

# 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 were compared and structure-property-relationships were discussed. **Polyolefins J (2018) 5: 157-165**

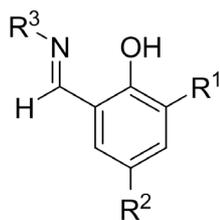
**Keywords:** Zirconium phenoxyimine complexes; catalytic ethylene polymerization; structure-property-relationship studies.

## INTRODUCTION

In the past 20 years, transition metal phenoxyimine complexes (FI complexes, Figure 1) have been 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.

Phenoxyimine compounds can be obtained from condensation reactions of substituted salicylaldehydes and amines. Modifications are possible in three positions indicated as R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>. The bulkiness of the substituent R<sup>1</sup> 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<sup>2</sup> 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

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**Figure 1.** General structure of phenoxyimine compounds.

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 toward 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 configured 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 <sup>1</sup>H NMR spectra are referred to the residual proton signal of the solvent ( $\delta = 7.24$  ppm for CDCl<sub>3</sub>;  $\delta = 5.32$  ppm for CD<sub>2</sub>Cl<sub>2</sub>,  $\delta = 7.15$  ppm for C<sub>6</sub>D<sub>6</sub>) and in <sup>13</sup>C NMR spectra to the solvent signal ( $\delta = 77.0$  ppm for CDCl<sub>3</sub>;  $\delta = 53.5$  ppm for CD<sub>2</sub>Cl<sub>2</sub>;  $\delta = 128.0$  ppm for C<sub>6</sub>D<sub>6</sub>).

### 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  $\mu$ m, flow 75 ml/min, split ratio 50:1) was used for separation and 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 tetrahydrofuran (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) were 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%.

<sup>1</sup>H NMR: 11.84 s (<sup>1</sup>H, OH), 9.72 s (<sup>1</sup>H, O=C-H), 7.43 - 7.47 m (<sup>1</sup>H, Ar-H), 7.25 - 7.29 m (<sup>1</sup>H, Ar-H), 6.86 t (<sup>1</sup>H, Ar-H), 1.38 s (9H, <sup>1</sup>Bu-CH<sub>3</sub>). <sup>13</sup>C NMR: 197.2 (O=C-H), 161.1, 138.0, 120.7 (C<sub>q</sub>), 134.1, 132.0, 119.3 (Ar-CH), 34.8 (C<sub>q</sub>), 29.2 (<sup>1</sup>Bu-CH<sub>3</sub>). MS m/z: 178 M<sup>+</sup> (26), 163 M - Me (100), 135 M - C<sub>3</sub>H<sub>7</sub> (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 calcium carbonate (10.76 mmol) were added. The reaction mixture was stirred for one day at room temperature. After that, the excess calcium carbonate was filtered off. The filtrate was evaporated to 20% and a 5% solution of sodium hydrogen sulfite (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%.

$^1\text{H}$  NMR: 11.82 s ( $^1\text{H}$ , OH), 9.85 s ( $^1\text{H}$ , O=C-H), 7.52 d ( $^1\text{H}$ , Ar-H), 7.38 d ( $^1\text{H}$ , Ar-H), 1.42 s (9H,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 197.1 (O=C-H), 161.2, 138.2, 120.6 ( $\text{C}_q$ ), 134.1, 132.0 (Ar-CH), 74.7 ( $\text{C}_q$ , C-I), 34.8 ( $\text{C}_q$ ), 29.2 ( $^t\text{Bu-CH}_3$ ). MS m/z: 304  $\text{M}^+$  (65), 289 M - Me (100), 261 M -  $\text{C}_3\text{H}_7$  (40).

