ORIGINAL PAPER

# The effect of iodo substituents in bis(phenoxyimine) zirconium complexes on the catalytic performance of homogeneous ethylene polymerization reactions

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## ABSTRACT

Eight different zirconium phenoxyimine complexes were synthesized, characterized and tested as catalysts for ethylene polymerization. The phenoxyimine compounds were prepared by condensation of substituted salicylaldehydes with aliphatic and aromatic amines, the substituted salicylaldehydes from ortho substituted phenols and paraformaldehyde. The introduction of iodo substituents was achieved either by iodination of the aldehyde component followed by condensation with amines or the iodination of the aldehyde after the condensation with amines or the iodination via condensation with iodo substituted amines. Deprotonation of the hydroxy function of phenoxyimine compounds and reaction with zirconium tetrachloride gave mononuclear bis(phenoxyimine) zirconium complexes in good yields. These complexes were activated with methylaluminoxane (MAO) and applied for ethylene polymerization. The performances of the various catalysts are compared and structure-property-relationships are discussed.

**Keywords:** Zirconium phenoxyimine complexes; Catalytic ethylene polymerization; Structure-property-relationship studies.

## INTRODUCTION

In the past 20 years transition metal phenoxyimine complexes (FI complexes) established as attractive catalyst precursors in catalytic olefin polymerization and oligomerization reactions [1-31]. Various substituents at various positions of phenoxyimine ligands allow structure-property-relationship studies and tailoring of the corresponding catalyst molecules [22]. The asymmetric chelate structure can play an important role when prochiral olefins like propene are polymerized.

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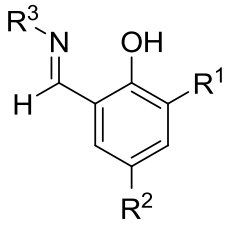



**Figure1.** General structure of phenoxyimine compounds.

Phenoxyimine compounds can be obtained from condensation reactions of substituted salicylaldehydes and amines. Modifications are possible in three positions indicated as $R^1$, $R^2$ and $R^3$. The bulkiness of the substituent $R^1$ is responsible for the polymerization activity of the respective zirconium complex. Cumyl, adamantyl and tert-butyl substituents are suitable candidates for high activities. A substituent $R^2$ in para position of the hydroxyl group has not much influence on the activity but on the molecular weight of the resulting polymers. For condensation reactions, aromatic and aliphatic amines can be used. To obtain bis(phenoxyimine) zirconium complexes from phenoxyimine compounds, the hydroxyl groups are deprotonated, followed by treatment of the phenolate salts with zirconium tetrachloride. The metal centre is coordinated octahedrally by two phenoxyimine and two chloro ligands. There exist five possible isomers depending on the positions of the three hetero atoms N, Cl and O to each other. The binding energies have been calculated by the Fujita group for all five isomers [17]. In the energetically favored isomer both the nitrogen and the chloro atoms are cis configurated while the oxygen atoms are in trans positions. The cis configuration of the chloro ligands is the prerequisite for polymerization activity of the complexes after activation with MAO and all three energetically favorable isomers display this configuration.

## EXPERIMENTAL

### NMR spectroscopy

The spectrometers Bruker ARX 250 and Varian (Inova 400) were 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 $^1$H NMR spectra are referred to the residual proton signal of the solvent ($\delta$ = 7.24 ppm for $CDCl_3$; $\delta$ = 5.32 ppm for $CD_2Cl_2$, $\delta$ = 7.15 ppm for $C_6D_6$) and in $^{13}$C NMR spectra to the solvent signal ($\delta$ = 77.0 ppm for $CDCl_3$; $\delta$ = 53.5 ppm for $CD_2Cl_2$; $\delta$ = 128.0 ppm for $C_6D_6$).

### GC/MS spectroscopy

GC/MS spectra were recorded with a Thermo Focus gas chromatograph in combination with a Thermo DSQ mass detector. A 30 m HP-5MS fused silica column (film 0.25 µm, flow 75 ml/min, split ratio 50:1), helium (4.6) was applied as the carrier gas. Using a 30 m column, the routinely performed temperature program started at 50°C (2 min). After a heating phase of 24 min (10K/min, final temperature 290°C) the end temperature was held for 15 min (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.

**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.

**Elemental analysis**

The analyses were performed with a VarioEI 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).

**Synthesis**

*Synthesis of 3-tert-butyl-salicylaldehyde (**1**)*

To 2-tert-butylphenol (50 mmol), dissolved in tetrahydrofurane (40 ml), methyl magnesium bromide (55.5 mmol, 3 M in diethylether) was added. After stirring for two hours at room temperature the gas production ended and 90% of the solvent was removed in vacuo. Then toluene (100 ml), triethylamine (72 mmol) and paraformaldehyde (125 mmol) was added. The reaction mixture was stirred for two hours at 88°C. After cooling down the yellow fluorescing solution was hydrolysed with cold hydrochloric acid (250 ml, 1 M in water). The organic phase was removed and dried over sodium sulphate. The solvent was evaporated and 3-tert-butylaldehyde was obtained from high vacuum distillation. Yield: 85%.

$^{1}$H NMR: 11.84 s (1H, OH), 9.72 s (1H, O=C-H), 7.43 - 7,47 m (1H, Ar-H), 7.25 - 7,29 m (1H, Ar-H), 6.86 t (1H, Ar-H), 1.38 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 197.2 (O=C-H), 161.1, 138.0, 120.7 ($C_q$), 134.1, 132.0, 119.3 (Ar-CH), 34.8 ($C_q$), 29.2 ($^{t}$Bu-$CH_3$). MS *m/z*: 178 $M^{\cdot+}$ (26), 163 M - Me (100), 135 M - $C_3H_7$ (39)

*General synthesis route for the iodination of 3-tert-butyl-salicylaldehyde derivatives **2** and **10***

3-tert-Butyl-salicylaldehyde or its derivatives (8.21 mmol) was dissolved in a mixture of methanol and methylene chloride (100 ml, ratio: 3:7). Then, benzyl trimethyl ammonium dichloroiodate (8.98 mmol) and anhydrous calciumcarbonate (10.76 mmol) was added. The reaction mixture was stirred for one day at room temperature. After that, the excess calciumcarbonate was filtered off. The filtrate was evaporated to 20% and a 5% solution of sodium hydrogensulfite (20 ml) in water was added for decomposition of the excess benzyl trimethyl ammonium dichloroiodate. The organic phase was extracted with diethylether and dried over sodium sulfate. The solvent was removed in vacuo and the product was obtained from recrystallisation in n-pentane. Yield: 59 - 92%.

