



Ti (IV) Complexes of Some Heterocyclic Ligands Synthesis, Characterization and Ethylene Polymerization Activity

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ABSTRACT

31 complexes of bis - (benzimidazole, benzothiazole and benzoxazole) compounds with Ti (IV) metal centers were synthesized, characterized, activated with methylalumoxane (MAO) and then tested for catalytic ethylene polymerization. The activities of the various catalysts were found to be functions of the hetero atoms in the ligand frameworks. The highest activity was obtained with 39 / MAO (573 kg PE / mol cat. h). The produced polyethylenes showed high molecular weights (up to 1.5×10^6 g/mol) and broad molecular weight distributions (PD = 65). This could result from different interactions of the MAO counterion with the heteroatoms of the catalyst ligand generating different active sites.

Key words: Heterocyclic Ligands, Catalyst, Ethylene Polymerization.

INTRODUCTION

A review of the literature revealed that 1,2-bis(2-benzothiazolyl)benzene and 1,2-bis(2-benzothiazolyl)ethane are frequently used as ligands and a considerable number of their complexes with late transition metals are reported¹⁻⁶. Also, the nickel(II), cobalt(II) and copper(II) coordination chemistry of some tetradentate ligands involving benzothiazole functional groups has been published⁷. In all cases involving benzothiazoles as functional groups the ligands behave as nitrogen

donors, except in a few cases involving bridging benzothiazole⁸, in which it is assumed to behave as a bidentate ligand involving both N and S donation. The ligand 2, 6-bis (2-benzothiazolyl) pyridine^{9, 10}, has been shown to behave as an N-3 donor in its complexes with manganese (II), iron (II) and nickel (II). 2,6-Bis(benzimidazolyl)pyridine^{1, 11-23}, and 2,6-bis (benzoxazolyl)pyridine²⁴, derivatives have been reported as ligands for transition metals in order to investigate the complexes for their structures and properties.

In polyolefin chemistry, an increasing interest has been focused on the exploration and development of homogeneous transition metal catalysts, as a result of an increasing demand for polyethylene²⁵⁻³⁰. The vanadium complexes of bis(benzimidazole)amine tridentate ligands [N, N, N], were reported as active

ethylene polymerization catalysts after activation with simple alkylaluminum compounds³¹. 2,6-Bis(2-benzimidazolyl)pyridine zirconium dichloride / MAO polymerizes methylacrylate³². Recently,³³⁻³⁹ we reported the ethylene polymerization activity of benzimidazole, benzothiazole, benzoxazole and 2-(benzimidazolyl) pyridine titanium zirconium and vanadium complexes. Herein we report on the effect of hetero atom on the activity of zirconium, complexes of bis (benzimidazole), benzothiazole, and benzoxazole), and their behaviour towards ethylene polymerization after activation with methylaluminoxane (MAO).

No.	Bridging unit (B)	X	R ₁	R ₂
1	-	S	H	H
2	-	O	H	H
3	-	O	CH ₃	H
4	-	NH	H	H
5	-	NH	CH ₃	H
6	CH ₂	S	H	H
7	CH ₂	O	H	H
8	CH ₂	O	CH ₃	H
9	CH ₂	O	H	CH ₃
10	CH ₂	NH	H	H
11	CH ₂	NH	CH ₃	H
12	CH ₂	NH	Cl	H
13	CH ₂ CH ₂	S	H	H
14	CH ₂ CH ₂	O	H	H
15	CH ₂ CH ₂	O	H	CH ₃
16	CH ₂ CH ₂	O	CH ₃	H
17	CH ₂ CH ₂	NH	H	H
18	CH ₂ CH ₂	NH	CH ₃	H
19	CH ₂ CH ₂	NH	Cl	H
20	1,2-phenylene	S	H	H
21	1,2-phenylene	O	H	H
22	1,2-phenylene	O	CH ₃	H
23	1,2-phenylene	O	H	CH ₃
24	1,2-phenylene	NH	H	H
25	1,2-phenylene	NH	CH ₃	H
26	1,2-phenylene	NH	Cl	H
27	4-Me-1,2-phenylene	S	H	H
28	4-Me-1,2-phenylene	O	H	H
29	4-Me-1,2-phenylene	NH	H	H
30	4-Me-1,2-phenylene	NH	CH ₃	H
31	4-Me-1,2-phenylene	NH	Cl	H

RESULTS AND DISCUSSION

General synthesis of ligand precursors

The condensation reaction of a dicarboxylic acid or an acid anhydride with diamine compound in preheated polyphosphoric acid is a well established procedure for the preparation of the imidazole based ligand precursors^{20, 40, 41} in high yields (Scheme 1).

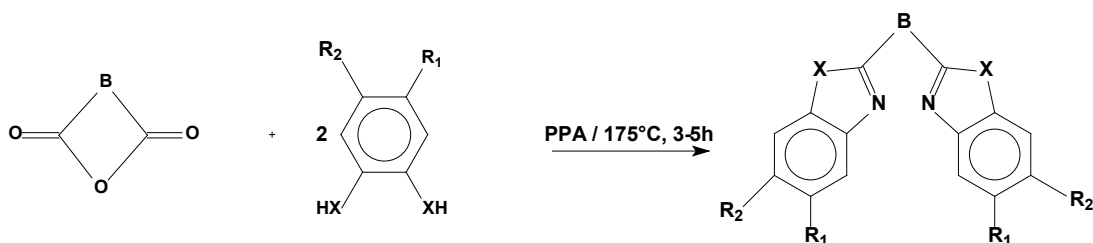
Synthesis of titanium complexes 32-62

The complexes were synthesized according to Scheme 2. The titanium complexes were prepared by ligand displacement reactions. The reaction of the Tetrahydrofuran adducts of titanium tetrachloride with the corresponding ligand precursor in methylene chloride resulted in an immediate colour change and the complexes could be isolated in very high yields (80-95 %). The complexes were characterized by NMR, mass spectrometry and elemental analysis.

Characterization

NMR spectroscopy

The ligand precursors were characterized by NMR spectroscopy using DMSO and CD₂Cl₂ as solvents. Table 2 includes the ¹H and ¹³C NMR data for compounds 1-31. For example, the ¹H NMR



Scheme 1: Synthesis of ligand precursors 1-31.

spectrum of compound **15** (Figure. 1) shows five signals, the doublet at $\delta = 7.54$ ppm [d, 2H, $J_{H,H} = 8.1$ Hz] assigned to H2, the signal at $\delta = 7.35$ ppm [s, 2H] assigned to aromatic protons H1, the doublet at $\delta = 7.16$ ppm [d, 2H, $J_{H,H} = 8.1$ Hz] corresponds to two

protons H3. At $\delta = 3.54$ ppm a singlet assigned to H4, and the signal upfield at $\delta = 2.50$ ppm assigned to the s1x protons of the methyl groups.