$^{10}\text{H}$  NMR: 14.36 s (br, 1H, OH), 8.24 s (1H, N=C-H), 7.51 d (1H, Ar-H), 7.38 d ( $^1\text{H}$ , Ar-H), 3.15 - 3.27 m ( $^1\text{H}$ , N-CH), 1.27 - 1.84 m (10H,  $\text{CH}_2$ ), 1.40 s (9H,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 161.6 (N=C-H), 160.7, 140.5, 120.8, 79.0 ( $\text{C}_q$ ), 140.0, 137.6 (Ar-CH), 67.4 (N-CH), 34.9 ( $\text{C}_q$ ), 34.3 (2C), 24.4, 22.4 (2C) ( $\text{CH}_2$ ), 29.0 ( $^t\text{Bu-CH}_3$ ). MS m/z: 385  $\text{M}^+$  (100), 370 M - Me (53), 342 M -  $\text{C}_3\text{H}_7$  (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, aniline (2.04 mmol) and a catalytic amount of para-toluene sulfonic acid, respectively, 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%.

$^3\text{H}$  NMR: 14.28 s (br, 1H, OH), 8.37 s ( $^1\text{H}$ , N=C-H), 7.32 dd ( $^1\text{H}$ , Ar-H), 7.11 dd ( $^1\text{H}$ , Ar-H), 6.81 t ( $^1\text{H}$ , Ar-H), 3.18 - 3.23 m ( $^1\text{H}$ , N-CH), 1.36 - 1.86 m (10H,  $\text{CH}_2$ ), 1.47 s (9H,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 163.0 (N=C-H), 160.7, 137.4, 118.8 ( $\text{C}_q$ ), 129.4, 129.1, 117.6 (Ar-CH), 67.5 (N-CH), 34.8 ( $\text{C}_q$ ), 34.3 (2C), 25.5, 24.5 (2C) ( $\text{CH}_2$ ), 29.4 ( $^t\text{Bu-CH}_3$ ). MS m/z: 259  $\text{M}^+$  (70), 244 M - Me (96), 216 M -  $\text{C}_3\text{H}_7$  (100).

$^4\text{H}$  NMR: 13.97 s (br,  $^1\text{H}$ , OH), 8.64 s ( $^1\text{H}$ , N=C-H),

7.42 - 7.46 m (3H, Ar-H), 7.26 - 7.33 m (4H, Ar-H), 6.91 t ( $^1\text{H}$ , Ar-H), 1.54 s (9H,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 163.4 (N=C-H), 160.6, 148.4, 137.7, 119.1 ( $\text{C}_q$ ), 130.7, 130.7, 130.4, 129.4, 126.8, 121.2, 118.4, 118.3 (Ar-CH), 35.0 ( $\text{C}_q$ ), 29.4 ( $^t\text{Bu-CH}_3$ ). MS m/z: 253  $\text{M}^+$  (57), 238 M - Me (100), 210 M -  $\text{C}_3\text{H}_7$  (91).

$^7\text{H}$  NMR: 13.71 s (br,  $^1\text{H}$ , OH), 8.48 s ( $^1\text{H}$ , N=C-H), 7.68 - 7.73 m (2H, Ar-H), 7.54 dd ( $^1\text{H}$ , Ar-H), 7.23 dd ( $^1\text{H}$ , Ar-H), 6.97 - 7.02 m (2H, Ar-H), 1.41 s (9H,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 162.0 (N=C-H), 160.3, 147.5, 140.7, 121.0, 91.9, 80.0 ( $\text{C}_q$ ), 139.1, 138.7, 138.5 (2C), 123.1 (2C) (Ar-CH), 35.0 ( $\text{C}_q$ ), 29.1 ( $^t\text{Bu-CH}_3$ ). MS m/z: 505  $\text{M}^+$  (100), 490 M - Me (56), 462 M -  $\text{C}_3\text{H}_7$  (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 %.

$^5\text{H}$  NMR: 13.95 s (br,  $^1\text{H}$ , OH), 8.52 s ( $^1\text{H}$ , 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,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 162.2 (N=C-H), 160.8, 148.3, 141.1 ( $\text{C}_q$ ), 139.2, 139.1, 129.9 (2C); 127.6, 121.6 (2C) (Ar-CH), 80.2 (C-I), 35.5 ( $\text{C}_q$ ), 29.6 ( $^t\text{Bu-CH}_3$ ). MS m/z: 379  $\text{M}^+$  (1), 364 M - Me (2), 336 M -  $\text{C}_3\text{H}_7$  (3), 77 Phe (100).