**2** $^{1}$H NMR: 11.82 s (1H, OH), 9.85 s (1H, O=C-H), 7.52 d (1H, Ar-H), 7.38 d (1H, Ar-H), 1.42 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 197.1 (O=C-H), 161.2, 138.2, 120.6 ($C_q$), 134.1, 132.0 (Ar-CH), 74.7 ($C_q$, C-I), 34.8 ($C_q$), 29.2 ($^{t}$Bu-$CH_3$). MS *m/z*: 304 $M^{\cdot+}$ (65), 289 M - Me (100), 261 M - $C_3H_7$ (40).

**10** $^{1}$H NMR: 14.36 s (br, 1H, OH), 8.24 s (1H, N=C-H), 7.51 d (1H, Ar-H), 7.38 d (1H, Ar-H), 3.15 - 3.27 m (1H, N-CH), 1.27 - 1.84 m (10H, $CH_2$), 1.40 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 161.6 (N=C-H), 160.7, 140.5, 120.8, 79.0 ($C_q$), 140.0, 137.6 (Ar-CH), 67.4 (N-CH), 34.9 ($C_q$), 34.3 (2C), 24.4, 22.4 (2C) ($CH_2$), 29.0 ($^{t}$Bu-$CH_3$). MS *m/z*: 385 $M^{\cdot+}$ (100), 370 M - Me (53), 342 M - $C_3H_7$ (78), 259 M - I (39).

*General synthesis route for the phenoxyimine compounds **3**, **4** and **7***

A salicylaldehyde derivative (1.7 mmol) was dissolved in toluene (70 ml). After addition of a substituted amine respectively aniline (2.04 mmol) and a catalytic amount of para-toluene sulfonic acid, the reaction mixture was stirred for three hours under reflux using a Dean-Stark trap. After cooling down to room temperature, the reaction mixture was filtered over sodium sulfate and silica. The solvent was removed till 1-2 ml were left followed by recrystallisation in ethanol. Yield: 84 - 90%.

**3** $^{1}$H NMR: 14.28 s (br, 1H, OH), 8.37 s (1H, N=C-H), 7.32 dd (1H, Ar-H), 7.11 dd (1H, Ar-H), 6.81 t (1H, Ar-H), 3.18 - 3.23 m (1H, N-CH), 1.36 - 1.86 m (10H, $CH_2$), 1.47 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 163.0 (N=C-H), 160.7, 137.4, 118.8 ($C_q$), 129.4, 129.1, 117.6 (Ar-CH), 67.5 (N-CH), 34.8 ($C_q$), 34.3 (2C), 25.5, 24.5 (2C) ($CH_2$), 29.,4 ($^{t}$Bu-$CH_3$). MS *m/z*: 259 $M^{\cdot+}$ (70), 244 M - Me (96), 216 M - $C_3H_7$ (100).

**4** $^{1}$H NMR: 13.97 s (br, 1H, OH), 8.64 s (1H, N=C-H), 7.42 - 7.46 m (3H, Ar-H), 7.26 - 7.33 m (4H, Ar-H), 6.91 t (1H, Ar-H), 1.54 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 163.4 (N=C-H), 160.6, 148.4, 137.7, 119.1 ($C_q$), 130.7, 130.7, 130.4, 129.4, 126.8, 121.2, 118.4, 118.3 (Ar-CH), 35.0 ($C_q$), 29.4 ($^{t}$Bu-$CH_3$). MS *m/z*: 253 $M^{\cdot+}$ (57), 238 M - Me (100), 210 M - $C_3H_7$ (91).

**7** $^{1}$H NMR: 13.71 s (br, 1H, OH), 8.48 s (1H, N=C-H), 7.68 - 7.73 m (2H, Ar-H), 7.54 dd (1H, Ar-H), 7.23 dd (1H, Ar-H), 6.97 - 7.02 m (2H, Ar-H), 1.41 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 162.0 (N=C-H), 160.3, 147.5, 140.7, 121.0, 91.9, 80.0 ($C_q$), 139.1, 138.7, 138.5 (2C), 123.1 (2C) (Ar-CH), 35.0 ($C_q$), 29.1 ($^{t}$Bu-$CH_3$). MS *m/z*: 505 $M^{\cdot+}$ (100), 490 M - Me (56), 462 M - $C_3H_7$ (54).

*General synthesis route for the phenoxyimine compounds **5**, **6**, **8** and **9***

3-tert-Butyl-salicylaldehyde (15 mmol), the amine compound (30 mmol) and molecular sieves (15 g, 3 Å) were dissolved in toluene (100 ml) and stirred 48-72 hours at room temperature. After filtration over sodium sulphate the solvent was removed. The residue was extracted with n-pentane and dried over sodium sulphate. The solvent was removed in vacuo and pure products were obtained. Yield: 49 - 98 %.

**5** $^{1}$H NMR: 13.95 s (br, 1H, OH), 8.52 s (1H, N=C-H), 7.55 dd (2H, Ar-H), 7.37 - 7.45 m (2H, Ar-H), 7.23 - 7.32 m (3H, Ar-H), 1.42 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 162.2 (N=C-H), 160.8, 148.3, 141.1 ($C_q$), 139.2, 139.1, 129.9 (2C); 127.6, 121.6 (2C) (Ar-CH), 80.2 (C-I), 35.5 ($C_q$), 29.6 ($^{t}$Bu-$CH_3$). MS *m/z*: 379 $M^{\cdot+}$ (1), 364 M - Me (2), 336 M - $C_3H_7$ (3), 77 Phe (100).

**6** $^{1}$H NMR: 13.67 s (br, 1H, OH), 8.58 s (1H, N=C-H), 7.70 - 7.73 m (2H, Ar-H), 7.39 dd (1H, Ar-H), 7.23 dd (1H, Ar-H), 7.01 - 7.04 m (2H, Ar-H), 6.87 t (1H, Ar-H), 1.45 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 163.7 (N=C-H), 160.5, 148.1, 137.7, 118.9, 91.3 ($C_q$), 138.4, 130.8, 130.7 (2C), 123.2, 118.5 (2C) (Ar-CH), 34.9 ($C_q$), 29.3 ($^{t}$Bu-$CH_3$). MS *m/z*: 379 $M^{\cdot+}$ (66), 364 M - Me (100), 336 M - $C_3H_7$ (79).

**8** $^{1}$H NMR: 14.24 s (br, 1H, OH), 8.40 s (1H, N=C-H), 7.50 d (1H, Ar-H), 7.22 d (1H, Ar-H), 6.98 t (1H, Ar-H), 6.06 - 6.21 m (1H, =CH), 5.35 m (2H, =$CH_2$), 4.28 m (2H, $CH_2$), 1.68 s (9H, $^{t}$Bu-$CH_3$). $^{13}$C NMR: 166.5

(N=C-H), 160.7, 137.5, 118.9 ($C_q$), 135.8 (CH), 129.9, 129.6, 118.1 (Ar-CH), 116.6 (=$CH_2$), 61.4 ($CH_2$), 35.1 ($C_q$), 297 ($^t$Bu-$CH_3$). MS *m/z*: 217 $M^{\cdot+}$ (52), 202 M - Me (100), 174 M - $C_3H_7$ (85).