Complex No.	Bridging unit (B)	X	R ₁	R ₂
32	-	S	H	H
33	-	O	H	H
34	-	O	CH ₃	H
35	-	NH	H	H
36	-	NH	CH ₃	H
37	CH ₂	S	H	H
38	CH ₂	O	H	H
39	CH ₂	O	CH ₃	H
40	CH ₂	O	H	CH ₃
41	CH ₂	NH	H	H
42	CH ₂	NH	CH ₃	H
43	CH ₂	NH	Cl	H
44	CH ₂ CH ₂	S	H	H
45	CH ₂ CH ₂	O	H	H
46	CH ₂ CH ₂	O	CH ₃	H
47	CH ₂ CH ₂	O	H	CH ₃
48	CH ₂ CH ₂	NH	H	H
49	CH ₂ CH ₂	NH	CH ₃	H
50	CH ₂ CH ₂	NH	Cl	H
51	1,2-phenylene	S	H	H
52	1,2-phenylene	O	H	H
53	1,2-phenylene	O	CH ₃	H
54	1,2-phenylene	O	H	CH ₃
55	1,2-phenylene	NH	H	H
56	1,2-phenylene	NH	CH ₃	H
57	1,2-phenylene	NH	Cl	H
58	4-Me-1,2-phenylene	S	H	H
59	4-Me-1,2-phenylene	O	H	H
60	4-Me-1,2-phenylene	NH	H	H
61	4-Me-1,2-phenylene	NH	CH ₃	H
62	4-Me-1,2-phenylene	NH	Cl	H

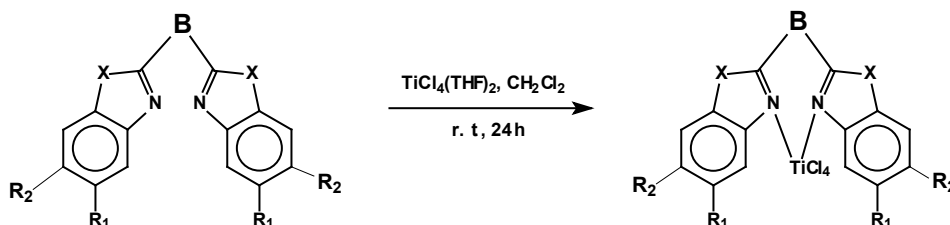
The ¹³C NMR spectrum of compound **15** (Figure. 2) shows nine signals. The two signals downfield at $\delta = 165.5$ ppm and at $\delta = 149.4$ ppm correspond to the carbon atoms 7 and 1 respectively. Each of the five signals at $\delta = 141.8, 134.43, 125.9, 119.7,$ and 109.9 ppm corresponds to two carbon atoms (6, 3, 4, 5 and 2 respectively) of the aromatic rings. The carbon atoms of the bridging group appear upfield at $\delta = 25.7$ ppm. The methyl carbon appears at $\delta = 21.3$ ppm

The ¹H NMR spectrum of complex **46** (Figure.3) shows four resonance signals. The doublet at $\delta = 7.52$ ppm [d, 2H, $J_{H,H} = 8.1$ Hz] assigned to H2,, the signal at $\delta = 7.48$ ppm [s, 2H,] can be assigned to H1, the doublet at $\delta = 7.14$ ppm is assigned to H3. The bridging group protons H4 can be observed as a singlet at $\delta = 3.50$ ppm. The singlet at $\delta = 2.42$ ppm is assigned to the methyl protons H5.

The ¹³C NMR spectrum of complex **46** (Figure. 4) shows nine resonance signals each corresponding to two carbon atoms. The signals at $\delta = 167.2, 149.7, 142.3, 136.0, 127.6, 119.5, 111.2, 25.6$ and 21.4 ppm can be assigned to the carbon atoms C7, C1, C6, C3, C4, C5, C2, C8, and C9 respectively.

Mass spectroscopy

The ligand precursors were also characterized by their mass spectra. The mass spectrum of compound **15** shows the molecular ion peak $m/z = 292$ and $m/z = 146$ ($M^+ - C_9H_8NO$). The ion with the mass $m/z = 132$ can be assigned to (C_8H_6NO), (the full fragmentation pattern is shown in Figure 5).



Scheme 2: Synthesis of the coordination compounds 32-62

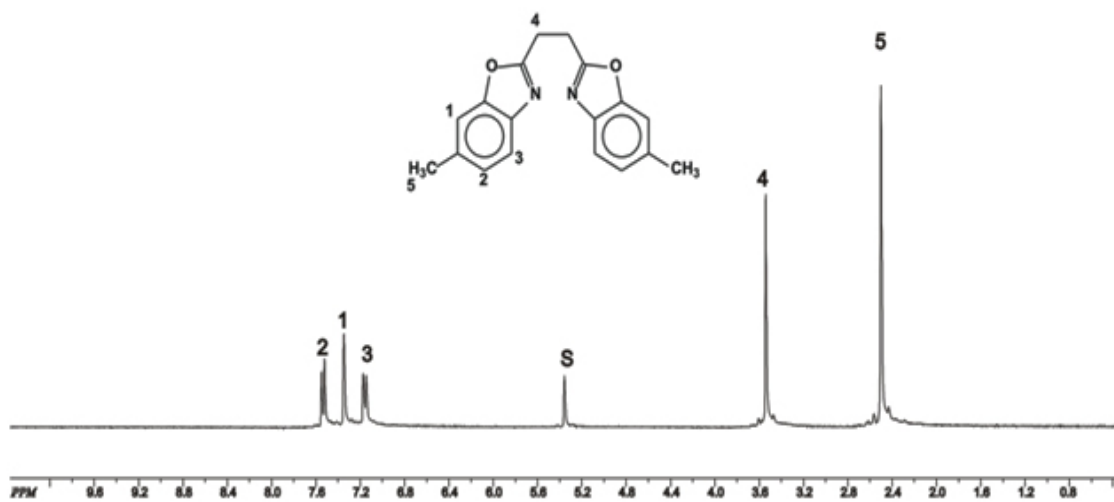
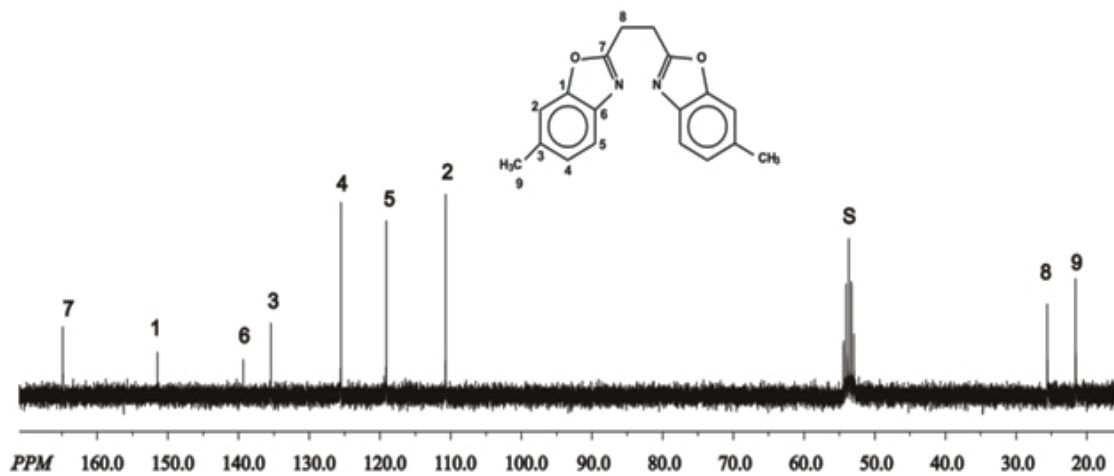
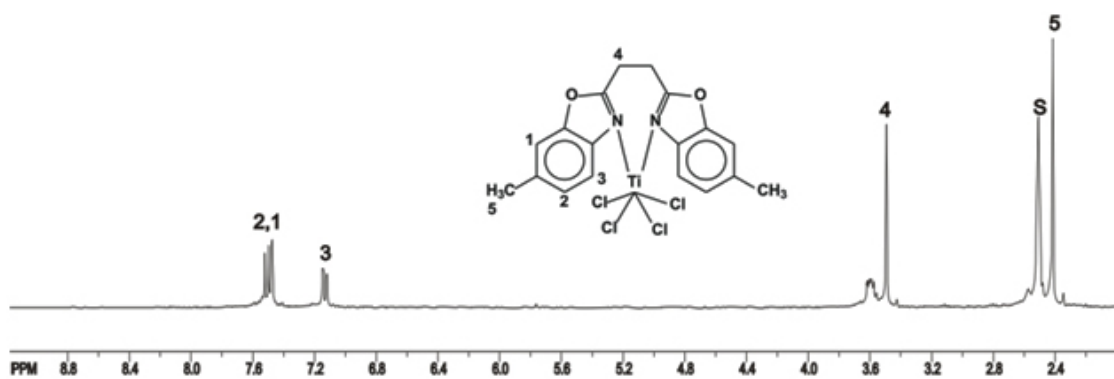
Fig.1: ^1H NMR spectrum of compound 15 in deuterated CD_2Cl_2 Fig. 2: ^{13}C NMR spectrum of compound 15Fig. 3: ^1H NMR spectrum of complex 46

Figure 6 shows the mass spectrum of complex **46**. The molecular ion peak $m/z = 482$. The ion with $m/z = 449$ represents the loss of one

chloride, the ions with $m/z = 411$ result from the loss of two chlorides. The ion with $m/z = 292$ represents the mass of the free ligand.