$^6\text{H}$  NMR: 13.67 s (br,  $^1\text{H}$ , OH), 8.58 s ( $^1\text{H}$ , N=C-H), 7.70 - 7.73 m (2H, Ar-H), 7.39 dd ( $^1\text{H}$ , Ar-H), 7.23 dd ( $^1\text{H}$ , Ar-H), 7.01 - 7.04 m (2H, Ar-H), 6.87 t ( $^1\text{H}$ , Ar-H), 1.45 s (9H,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 163.7 (N=C-H), 160.5, 148.1, 137.7, 118.9, 91.3 ( $\text{C}_q$ ), 138.4, 130.8, 130.7 (2C), 123.2, 118.5 (2C) (Ar-CH), 34.9 ( $\text{C}_q$ ), 29.3 ( $^t\text{Bu-CH}_3$ ). MS m/z: 379  $\text{M}^+$  (66), 364 M - Me (100), 336 M -  $\text{C}_3\text{H}_7$  (79).

$^8\text{H}$  NMR: 14.24 s (br,  $^1\text{H}$ , OH), 8.40 s ( $^1\text{H}$ , N=C-H), 7.50 d ( $^1\text{H}$ , Ar-H), 7.22 d ( $^1\text{H}$ , Ar-H), 6.98 t ( $^1\text{H}$ , Ar-H), 6.06 - 6.21 m ( $^1\text{H}$ , =CH), 5.35 m (2H, = $\text{CH}_2$ ), 4.28 m (2H,  $\text{CH}_2$ ), 1.68 s (9H,  $^t\text{Bu-CH}_3$ ).  $^{13}\text{C}$  NMR: 166.5 (N=C-H), 160.7, 137.5, 118.9 ( $\text{C}_q$ ), 135.8 (CH), 129.9, 129.6, 118.1 (Ar-CH), 116.6 (=CH<sub>2</sub>), 61.4 (CH<sub>2</sub>), 35.1 ( $\text{C}_q$ ), 29.7 ( $^t\text{Bu-CH}_3$ ). MS m/z: 217  $\text{M}^+$  (52), 202 M - Me (100), 174 M -  $\text{C}_3\text{H}_7$  (85).

$^9\text{H}$  NMR: 13.5 s (br,  $^1\text{H}$ , OH), 8.30 s ( $^1\text{H}$ , N=C-H), 7.54 d ( $^1\text{H}$ , Ar-H), 7.43 d ( $^1\text{H}$ , Ar-H), 6.06 - 6.21 m

(<sup>1</sup>H, =CH), 5.43 m (2H =CH<sub>2</sub>), 4.35 m (2H, CH<sub>2</sub>), 1.38 s (9H, <sup>1</sup>Bu-CH<sub>3</sub>). <sup>13</sup>C NMR: 166.8 (N=C-H), 160.0, 140.6, 120.4 (C<sub>q</sub>), 138.6 (=CH), 129.7, 128.9 (Ar-H), 117.5 (=CH<sub>2</sub>), 79.6 (C-I), 35.0 (C<sub>q</sub>), 29.1 (<sup>1</sup>Bu-CH<sub>3</sub>). MS m/z: 343 M<sup>+</sup> (49), 328 M - Me (29), 300 M - C<sub>3</sub>H<sub>7</sub> (40), 217 M - I (9).

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

The phenoxyimine compound (6 mmol) was dissolved in tetrahydrofuran at room temperature. Then, sodium hydride (6 mmol), suspended in tetrahydrofuran, 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<sup>+</sup> (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<sup>+</sup> (52), 631 M - Cl (13), 613 M - Cl - H - Me (100), 414 M - ligand (18).