**9** $^1$H NMR: 13.5 s (br, 1H, OH), 8.30 s (1H, N=C-H), 7.54 d (1H, Ar-H), 7.43 d (1H, Ar-H), 6.06 - 6.21 m (1H, =CH), 5.43 m (2H =$CH_2$), 4.35 m (2H, $CH_2$), 1.38 s (9H, $^t$Bu-$CH_3$). $^{13}$C NMR: 166.8 (N=C-H), 160.0, 140.6, 120.4 (Cq), 138.6 (=CH), 129.7, 128.9 (Ar-H), 117.5 (=$CH_2$), 79.6 (C-I), 35.0 ($C_q$), 29.1 ($^t$Bu-$CH_3$). MS *m/z*: 343 $M^+$ (49), 328 M – Me (29), 300 M – $C_3H_7$ (40) , 217 M – I (9).

*Synthesis of the bis(phenoxyimine) zirconium complexes **11** - **18***

The phenoxyimine compound (6 mmol) was dissolved in tetrahydrofurane at room temperature. Then sodium hydride (6 mmol), suspended in tetrahydrofurane, was added. The reaction mixture was stirred for one hour at room temperature until the hydrogen gas production ended. After addition of zirconium tetrachloride (3 mmol) stirring was continued for twenty hours at room temperature. The solvent was then evaporated in vacuo and methylene chloride (30 ml) was added. The mixture was filtered over sodium sulfate. After evaporating the solvent to 5 ml, n-pentane (50 ml) was added and the complexes precipitated from the solution. Washing 3 times with n-pentane and drying in vacuo finally gave the complexes. Yields: 80 - 90%.

**11**: MS *m/z*: 678 $M^{\cdot+}$ (73), 641 M - Cl (63), 625 M - Cl - H - Me (69). Elemental analyses: Found: C, 60.8; H, 7.14; N, 4.11. Calc: C, 60.2; H, 7.13; N, 4.13.

**12** MS *m/z*: 660 $M^{\cdot+}$ (52), 631 M - Cl (13), 613 M - Cl - H - Me (100), 414 M - ligand (18).

**13** MS *m/z*: 918 $M^{\cdot+}$ (100), 881 M - Cl (18), 865 M - Cl - H - Me (90), 540 M - ligand (63). Elemental analysis: Found: C, 44.4; H, 3.75; N, 2.48. Calc: C, 44.5; H, 3.73; N, 3.05.

**14** MS *m/z*: 918 $M^{\cdot+}$ (67), 881 M - Cl (99), 866 M - Cl - Me (29). Elemental analysis: Found: C, 44.3; H, 3.79; N, 3.00. Calc: C, 44.5; H, 3.73; N, 3.05.

**15** $^1$H NMR: 8.54 s (2H, N=C-H), 7.70 - 7.77 m (4H, Ar-H), 7.59 dd (4H, Ar-H), 7.02 - 7.09 m (4H, Ar-H), 1.41 s (18H, $^t$Bu-$CH_3$). MS *m/z*: 1170 $M^{\cdot+}$ (100), 1117 M - Me - Cl - H (75), 1044 M - I (29), 969 M - Phe - I (33), 918 M - 2 I (31), 666 M - ligand (46).

**16** $^1$H NMR: 8.22 s (2H, N=C-H), 7.59 dd (2H, Ar-H), 7.26 dd (2H, Ar-H), 6.95 t (2H, Ar-H), 5.59 - 5.77 m (2H, =CH), 4.94 - 5.07 m (4H, =$CH_2$), 4.04 - 4.37 m (4H, $CH_2$), 1.50 s (18H, $^t$Bu-$CH_3$). MS *m/z*: 594 $M^{\cdot+}$ (59), 557 M - Cl (28), 541 M - Cl - H - Me (100). Elemental analysis: Found: C, 56.5; H, 6.05; N, 4.71. Calc: C, 56.6; H, 6.10; N, 4.71.

**17** $^1$H NMR: 8.15 s (2H, N=C-H), 7.81 dd (2H, Ar-H), 7.59 dd (2H, Ar-H), 5.29 - 5.33 m (2H, =CH), 4.92 - 5.15 m (4H, =$CH_2$), 4.04 - 4.32 m (4H, $CH_2$), 1.48 s (18H, $^t$Bu-$CH_3$). MS *m/z*: 846 $M^{\cdot+}$ (38), 809 M - Cl (10), 793 M - Cl - H - Me (23), 720 M - I (18), 669 M - Cl - H - Me - I (16), 504 M - Ligand (15). Elemental analyses: Found: C, 38.7; H, 4.24; N, 2.85. Calc: C, 39.7; H, 4.05; N, 3.31.

**18** MS *m/z*: 930 $M^{\cdot+}$ (43), 895 M - Cl (13), 879 M - Cl - H - Me (14), 545 M - ligand (20). Elemental analysis: Found: C, 43.2; H, 4.94; N, 2.92. Calc: C, 43.9; H, 4.98; N, 3.01.

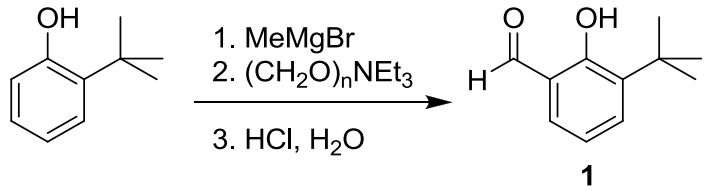
*Polymerisation of ethylene with the bis(phenoxyimine) zirconium complexes **11** - **18***

The zirconium complex (1-5 mg) was dissolved in 5 ml of toluene. Then the solution was filled into a flask containing 250 ml of n-pentane. A 1l Büchi autoclave was evacuated and refilled with argon several times and the mixture was added. Then after short evacuation, the autoclave was set under an ethylene pressure of 1 bar and methylaluminoxane (MAO, 30% in toluene, Zr:Al ratio = 1:500) was added to the solution. The mixture was then stirred for one hour at 35°C respectively 60°C applying an ethylene pressure of 10 bar. The ethylene pressure was released and, after cooling to room temperature, the polymer mixture was taken out of the reactor. The obtained polymer was washed with hydrochloric acid, water and acetone and was finally dried in vacuo.