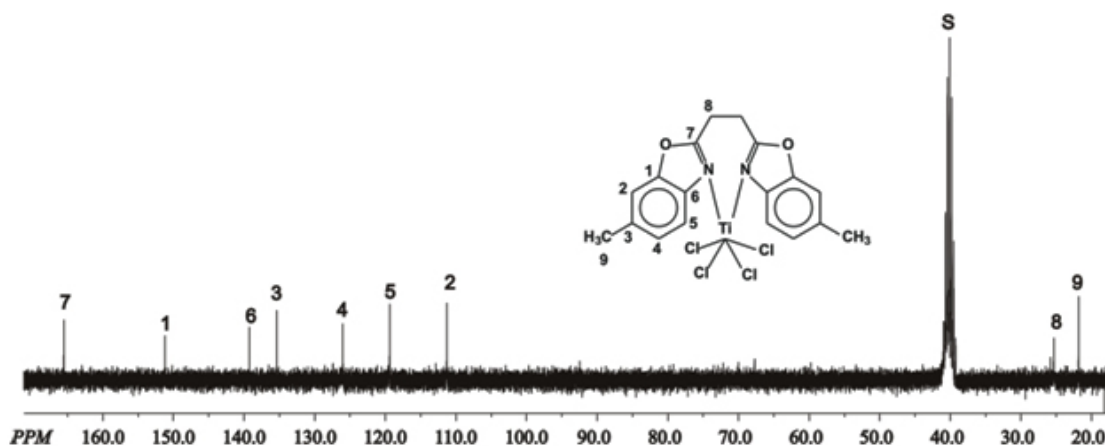


Fig. 4: ^{13}C NMR spectrum of complex **46**

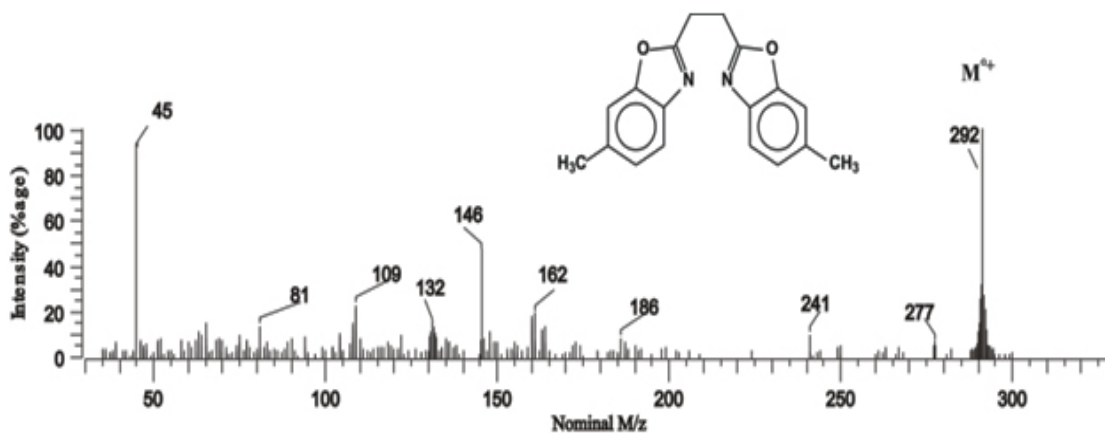


Fig. 5: Mass spectrum of compound **15**

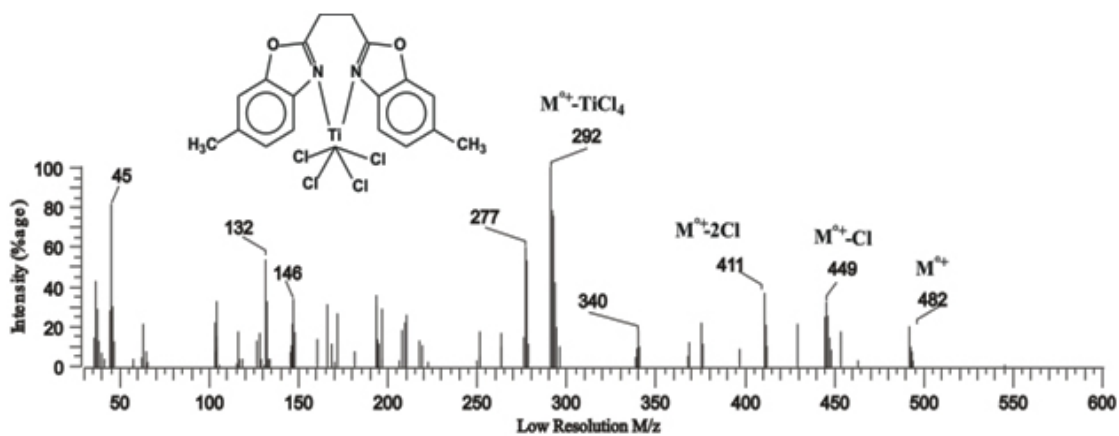


Fig. 6: Mass spectrum of complex **46**

Table 1: Elemental analysis data for heterocycles and their complexes.