13: MS m/z: 918 M<sup>+</sup> (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<sup>+</sup> (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: <sup>1</sup>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, <sup>1</sup>Bu-CH<sub>3</sub>). MS m/z: 1170 M<sup>+</sup> (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: <sup>1</sup>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<sub>2</sub>), 4.04 - 4.37 m (4H, CH<sub>2</sub>), 1.50 s (18H, <sup>1</sup>Bu-CH<sub>3</sub>). MS m/z: 594 M<sup>+</sup> (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: <sup>1</sup>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<sub>2</sub>), 4.04 - 4.32 m (4H, CH<sub>2</sub>), 1.48 s (18H, <sup>1</sup>Bu-CH<sub>3</sub>). MS m/z: 846 M<sup>+</sup> (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<sup>+</sup> (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.

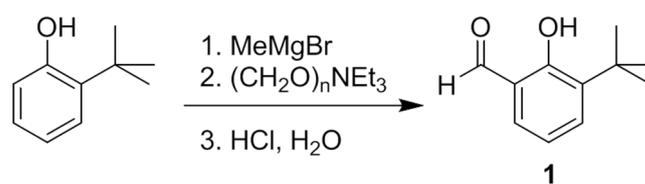
#### Polymerisation of ethylene with the bis(phenoxyimine) zirconium complexes 11 - 18

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 and 60°C, respectively, 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.

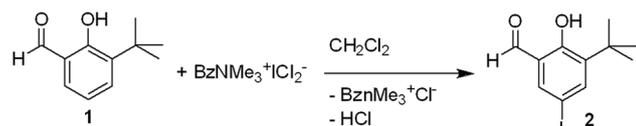
## RESULTS AND DISCUSSION

### 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).



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



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

### Introduction of iodo substituents

For introducing an 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 phenoxyimine compounds

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

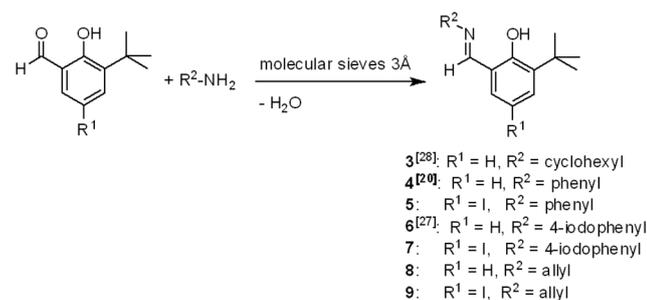
1. The condensation reaction of a substituted salicylaldehyde with an aliphatic or aromatic amine in toluene to give the phenoxyimine compound under azeotropic water separation [28].
2. The reaction of the substituted salicylaldehyde with a small excess of an aliphatic or aromatic amine in the presence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

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

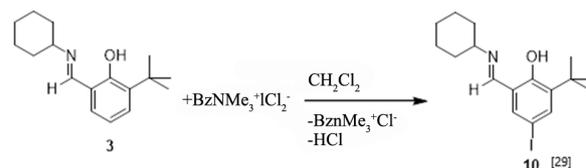
Iodo substituents can be introduced into phenoxyimine compounds in an additional step (see scheme 4). This procedure only works for phenoxyimine compounds bearing a saturated substituent at the imine group. Aromatic and olefinic substituents are iodinated at the double bonds.

### Synthesis of bis(phenoxyimine) zirconium complexes

The phenoxyimine compounds are deprotonated with sodium hydride in tetrahydrofuran and treated with zirconium tetrachloride (Scheme 5). The low yields



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

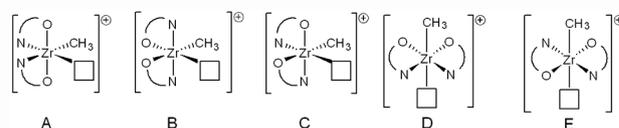


**Scheme 4.** Iodination of phenoxyimine compounds [29].

are due to hydrolysis reactions.