## RESULTS AND DISCUSSION

### Synthesis of substituted salicylaldehydes

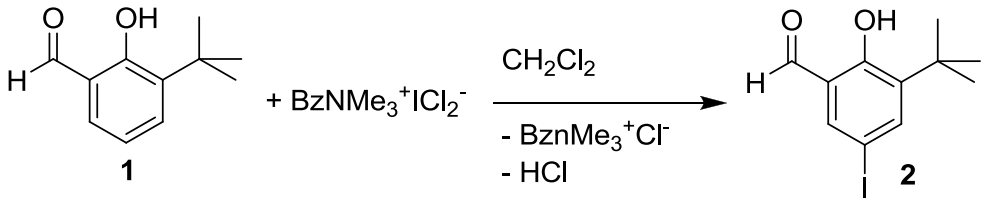
To obtain 3-substituted salicylaldehydes, phenols containing one unsubstituted ortho-position, are deprotonated in tetrahydrofuran with a Grignard reagent. The following reaction with para formaldehyde in toluene and subsequent hydrolysis leads to the salicylaldehydes [20].




**Scheme 1.** Synthesis of substituted salicylaldehydes.

### Introduction of iodo substituents

For introducing a iodo substituent in para-position to the hydroxyl group, 3-tert-butylsalicylaldehyde was treated with benzyl trimethyl ammonium dichloroiodate in methanol to give 3-tert-butyl-5-iodo-salicylaldehyde [17].



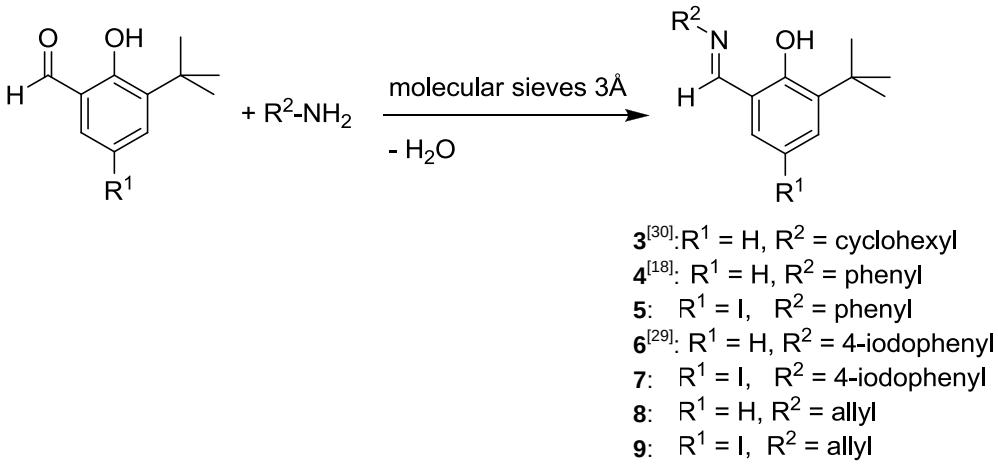

**Scheme 2**. Synthesis of 3-tert-butyl-5-iodosalicylaldehyde (**2)**.

### Synthesis of phenoxyimine compounds

The synthesis of phenoxyimine compounds was achieved following two different routes:

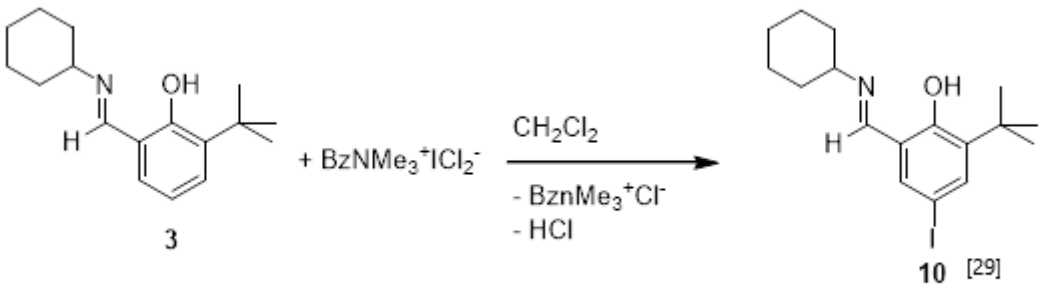
1. The condensation reaction of a substituted salicylaldehyde with an aliphatic or aromatic amine in toluene to give the phenoxyimine compound under azeotropic water separation [28].
2. The substituted salicylaldehyde is reacted with a small excess of an aliphatic or aromatic amine in the presence of molecular sieves (3Å) in toluene at room temperature.

The second method is milder and produces less undesired side products.




**Scheme 3.** Synthesis of phenoxyimine compounds.

Iodo substituents can be introduced into phenoxyimine compounds in an additional step.

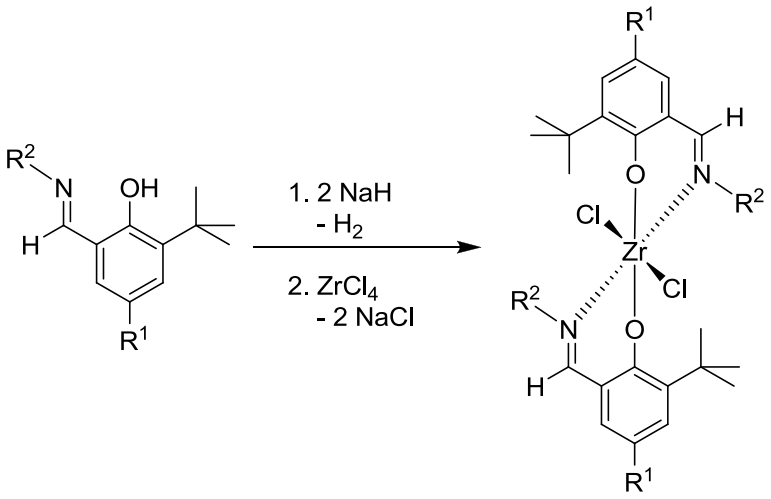



**Scheme 4:** Iodination of phenoxyimine compounds [29].

This procedure only works for phenoxyimine compounds bearing a saturated substituent at the imine group. Aromatic and olefinic substituents are iodinated at the double bonds.

**Synthesis of bis(phenoxyimine) zirconium complexes**

The phenoxyimine compounds are deprotonated with sodium hydride in tetrahydrofuran and treated with zirconium tetrachloride. The low yields are due to hydrolysis reactions.




| starting compound | $R^1$ | $R^2$ | product |
|---|---|---|---|
| **3**[30] | H | cyclohexyl | **11**[30] |
| **4**[14] | H | phenyl | **12**[14] |
| **5** | I | phenyl | **13** |
| **6**[29] | H | 4-iodophenyl | **14**[29] |
| **7** | I | 4-iodophenyl | **15** |
| **8** | H | allyl | **16** |
| **9** | I | allyl | **17** |
| **10**[29] | I | cyclohexyl | **18**[29] |

**Scheme 5.** Synthesis of bis(phenoxyimine) zirconium complexes.

**Spectroscopic characterisation of the bis(phenoxyimine) zirconium complexes**

All synthesised bis(phenoxyimine) complexes have been characterized with mass spectroscopy and elemental analysis. $^1$H NMR spectra could not be obtained from all complexes due to their poor solubility.