Compound No.	General Formula	Calculated			Found		
		C	H	N	C	H	N
1	C ₁₄ H ₈ N ₂ S ₂	62.7	3.0	10.4	62.9	2.8	10.6
2	C ₁₄ H ₈ N ₂ O ₂	71.2	3.4	11.9	70.8	3.6	12.1
3	C ₁₆ H ₁₂ N ₂ O ₂	72.7	4.5	10.6	72.4	4.7	10.8
4	C ₁₄ H ₁₀ N ₄	71.8	4.3	23.9	71.6	4.5	24.1
5	C ₁₆ H ₁₄ N ₄	73.3	5.3	21.4	72.9	5.5	21.1
6	C ₁₅ H ₁₀ N ₂ S ₂	63.8	3.5	9.9	63.6	3.4	10.2
7	C ₁₅ H ₁₀ N ₂ O ₂	72.0	4.0	11.2	71.8	4.2	11.4
8	C ₁₇ H ₁₄ N ₂ O ₂	73.4	5.0	10.1	73.6	5.1	9.8
9	C ₁₇ H ₁₄ N ₂ O ₂	73.4	5.0	10.1	73.6	5.1	9.8
10	C ₁₅ H ₁₂ N ₄	72.6	4.8	22.6	71.8	4.6	22.4
11	C ₁₇ H ₁₆ N ₄	73.9	5.8	20.3	73.7	6.0	20.1
12	C ₁₅ H ₁₀ N ₄ Cl ₂	64.9	4.1	9.5	65.2	4.4	9.1
13	C ₁₆ H ₁₂ N ₂ S ₂	64.9	4.1	9.5	65.2	3.9	9.6
14	C ₁₆ H ₁₂ N ₂ O ₂	72.7	4.6	10.6	72.9	4.5	10.5
15	C ₁₈ H ₁₆ N ₂ O ₂	74.0	5.5	9.6	73.7	5.8	9.9
16	C ₁₈ H ₁₆ N ₂ O ₂	74.0	5.5	9.6	73.8	5.7	9.6
17	C ₁₆ H ₁₄ N ₄	73.3	5.3	21.4	72.9	5.4	21.4
18	C ₁₈ H ₁₈ N ₄	74.5	6.2	19.3	74.8	5.9	19.6
19	C ₁₆ H ₁₂ N ₄ Cl ₂	58.0	3.6	16.9	58.2	3.7	17.1
20	C ₂₀ H ₁₂ N ₂ S ₂	68.8	3.5	8.1	69.7	3.5	8.2
21	C ₂₀ H ₁₂ N ₂ O ₂	76.9	3.9	9.0	77.1	3.7	8.8
22	C ₂₂ H ₁₆ N ₂ O ₂	77.7	4.7	8.2	77.7	4.7	8.4
23	C ₂₂ H ₁₆ N ₂ O ₂	77.7	4.7	8.2	77.7	4.7	8.4
24	C ₂₀ H ₁₄ N ₄	77.4	4.5	18.1	77.4	4.5	18.1
25	C ₂₂ H ₁₈ N ₄	78.1	5.3	16.6	78.6	5.2	17.1
26	C ₂₀ H ₁₂ N ₄ Cl ₂	63.3	3.2	14.8	64.1	3.5	15.2
27	C ₂₁ H ₁₄ N ₂ S ₂	70.4	3.9	7.8	69.8	4.1	7.5
28	C ₂₁ H ₁₄ N ₂ O ₂	77.3	4.3	8.6	76.9	4.6	8.9
29	C ₂₁ H ₁₆ N ₄	77.8	4.9	17.3	78.1	5.2	17.6
30	C ₂₃ H ₂₀ N ₄	78.4	5.7	15.9	78.1	5.5	16.2
31	C ₂₁ H ₁₄ N ₄ Cl ₂	64.1	3.6	14.2	64.5	3.9	13.9
32	C ₁₄ H ₈ N ₂ S ₂ TiCl ₄	36.7	1.8	6.1	36.2	1.7	5.9
33	C ₁₄ H ₈ N ₂ O ₂ TiCl ₄	39.4	1.9	6.6	39.8	1.8	6.7
34	C ₁₆ H ₁₂ N ₂ O ₂ TiCl ₄	42.3	2.6	6.2	41.9	2.3	5.9
35	C ₁₄ H ₁₀ N ₄ TiCl ₄	39.6	2.4	13.2	39.1	2.6	13.7
36	C ₁₆ H ₁₄ N ₄ TiCl ₄	42.4	3.1	12.4	42.7	2.9	12.2
37	C ₁₅ H ₁₀ N ₂ S ₂ TiCl ₄	38.1	2.1	5.9	38.4	2.1	5.6
38	C ₁₅ H ₁₀ N ₂ O ₂ TiCl ₄	40.9	2.3	6.4	40.8	2.0	6.4
39	C ₁₇ H ₁₄ N ₂ O ₂ TiCl ₄	42.7	2.9	5.9	42.3	3.0	5.4
40	C ₁₇ H ₁₄ N ₂ O ₂ TiCl ₄	42.7	2.9	5.9	42.6	2.7	5.5
41	C ₁₅ H ₁₂ N ₄ TiCl ₄	41.9	2.8	13.0	42.2	2.6	13.4
42	C ₁₇ H ₁₆ N ₄ TiCl ₄	43.8	3.4	12.0	43.5	3.8	11.7
43	C ₁₅ H ₁₀ N ₄ Cl ₂ TiCl ₄	35.5	2.0	11.0	35.2	2.1	10.8
44	C ₁₆ H ₁₂ N ₂ S ₂ TiCl ₄	39.5	2.5	5.8	39.3	2.5	5.4
45	C ₁₆ H ₁₂ N ₂ O ₂ TiCl ₄	42.3	2.6	6.2	42.0	2.2	5.9

46	$C_{18}H_{16}N_2O_2 TiCl_4$	44.8	3.3	5.8	44.7	3.4	5.6
47	$C_{18}H_{16}N_2O_2 TiCl_4$	44.8	3.3	5.8	45.2	3.1	5.9
48	$C_{16}H_{14}N_4 TiCl_4$	42.5	3.1	12.4	42.3	3.3	12.8
49	$C_{18}H_{18}N_4 TiCl_4$	45.0	3.8	11.7	45.6	3.5	11.4
50	$C_{16}H_{12}N_4Cl_2 TiCl_4$	36.9	2.3	10.7	36.8	2.6	10.9
51	$C_{20}H_{12}N_2S_2 TiCl_4$	44.9	2.2	5.2	45.3	1.9	4.9
52	$C_{20}H_{12}N_2O_2 TiCl_4$	47.8	2.4	6.6	47.4	2.7	6.8
53	$C_{22}H_{16}N_2O_2 TiCl_4$	49.8	3.0	5.3	49.7	2.9	5.5
54	$C_{22}H_{16}N_2O_2 TiCl_4$	49.8	3.0	5.3	49.2	3.3	5.6
55	$C_{20}H_{14}N_4 TiCl_4$	48.0	2.8	11.2	48.5	2.4	11.5
56	$C_{22}H_{18}N_4 TiCl_4$	50.0	3.4	10.6	49.8	3.5	10.1
57	$C_{20}H_{12}N_4Cl_2 TiCl_4$	42.3	2.1	9.9	42.5	1.9	9.5
58	$C_{21}H_{14}N_2S_2 TiCl_4$	46.0	2.6	5.1	46.3	2.9	4.8
59	$C_{21}H_{14}N_2O_2 TiCl_4$	48.8	2.7	5.4	47.9	3.0	5.2
60	$C_{21}H_{16}N_4 TiCl_4$	49.0	3.1	10.9	48.7	3.4	10.7
61	$C_{23}H_{20}N_4 TiCl_4$	50.9	3.7	10.3	51.3	3.4	10.6
62	$C_{21}H_{14}N_4Cl_2 TiCl_4$	43.3	2.4	9.6	43.7	2.6	9.4

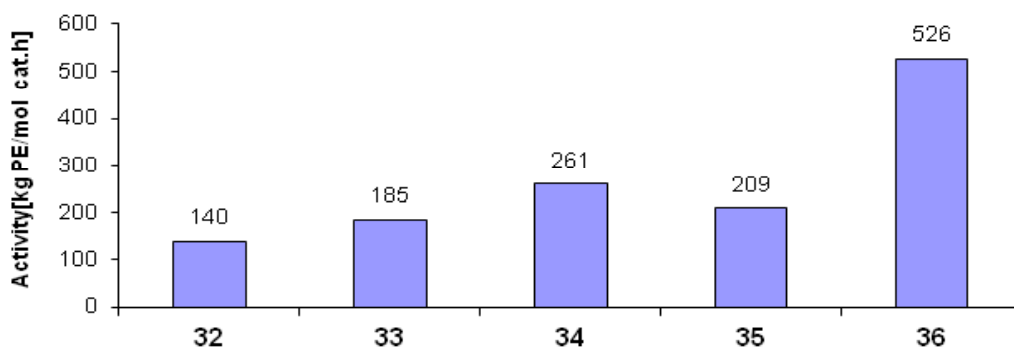


Fig. 7: Activities of bis (benzothiazolyl, benzoxazolyl, benzimidazolyl) titanium complexes