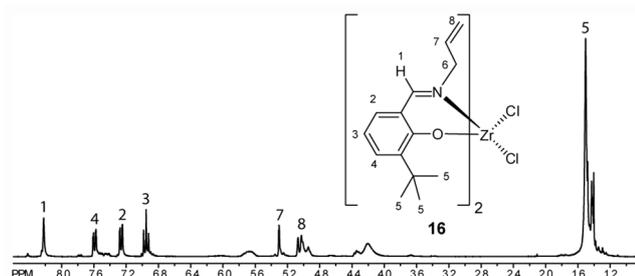
### Spectroscopic characterisation of the bis(phenoxyimine) zirconium complexes

All synthesised bis(phenoxyimine) complexes have been characterized with mass spectroscopy and elemental analysis. <sup>1</sup>H NMR spectra could not be obtained from all complexes due to their poor solubility. In the following, the <sup>1</sup>H NMR (Figure 2) and mass spectra (Figure 3) of complex 16 are discussed. A comparison of the <sup>1</sup>H NMR spectra of compounds 8 and 16 in CD<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub> 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 C<sub>6</sub> 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 dif-



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

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



**Figure 2.**  $^1\text{H}$  NMR spectrum of complex 16 in  $\text{CD}_2\text{Cl}_2$ .

ferent isomers.

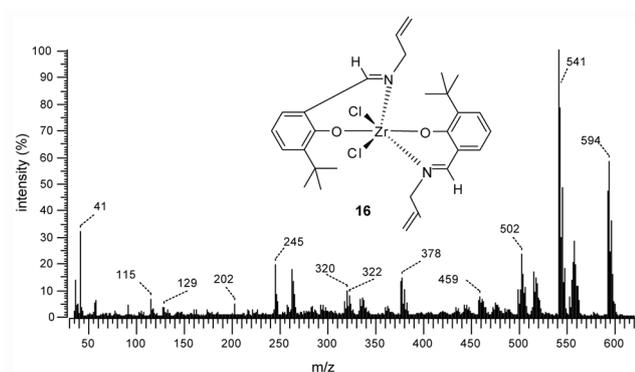
The mass spectrum of complex 16 shows the molecule ion at  $m/z = 594$ . The loss of an HCl molecule leads to the fragment with  $m/z = 557$ . The base peak at  $m/z = 541$  results from the loss of an HCl molecule and a methyl group.

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

The synthesized phenoxyimine complexes were tested in homogeneous ethylene polymerisation reactions. Methylaluminumoxane (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  $\text{PD} = M_w/M_n$ , molecular weight  $M_n$  and  $M_w$ ) are summarized in Table 1.

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

**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

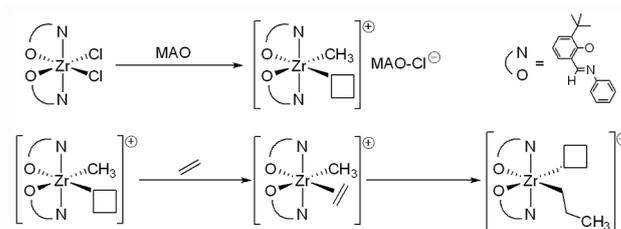
Like for the neutral bis(phenoxyimine) zirconium complexes, five isomers of the active species are formed (Figure 5). Since all possible coordination sites need to be cis, isomers D and E are out of question for the polymerisation experiments since the coordination sites are trans to each other. Isomer A is energetically favored.

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] (see Figure 6).

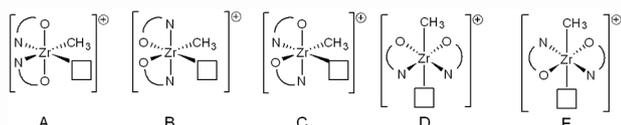
### Comparison of the activities of the bis(phenoxyimine) zirconium complexes

The comparison of the activities of complexes 16, 12 and 11/MAO (Figure 7) 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.