In the following, the $^1$H NMR (Figure 2) and mass spectra (Figure 3) of complex **16** are discussed. A comparison of the $^1$H NMR spectra of compounds **8** and **16** in $CD_2Cl_2$ shows that the proton of the phenolic hydroxy group has disappeared in complex **16**. This is a strong evidence for complex formation. The broad singlet at δ = 5.68 ppm indicates the proton of the carbon atom C7 in the aliphatic side chain. The signal for the solvent $CD_2Cl_2$ is visible at δ = 5.32 ppm. Both protons on the carbon atom C8 give a multiplet at δ = 4.94 - 5.07 ppm and the two protons on carbon atom C6 are represented by the signal at δ = 4.04 - 4.37 ppm. The proton of the imino group gives a signal at δ = 8.22 ppm. The doublets at δ = 7.59 and 7.26 ppm can be assigned to the protons H4 and H2 at the salicylaldehyde ring. H3 appears as a virtual triplet at δ = 6.95 ppm. The singlet at δ = 1.50 ppm results from the protons of the tert-butyl group. The smaller signals visible in the spectrum can be assigned to different isomers.

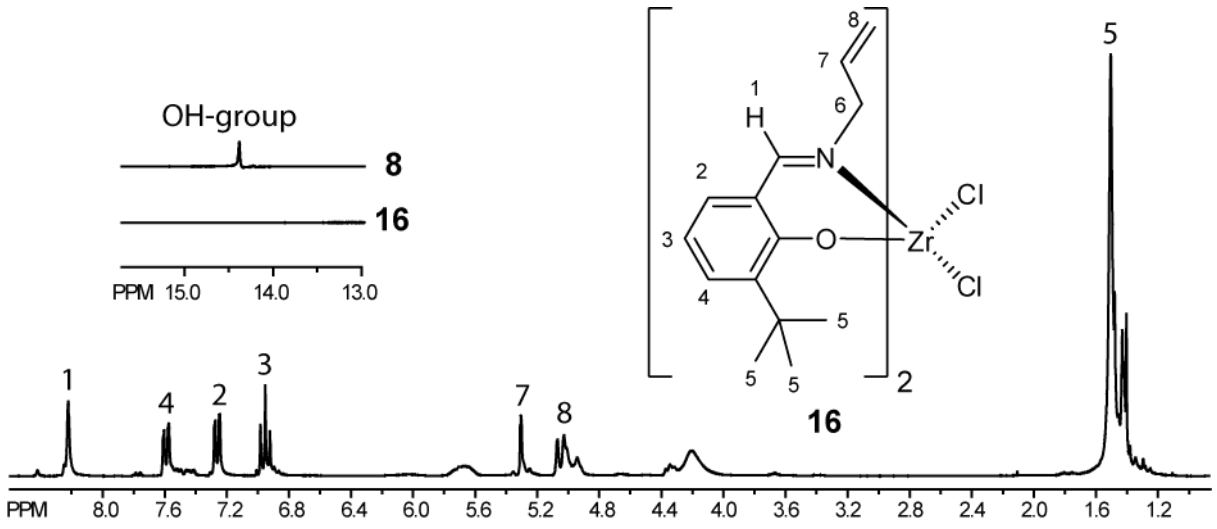



**Figure 2.** $^{1}$H NMR spectrum of complex **16** in $CD_2Cl_2$.

The mass spectrum of complex **16** shows the molecule ion at m/z = 594. The loss of an HCl molecule leads to the fragment with m/z = 557. The base peak at m/z = 541 results from the loss of an HCl molecule and a methyl group.

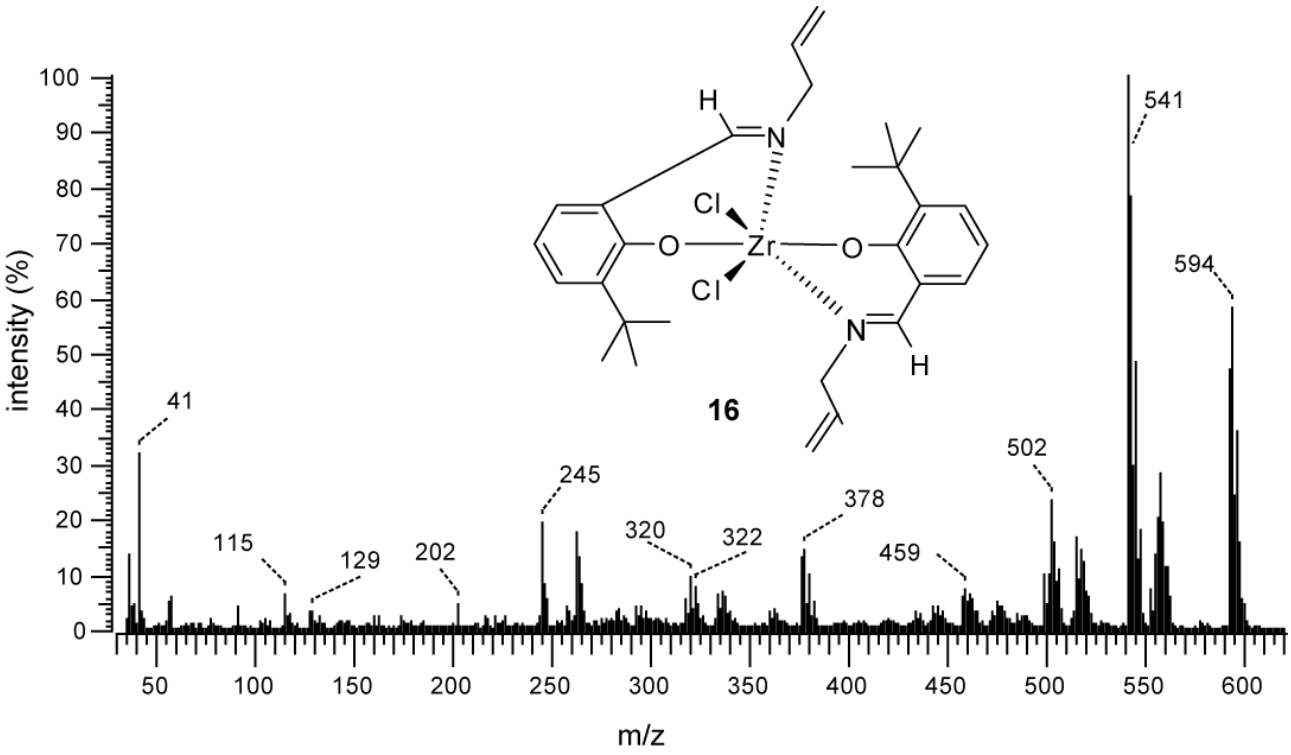



**Figure 3.** Mass spectrum of complex **16**.

**Ethylene polymerization with bis(phenoxyimine) zirconium complexes**

The synthesized phenoxyimine complexes were tested in homogeneous ethylene polymerisation reactions. Methylaluminoxane (MAO) was used as cocatalyst (Zr : Al = 1 : 500). All polymerisation experiments were carried out under an ethylene pressure of 10 bar for 1 hour at a temperature of 35°C. At 60°C, the catalysts decomposed. As a solvent, n-pentane was used. The activities of complexes **11 - 18** together with the data

from the gel permeation chromatography (GPC, polydispersity PD = $M_w/M_n$, molecular weight $M_n$ and $M_w$) are summarized in Table 1.