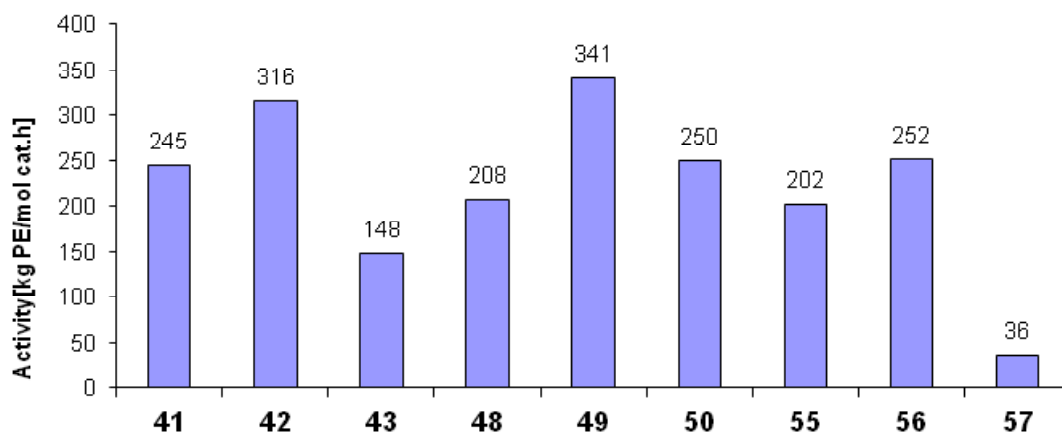


Fig. 8: Effect of bridging unit and substituent type on the activities of bis (benzimidazolyl) titanium complexes

Elemental analysis

The elemental analysis data of the synthesized ligands and their complexes are given in (Table 1). The data shows the formation of metal complexes in a 1: 1 (M: L) molar ratio.

Polymerization results

All coordination compounds were activated with MAO according to the mechanism proposed for the activation of metallocene^{42, 43} and 2,6-bis(imino)pyridine iron (II)⁴⁴ catalyst precursors.

The complexes of titanium with ligands derived from bis (benzimidazolyl), bis (benzoxazolyl)

Table 2: Polymerization activities of complexes 32-62

No.	Activity [kg/ mol cat. h]
32	140
33	185
34	261
35	209
36	526
37	279
38	472
39	573
40	374
41	245
42	316
43	148
44	155
45	239
46	386
47	205
48	208
49	341
50	250
51	210
52	355
53	402
54	110
55	202
56	252
57	36
58	260
59	176
60	204
61	315
62	88

and bis (benzothiazolyl) compounds showed variable activities for ethylene polymerization (Table 2).

The activities are greatly influenced by the hetero atoms in addition to the ligand environment.

2,2-bis(benzimidazolyl), 1,1-Bis (benzimidazolyl) methane, 1,2-bis(benzimidazolyl) ethane and 1,2-bis(benzimidazolyl) benzene titanium complexes act as catalysts for ethylene polymerization, after activation with methylaluminoxane (MAO). They showed variable activities under different polymerization conditions.

The titanium complexes generally show moderate to good activities compared to the benchmark complexes zirconocene (Cp₂ZrCl₂).

The titanium complexes derived from the ligand systems 2, 2-bis (benzothiazolyl **32**, benzoxazolyl (**33**, **34**) and benzimidazolyl (**35**, **36**) (Figure 7) shows the following activity order **35 / MAO > 33 / MAO > 32 / MAO**. The methyl substituted complexes **34** and **36** show higher activities compared to the unsubstituted complexes **33** and **35**. The different behaviours most probably occur due to the structure of the ligands in which the steric bulk and the electronic state greatly influence the activities of the complexes.

Among the titanium complexes with 1, 1-bis (benzimidazolyl) methane ligands, the activities of the systems decrease in the order **41/MAO > 42/MAO > 43/MAO** (see Figure 8). This result is in contrast to the fact that complexes with both large steric bulk and high electron withdrawing effect will have the highest activities. Complex **43** with a chloro-substituent in *meta* position to the imino nitrogen atoms shows a reduced activity, while complex **42** with a methyl group in the same position shows a somewhat higher activity. One explanation could be the fact that chlorine as a Lewis base can block the active sites of a neighbouring catalyst molecule.

The unsubstituted complex **41** shows the highest activity. The same trend is observed for the titanium complexes of 1, 2-bis (benzimidazolyl) benzene: **55/MAO > 56/MAO > 57/MAO**.

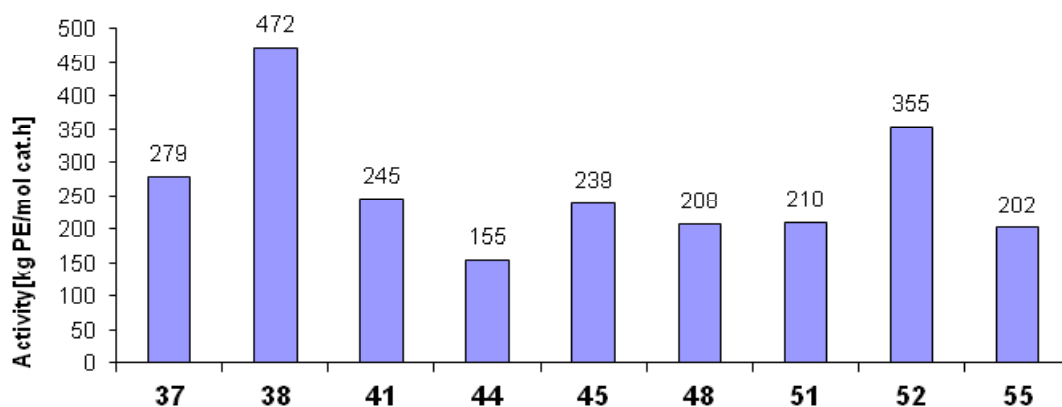


Fig. 9: Activities of benzothiazolyl (37, 44, 51), benzoxazolyl (38, 45, 52) and benzimidazolyl (41, 48, 55) titanium complexes

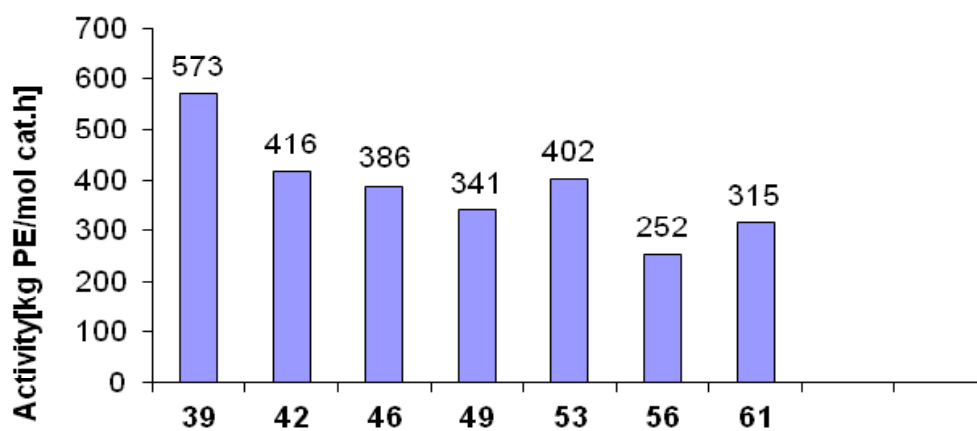


Fig. 10: Effect of methyl substituent on the activities of benzoxazole (39, 46, 53) and benzimidazole (42, 49, 56, 61)

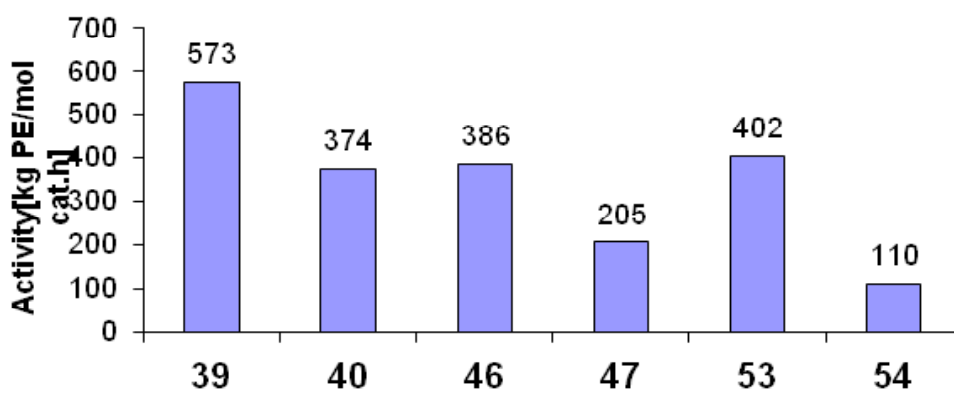


Fig. 11: Effect of substituent position on the activities of benzoxazolyl titanium complexes

For the titanium complexes derived from 1, 2-bis (benzimidazolyl) ethane, the activities decrease in the following order: **49/MAO** > **50/MAO** > **48/MAO** (Figure 8).