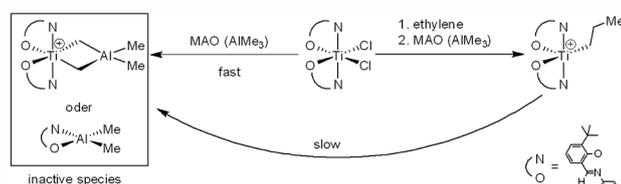
The introduction of an iodo substituent in para-position to the former hydroxyl group has different



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



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



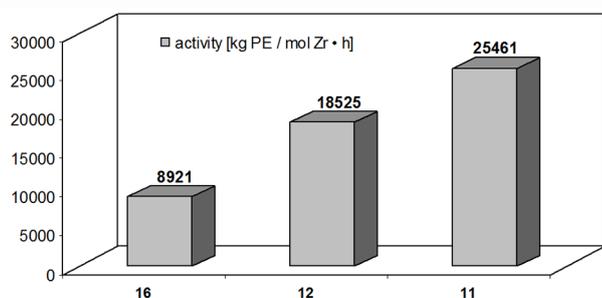
**Figure 6.** Activation and deactivation of bis(phenoxyimine) zirconium complexes.[20].

influences on the polymerization behaviour. 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 (see Figure 8).

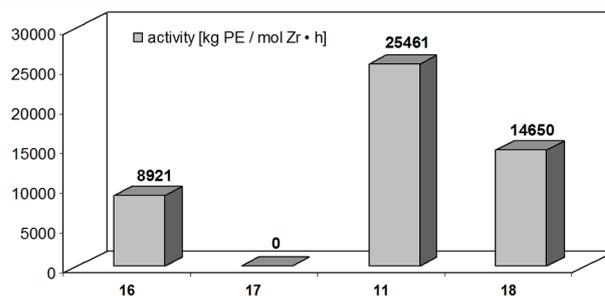
The bis(phenoxyimine) zirconium complexes containing phenyl substituents on the nitrogen atoms show a completely different behaviour (see Figure 9). Here, the mono iodinated complex 14 shows the lowest activity. Complex 13 with the iodo substituent in para-position to the former hydroxyl group shows 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.

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

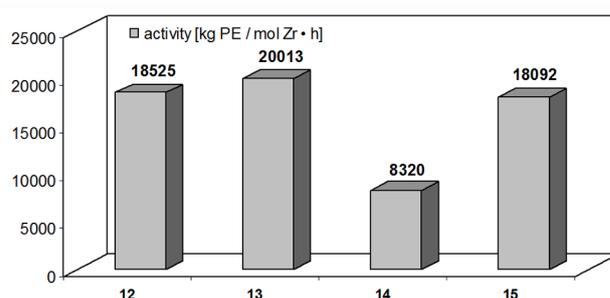
Phenoxyimine catalysts with cyclohexylimino, respectively allylimino substituents, mainly produce polyethylenes with lower polydispersities than cata-



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

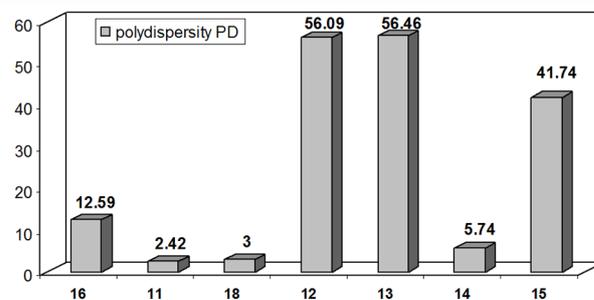


**Figure 8.** Activities of the bis(phenoxyimine) zirconium complexes 16, 17, 11 and 18/MAO.



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

lysts 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. polydispersity of the synthesized polyethylene was shown in Figure 10. An 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



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

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.

## 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 influenced the polydispersities, too. Complexes containing cyclohexylimino substituents gave polyethylenes with very low polydispersities, whereas complexes with unsubstituted phenyl substituents gave polyethylenes with high polydispersities. Broad polydispersities indicated 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.

## ACKNOWLEDGEMENTS

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