**Table 1.** Ethylene polymerization with the bis(phenoxyimine) zirconium complexes **11** - **19**. Polymerization conditions: solvent: 250 ml n-pentane, activator: MAO(Zr : Al = 1 : 500), 35°C, 10 bar ethylene, 1 h.

| complex | activity [kg PE/mol Zr · h] | $M_n$ [g/mol] | $M_w$ [g/mol] | PD |
|---|---|---|---|---|
| **11** | 25461 | 12460 | 30220 | 2.42 |
| **12** | 18525 | 5921 | 332089 | 56.09 |
| **13** | 20013 | 2276 | 128517 | 56.46 |
| **14** | 8320 | 7260 | 41700 | 5.74 |
| **15** | 18090 | 3383 | 141204 | 41.74 |
| **16** | 8953 | 8041 | 101203 | 12.59 |
| **17** | 0 | - | - | - |
| **18** | 14650 | 10700 | 32150 | 3.00 |

**General notes to ethylene polymerization with bis(phenoxyimine) zirconium complexes**

The mechanism of the ethylene polymerisation with bis(phenoxyimine) zirconium complexes is supposed to be the same as the mechanism for metallocene complexes (see Figure 4).

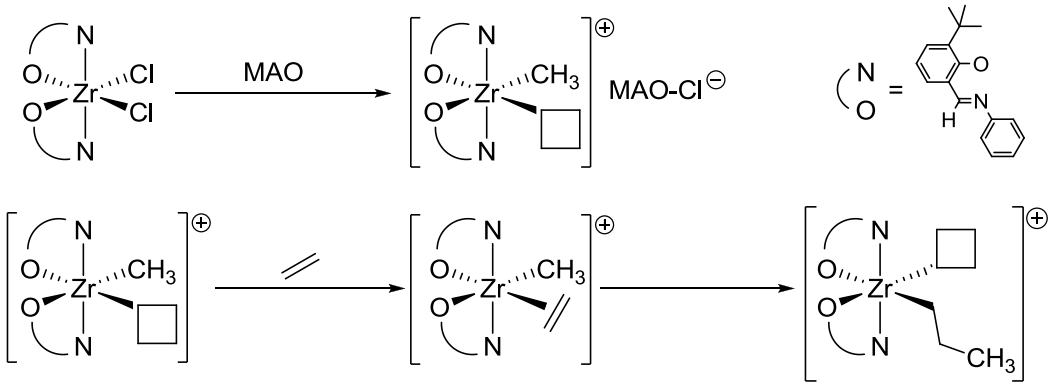



**Figure 4**. Mechanism of the polymerization of ethylene with bis(phenoxyimine) zirconium catalysts.

Like for the neutral bis(phenoxyimine) zirconium complexes, five isomers of the active species are formed. Since all possible coordination sites need to be cis, isomers D and E are out of question for the polymerisation experiments since the coordination sites are trans to each other. Isomer A is energetically favored.

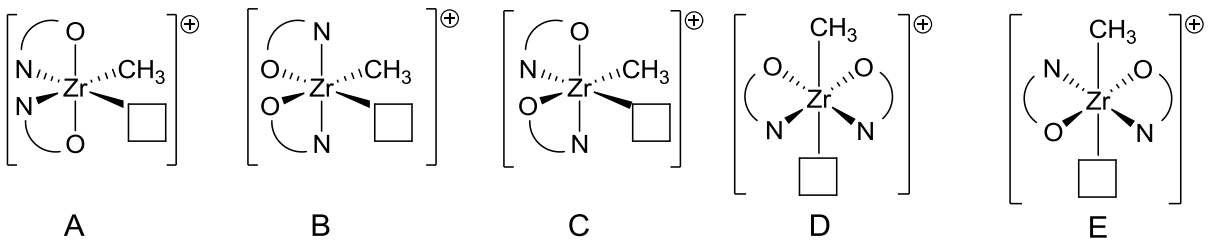



**Figure 5.** Possible isomers of the active species of bis(phenoxyimine) zirconium complexes.

Bis(phenoxyimine) zirconium complexes have a specific feature after activation with aluminoxanes. They are only active, when the activation with MAO occurs under an ethylene atmosphere. If this is not the case, one of the two phenoxyimine ligands migrates to an aluminum centre, blocks it and deactivates the polymerisation ability of its own complex [31].

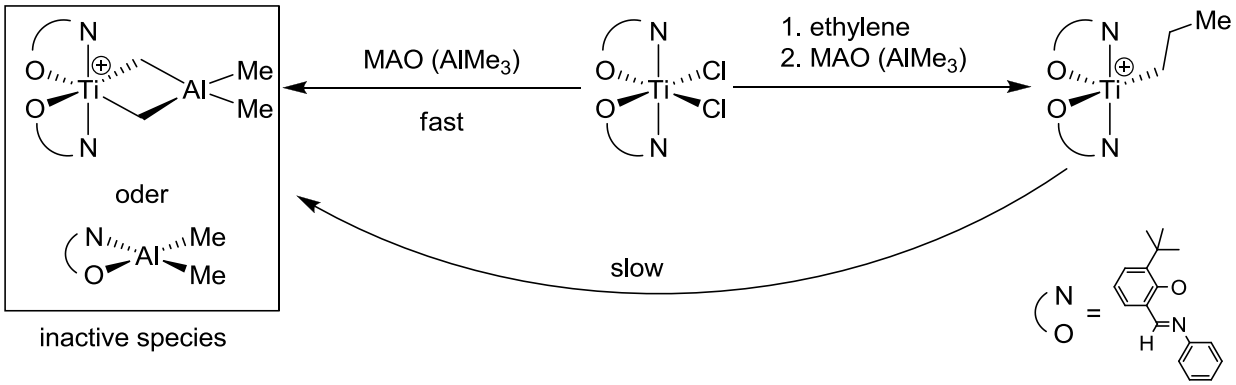



**Figure 6.** Activation and deactivation of bis(phenoxyimine) zirconium complexes.[20].

**Comparison of the activities of the bis(phenoxyimine) zirconium complexes**

The comparison of the activities of complexes ***16, 12 and 11****/MAO* shows that the activity of the complex with the aliphatic side chain is the lowest (8921 kg PE / mol Zr h). The phenyl substituent increases the activity and the best activity is achieved with complex **11**/MAO. Obviously the electron pushing effect of the cyclohexyl substituent has a positive influence on the polymerization activity.