Ethylene polymerization reactions with complexes of titanium with the ligand systems 1,1-bis(benzothiazolyl)methane, 1,2-bis(benzothiazolyl)

ethane, and 1,2-bis(benzothiazolyl)benzene. The activities of titanium complexes decrease in the order of 1, 1-bis (benzothiazolyl)methane (**37**) > 1,2-bis(benzothiazolyl)benzene (**51**) > 1,2-bis(benzothiazolyl) ethane (**44**) (Figure 9). This order of activity can be accounted for by structural variations of the ligand systems.

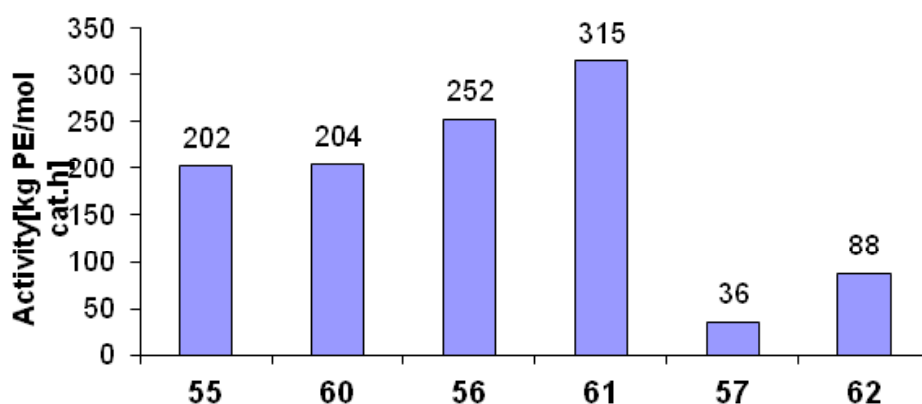


Fig. 12: Effect of substituent type on the activities of bis (benzimidazolyl) benzene titanium complexes

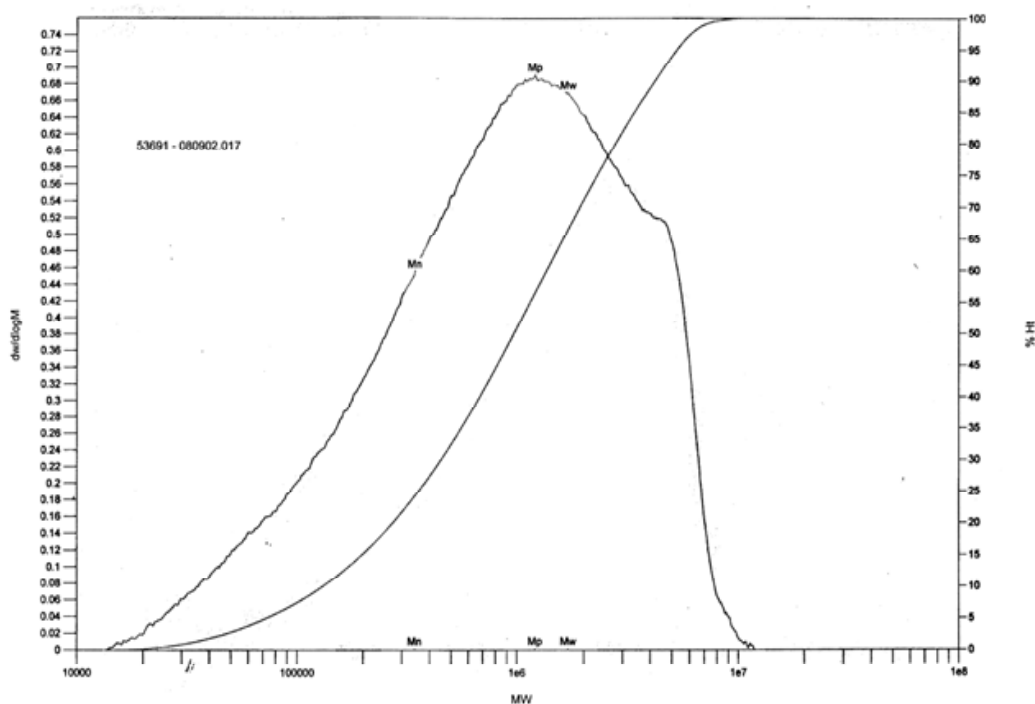


Fig. 13: GPC profile for polyethylene produced with catalyst 55 / MAO

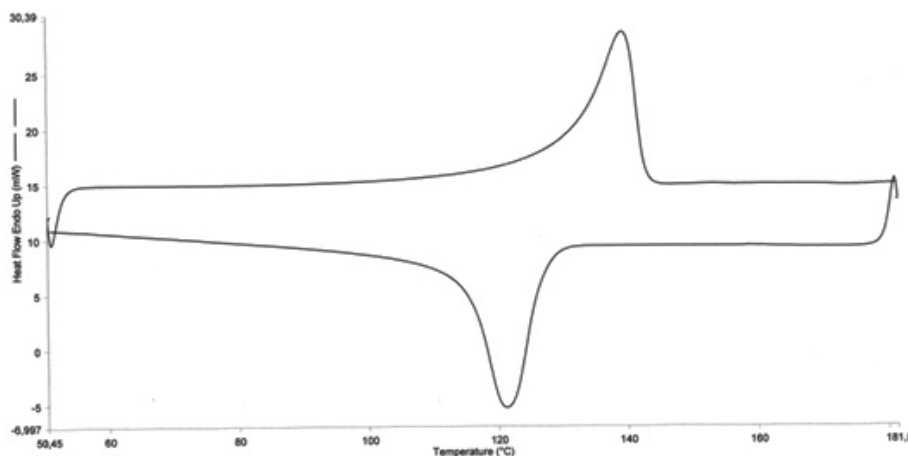


Fig. 14: DSC curve for the polyethylene produced with the catalyst 55 / MAO

The activity of unsubstituted (benzothiazolyl, benzoxazolyl and benzimidazolyl) titanium complexes (Figure 9) shows great dependence on both heteroatom and bridging units. For example the complexes derived from the ligand systems bis(benzothiazolyl) methane **37** > 1, 1-bis(benzothiazolyl) methane **51** > 1, 2-bis(benzothiazolyl) benzene **51** > 1, 2-bis(benzothiazolyl) ethane **44**. The bis(benzoxazolyl, benzimidazolyl) derived titanium complexes shows the same activity order 1, 1-bis(benzoxazolyl) methane **38** > 1, 2-bis(benzoxazolyl) ethane **45** > 1, 2-bis(benzoxazolyl) benzene **52**. 1, 1-bis(benzimidazolyl) methane **41** > 1, 2-bis(benzimidazolyl) ethane **48** > 1, 2-bis(benzimidazolyl) benzene **55**. The similar activity order of O, N containing ligands can be attributed to the similarities between the two hetero atoms. The 1,1-bis(benzoxazolyl) methane complex **38** shows a higher activity than the 1,2-bis(benzoxazolyl) benzene complex **52** and the 1,2-bis(benzoxazolyl) ethane complex **45**. They show higher activities than those obtained from the benzothiazole ligand of the same type (Figure 9). This is most probably due to extra stabilization of the active species caused by the strong electronegative oxygen atom leading to an increase in electrophilicity of the metal center.

The methyl substituted bis-(benzoxazolyl, and benzimidazolyl) titanium complexes (Figure 10)

Shows that, the bis benzoxazolyl complexes were more active than the bis benzimidazolyl

complexes, for example the catalyst system **39** / MAO shows an activity of 573 [kg/ mol cat. h] while the catalyst derived from 1, 1, bis(benzimidazolyl) methane **42** / MAO shows an activity of 416 [kg/ mol cat. h].

The methyl substituted bis-benzoxazole titanium complexes (Figure 11) behave differently depending on the position of the methyl group at the phenyl ring of the benzoxazolyl moiety. When the methyl group is introduced in the *meta*-position to the imino-nitrogen atom (**39**, **46**, **53**) it leads to an increase of the activity due to both electronic and steric effects. On the other hand, when the methyl group is introduced in the *para* position (**40**, **47**, **54**) with respect to the imino nitrogen atom, the activities drop because the electron density on the nitrogen atom increases and consequently the nucleophilicity of the central metal atom increases which weakens the interaction between the metal atom and the p-electrons of the ethylene monomer and hence this decreases the rate of ethylene insertion in the chain-growth steps^{27, 45}.

The activities of bis (benzimidazolyl) benzene titanium complexes (**55**, **56**, and **57**) and bis (benzimidazolyl) - 4-methyl benzene titanium complexes (**60**, **61**, and **62**) (Figure 11) revealed that the chloro substituted complexes are more active than the methyl substituted complexes. However both chloro and methyl substituted complexes of bis (benzimidazolyl) benzene (**56**, **57**) are much more

Table 3: ¹H NMR, ¹³C NMR and mass spectroscopic data of ligand precursors and complexes

No	¹ H NMR δ [ppm]	¹³ C NMR δ [ppm]	Mass m/z (%)
1	8.15(d,2H), 7.96(d,2H), 7.54(t,2H), 7.47(t,2H)	n.d.	268 M ²⁺ (100)
2	7.93(d,2H), 7.73(d,2H), 7.51(t,4H)	152.1, 151.2, 141.4, 127.8, 126.0, 121.8, 111.7	236 M ²⁺ (100)
3	7.63(s,2H), 7.11(d,2H), 6.98(d,2H) 2.37(s,6H)	155.4, 147.5, 141.3, 132.7,127.7,123.2, 108.6, 20.9	264 M ²⁺ (100)
4	12.22(br,2H, NH), 7.11- 6.99(m,8H)	156.0, 126.4, 123.8, 116.0	234 M ²⁺ (100)
5	12.32(br,2H,NH), 6.99- 6.96(m,2H), 6.87- 6.84(m,4H), 2.23(s,6H,CH ₃)	156.0, 155.6, 132.9, 126.1, 124.4, 123.2, 115.8, 115.6, 21.2	262 M ²⁺ (100)
6	8.04(d,2H), 7.95(d,2H), 7.47(t,2H), 7.43(t,2H), 5.05(s,2H,CH ₂)	167.0, 153.2, 135.9, 127.0, 125.9, 123.2, 122.9, 38.5	282 M ²⁺ (100)
7	7.70(d,2H), 7.50 (d,2H), 7.31(t,4H), 4.62(s,2H, CH ₂)	159.5, 151.5, 141.3, 125.5, 124.8, 120.4, 110.9, 29.6	250 M ²⁺ (100)
8	7.60(d,2H), 7.52(s,2H), 7.21(d,2H), 4.84(s,2H,CH ₂), 2.41(s,6H, 2CH ₃)	161.4, 149.5, 141.5, 134.7, 126.9, 120.2, 110.9, 29.4, 21.6	278 M ²⁺ (100)
9	7.59(d,2H), 7.52(s,2H), 7.19(d,2H), 4.82(s,2H,CH ₂), 2.46(s,6H,2CH ₃)	160.8, 151.5, 139.2, 136.0, 126.4, 119.7, 111.5, 29.3, 21.9	278 M ²⁺ (100)
10	12.41(s,2H, NH), 7.46(m,4H), 7.11(m,4H), 4.43(s,2H,CH ₂)	150.8, 138.4 122.9, 115.4, 29.8	248 M ²⁺ (100)
11	7.32(d,2H), 7.23(s,2H), 6.91(d,2H), 4.35(s,2H,CH ₂), 2.33(s,6H,CH ₃)	150.6, 139.2 137.9, 131.2, 123.5, 115.3, 114.7, 30.0, 21.9	276 M ²⁺ (100)
12	7.54(s,2H), 7.48(d,2H), 7.14(d,2H), 4.46(s,2H,CH ₂)	149.3, 134.7, 132.5, 129.6, 125.9, 116.6, 115.1, 26.8	317 M ²⁺ (100)
13	7.98(d,2H), 7.82(d,2H), 7.44(t,2H), 7.37(t,2H), 3.74(s,4H, 2CH ₂)	169.6, 153.5, 135.5, 126.4, 125.3, 123.0, 121.9, 33.6	296 M ²⁺ (100)
14	7.65(t,2H), 7.46(t,2H), 7.28(d,4H), 3.56(s,4H)	165.2, 151.2, 141.6, 125.2, 124.7, 120.2, 110.9, 25.7	264 M ²⁺ (100)
15	7.46(s,2H), 7.41(d,2H), 7.16(d,2H), 3.55(s,4H,2CH ₂), 2.47(s,6H,2CH ₃)	165.5, 149.4, 141.8, 134.3, 125.9, 119.7, 109.9, 25.7, 21.3	292 M ²⁺ (100)

16	7.53(d,2H), 7.35(s,2H), 7.16(d,2H), 3.54(s,4H,2CH ₂), 2.50(s,6H,2CH ₃)	164.8, 151.5, 139.3, 135.4, 125.5, 119.1, 110.7, 25.6, 21.6	292 M ⁺ (100)
17	7.57 (d,4H), 7.26 (t,4H), 3.56(s,4H,2CH ₂)	153.8, 135.4, 124.3, 114.6, 25.4	262 M ⁺ (100)
18	7.31 (d,2H), 7.22(s,2H), 6.90 (d,2H), 3.51 (s,4H,CH ₂), 2.33(s,6H,CH ₃)	154.2, 138.7, 137.4, 131.2, 123.5, 115.0, 114.5, 27.0, 21.9	290 M ⁺ (100)
19	7.50 (s,2H), 7.44(d,2H), 7.09(d,2H), 3.36 (s,4H,2CH ₂)	156.2, 140.6, 138.0, 126.3, 122.1, 116.2, 115.1 27.0	331 M ⁺ (100)
20	8.01(d,2H), 7.93- 7.90(dd,2H), 7.77(d,2H), 7.61-7.58(dd,2H), 7.44(t,2H), 7.33(t,2H)	166.4, 153.4, 136.6, 133.5, 131.6, 131.5, 127.2, 126.3, 123.8, 121.9	344 M ⁺ (100)
21	8.07(t,2H), 7.81(t,2H), 7.72(t,2H), 7.53(d,2H), 7.35(d,4H)	162.2, 151.0, 141.9, 132.5, 131.7, 127.4, 126.5, 125.5, 120.7, 111.5	312 M ⁺ (100)
22	8.13(t,2H), 7.84(d,2H), 7.52(s,2H), 7.44(d,2H), 7.19(d,2H), 2.40(s,6H,2CH ₃)	162.3, 149.4, 142.2, 134.9, 132.4, 131.6, 127.6, 127.4, 120.5, 110.9, 21.6	340 M ⁺ (100)
23	8.12-8.09(m,2H), 7.85-7.82(m,2H), 7.60(d,2H), 7.37(s,2H), 7.20(d,2H), 2.41(s,6H, 2CH ₃)	161.8, 151.4, 139.8, 136.5, 132.3, 131.7, 127.5, 126.7, 120.2, 111.4, 21.9	340 M ⁺ (100)
24	7.88 (d,1H), 7.80(d,1H), 7.69(t,2H), 7.64(s,2H, N-H), 7.61 (m,4H),7.26(m,4H),	151.6, 137.9, 133.5, 131.9, 129.4, 123.5, 115.5	310 M ⁺ (100)
25	8.05(s,2H), 7.78(s,2H,N-H), 7.63(s,2H), 7.56(d,2H), 7.35(s,2H), 7.00(d,2H), 2.37(s,6H,CH ₃)	151.6, 139.0, 137.8, 132.2, 132.0, 130.4, 129.9, 115.9, 115.1, 22.0	338 M ⁺ (100)
26	8.14 (s,2H), 7.61 (br,4H), 7.55 (d,2H), 7.12(d,2H)	154.3, 141.4, 138.9, 132.1, 130.4, 130.3, 126.6, 122.4, 117.1, 115.8	378 M ⁺ (100)
27	8.01-7.95(m,2H), 7.84- 7.79(m,3H), 7.74(s,1H), 7.48-7.44(m,3H), 7.38- 7.33(m,2H), 2.50(s,3H, CH ₃)	166.6, 166.5, 153.6, 153.5, 141.1, 136.8, 136.8, 133.5, 131.8, 131.2, 131.1, 131.0, 126.3, 126.2, 125.5, 125.4, 123.6, 123.5, 121.7, 121.6, 21.3	358 M ⁺ (100)
28	7.97(d,1H), 7.89(s,1H), 7.64(d,2H), 7.59(d,1H), 7.49(d,2H), 7.31(t,4H), 2.37(s,3H,CH ₃)	162.7, 162.6, 151.2, 151.1, 142.2, 142.1, 142.1, 132.1, 131.9, 131.19, 127.5, 125.5,	326 M ⁺ (100)