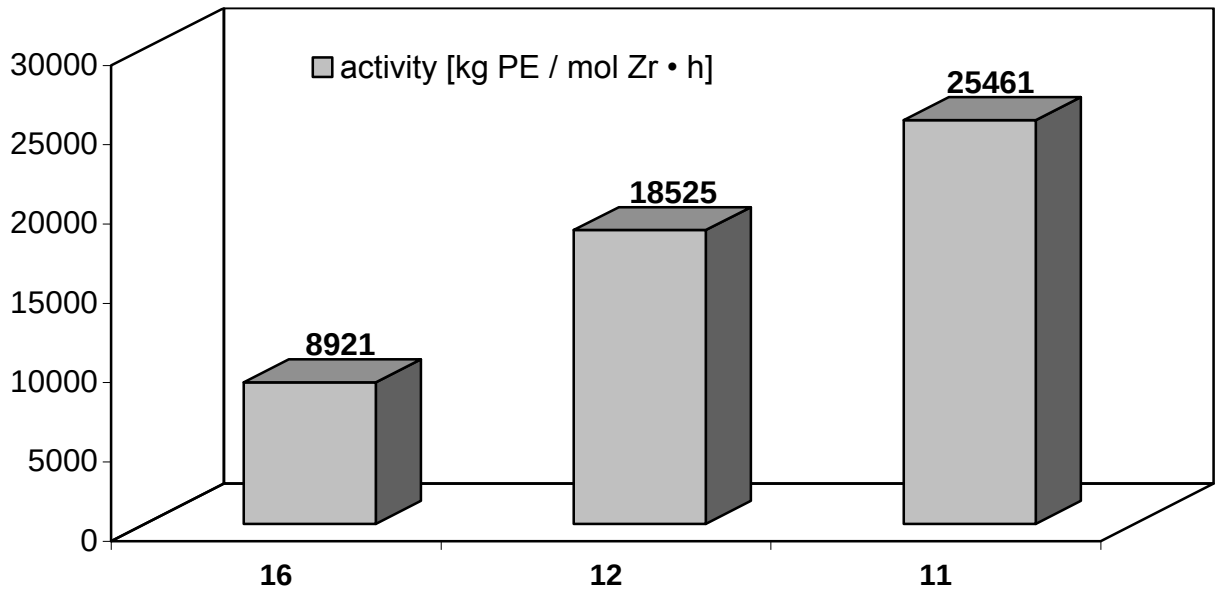



**Figure 7.** Activities of the bis(phenoxyimine) zirconium complexes **16/MAO**, **12/**MAO and **11**/MAO.

The introduction of a iodo substituent in para-position to the former hydroxyl group has different influences on the polymerization behavior.The iodo substituent of complex **18** leads to a significant lower polymerization activity compared to its non iodinated analogue **11**. Comparing complexes **16** and **17**, a complete loss of activity is observed.

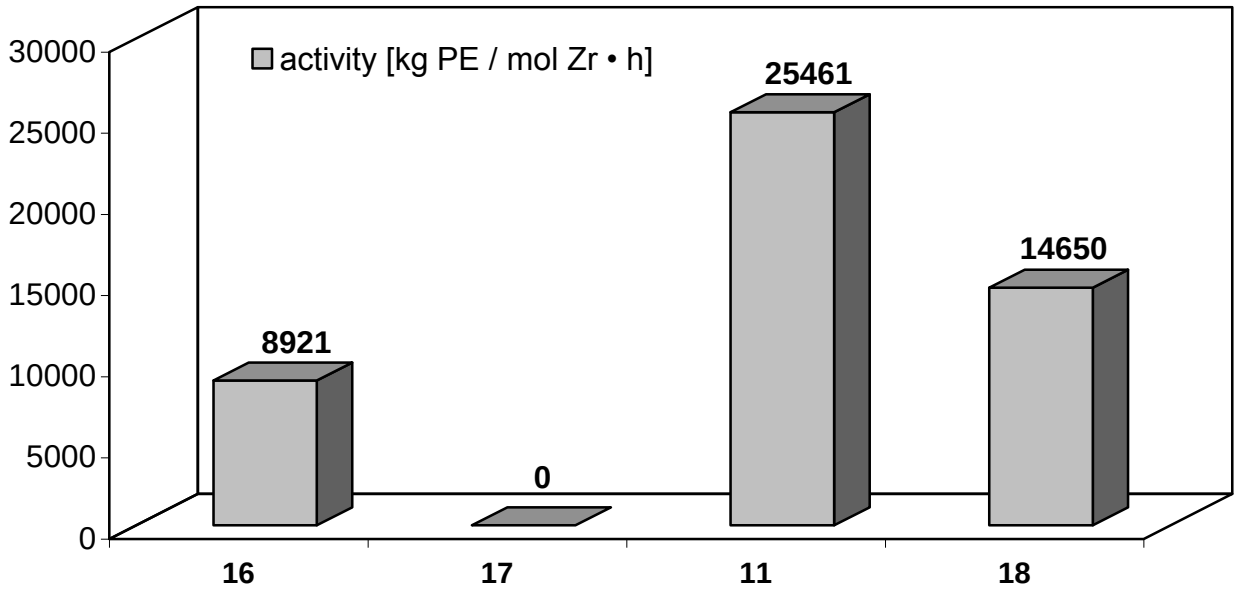



**Figure 8.** Activities of the bis(phenoxyimine) zirconium complexes **16**, **17**, **11** and **18**/MAO.

The bis(phenoxyimine) zirconium complexes containing phenyl substituents on the nitrogen atoms show a completely different behaviour. Here, the mono iodinated complex **14** shows the lowest activity. Complex **13** with the iodo substituent in para-position to the former hydroxyl group shows the highest activity. The activity of **15** with diiodo substituted ligands is about the same as observed for the complex without iodo substituents. The counterproductive effects of the iodo substituents and the positive effect of the phenyl substituent compensate each other.

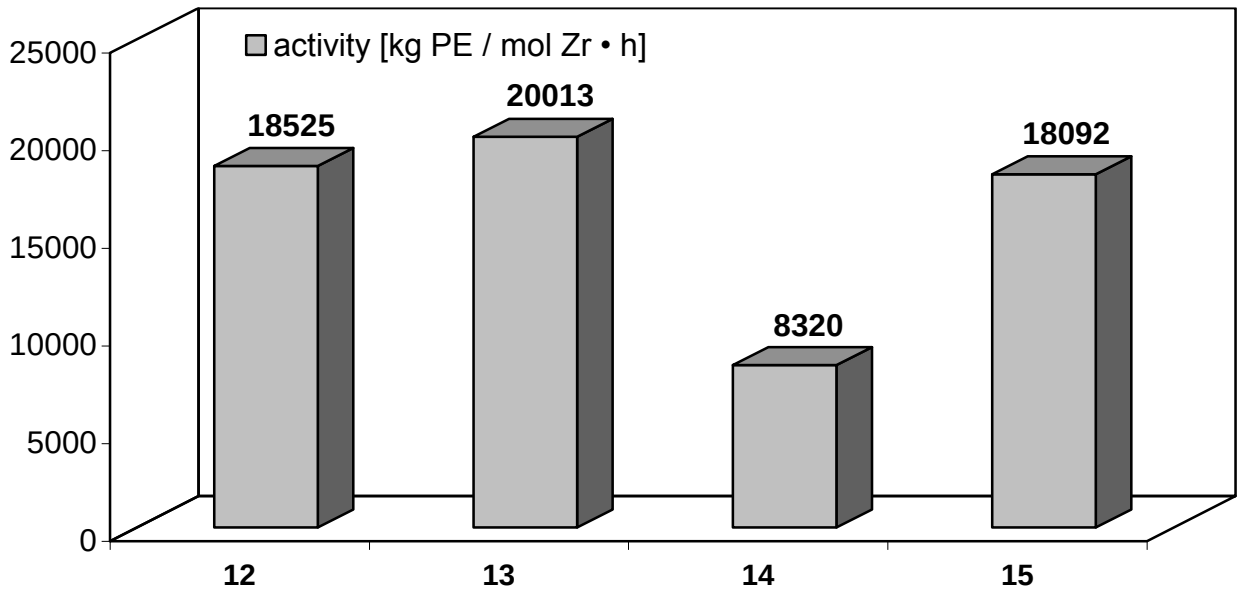



**Figure 9.** Activities of the bis(phenoxyimine) zirconium complexes **12**, **13**, **14** and **15**/MAO.

**Discussion of the GPC spectra of the polyethylenes obtained with the bis(phenoxyimine)zirconium complexes/MAO**

Phenoxyimine catalysts with cyclohexylimino, respectively allylimino substituents, mainly produce polyethylenes with lower polydispersities than catalysts with phenylimino substituents. If the phenoxyimine complex contains a 4-iodophenyl substituent, the polydispersity is again lower.The smaller the polydispersity, the smaller the molecular weight distribution in the GPC spectrum. Complex **11** produces a polyethylene with the smallest molecular weight distribution of the tested catalysts. A iodo substituent in para-position to the former hydroxyl group causes a small increase of the polydispersity. The same effect is observed for complexes **12** and **13**, whereas the polydispersity of the polyethylene is higher. The allylimino substituted complex **16** also has a very low value. Here a comparison with the iodinated complex **17** is not possible, because this complex was inactive in polymerization reactions of ethylene. In complex **15**, the opposite effect of the iodo substituents plays a role. The polydispersity of the obtained polyethylene is lower than for complexes **12** and **13** but still significantly higher as observed for the polymer produced with the 4-iodophenyl substituted complex **14**.

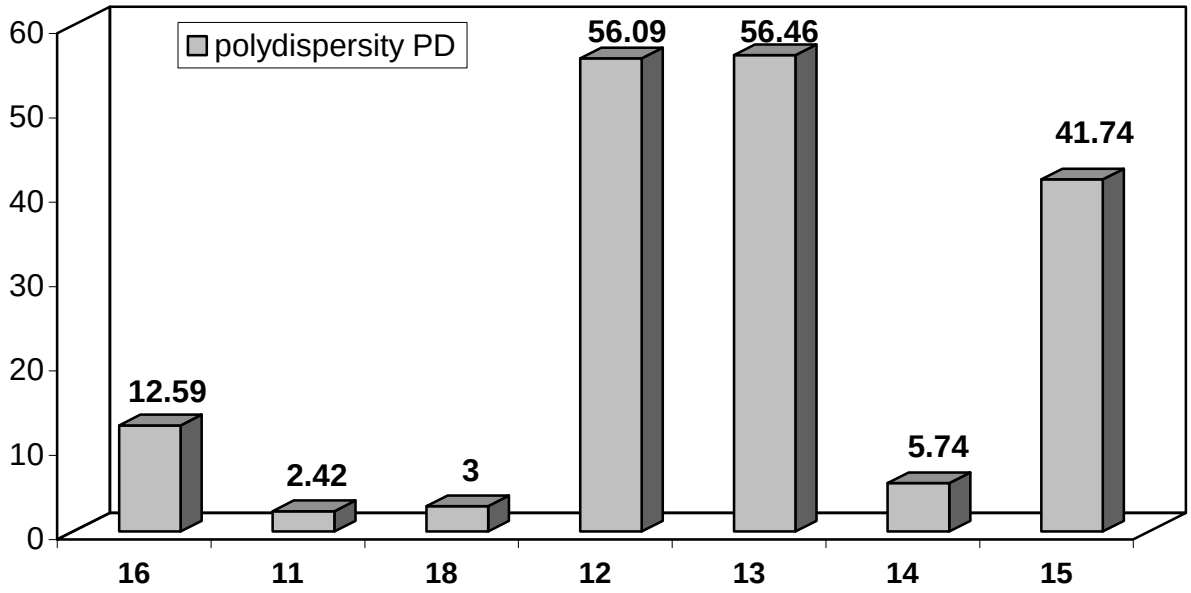



**Figure 10.** Polydispersities of the polyethylenes obtained with the bis(phenoxyimine) zirconium complexes **11** – **16/**MAO and **18**/MAO.

## CONCLUSION

All synthesized phenoxyimine complexes, in combination with MAO, were tested in homogeneous ethylene polymerization reactions. Clear differences in the activities for allyl, phenyl and cyclohexyl substituents at the imino groups were found. It was also shown that iodo substituents have various effects on the activities of the complexes depending on their positions at the ligand frameworks. The substituents influence the polydispersities, too. Complexes containing cyclohexylimino substituents give polyethylenes with very low polydispersities whereas complexes with unsubstituted phenyl substituents give polyethylenes with high polydispersities. Broad polydispersities indicate different active sites in the catalyst molecules. They could result from different interactions of the cationic catalyst and slightly modified MAO counter anions resulting from partial substitution of iodine substituents. There were limitations in the homogeneous polymerization reactions. The phenoxyimine complexes were only active at polymerization temperatures lower than 40°C and inactive at a polymerization temperature of 60°C. Furthermore, the complexes had to be activated in an ethylene atmosphere otherwise deactivation reactions occurred by ligand transfer to aluminum centres of the cocatalyst.

## ACKNOWLEDGEMENT

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