		125.4, 124.9, 124.6, 124.5, 120.4, 120.2, 110.7, 110.6, 21.4	
29	9.67(s,2H,N-H), 7.97(d,1H), 7.92(s,1H), 7.56-7.51(m,4H), 7.48-7.46(d,1H), 7.18- 7.15(m,4H), 2.40(s;3H,CH ₃)	152.1,152.0,140.3, 132.6, 132.5, 131.1, 131.0 129.9, 127.3, 122.8, 122.7, 115.2, 21.5	324 M ⁺ (100)
30	7.96(d,1H), 7.91(s,1H), 7.44- 7.43(m,3H), 7.35(s,2H), 6.98(d,2H), 2.42(s,3H,CH ₃), 2.36(s,6H,2CH ₃)	151.7,151.6,140.1, 132.5, 132.2, 132.1, 132.0, 131.0, 129.7, 127.2, 124.3, 124.2, 116.3, 115.5, 22.0, 21.4	352 M ⁺ (100)
31	8.09(d,1H), 8.04(s,1H), 7.62(d,2H), 7.56- 7.53(m,2H), 7.36(d,1H), 7.10(d,2H), 2.38(s,3H,CH ₃)	155.0,155.1, 141.7,141.6, 139.2,139.1, 132.5,132.1, 130.8,130.3, 127.6,126.3,126.2 122.2,122.1 117.0,116.9, 115.7,115.6, 21.4	393 M ⁺ (100)
32	8.23(d,2H), 7.97(d,2H), 7.56(t,2H), 7.50(t,2H)	n.d.	458 M ⁺ (20), 422 M ⁺ -Cl (10), 387 M ⁺ -2Cl (20), 317 M ⁺ -4Cl (20), 268 M ⁺ -TiCl ₄ (100)
33	7.95(dd,4H), 7.60- 7.56(m,4H)	152.3, 150.9, 141.3, 128.5, 126.7, 121.8, 112.4	425 M ⁺ (30), 390 M ⁺ -Cl (25), 321 M ⁺ -3Cl (10), 284 M ⁺ -4Cl (20), 236 M ⁺ -TiCl ₄ (100)
34	7.66(s,2H), 7.20(d,2H), 7.00(d,2H) 2.39(s,6H)	155.2, 147.7, 141.5, 132.6,127.5,123.0, 109.1, 21.1	454 M ⁺ (20), 418 M ⁺ -Cl (10), 383 M ⁺ -2Cl (10), 314 M ⁺ -4Cl (20), 264 M ⁺ -TiCl ₄ (100)
35	12.50(br,2H,NH), 7.40(d,4H), 7.15(t,4H)	156.1, 126.6, 123.8, 116.2	424 ⁺ (20), 352 M ⁺ -2Cl (20), 317 M ⁺ -3Cl (10),234 M ⁺ -TiCl ₄ (100)
36	12.12(br,2H,NH), 7.06(d,2H), 6.97(s,2H), 6.82(d,2H), 2.17(s,6H, 2CH ₃)	156.1, 155.8, 133.0, 126.2, 124.6, 124.1, 115.9, 115.7, 21.3	495 M ⁺ (10), 478 M ⁺ -CH ₃ (15), 423 M ⁺ -2Cl (20), 389 M ⁺ -3Cl (20), 352 M ⁺ -4Cl(20) 262 M ⁺ -ZrCl ₄ (50)

37	8.02(d,2H), 7.92(d,2H), 7.45(t,2H), 7.38(t,2H), 5.02(s,2H,CH ₂)	167.0, 153.2, 135.8, 127.0, 125.9, 123.2, 122.9, 38.4	472 M ²⁺ (20), 436 M ²⁺ -Cl (15), 401 M ²⁺ -2Cl (10), 365 M ²⁺ -3Cl (25), 282 M ²⁺ -TiCl ₄ (100) M ²⁺ -4Cl (20), 276 M ²⁺ -TiCl ₄ (100)
38	7.69(d,4H), 7.36(t,4H), 4.85(s,2H,CH ₂)	161.4, 151.2, 141.3, 126.1, 125.4, 120.4, 111.5, 29.3	438 M ²⁺ (20), 368 M ²⁺ -2Cl (10), 331 M ²⁺ -3Cl(10), 295 M ²⁺ -4Cl (15), 250 M ²⁺ -TiCl ₄ (100)
39	7.61(d,2H), 7.53(s,2H), 7.23(d,2H), 4.84(s,2H,CH ₂), 2.41(s,6H,2CH ₃)	161.5, 149.4, 141.5, 134.8, 127.0, 120.2, 111.0, 29.4, 21.7	468 M ²⁺ (15), 432 M ²⁺ -Cl (20),361 M ²⁺ -3Cl (30), 296 M ²⁺ -4Cl-2CH ₃ (25), 278 M ²⁺ - TiCl ₄ (100)
40	7.60(d,2H), 7.54(s,2H), 7.21(d,2H), 4.82(s,2H,CH ₂), 2.44(s,6H,2CH ₃)	160.8, 151.5, 139.1, 136.1, 126.5, 119.8, 111.5, 29.3, 21.9	468 M ²⁺ (20), 432 M ²⁺ -Cl (10), 361 M ²⁺ -3Cl (20), 296 M ²⁺ -4Cl-2CH ₃ (20), 278 M ²⁺ - TiCl ₄ (100)
41	7.52-7.49(m,4H), 7.52- 7.14(m,4H), 4.55(s,2H,CH ₂)	149.0, 135.4, 124.4, 115.1, 27.5	438 M ²⁺ (10), 402 M ²⁺ -Cl (20), 367 M ²⁺ -2Cl (20), 248 M ²⁺ -TiCl ₄ (100)
42	7.63(d,2H), 7.54(s,2H), 7.31(d,2H), 5.25(s,2H,CH ₂), 2.42(s,6H,2CH ₃)	146.3, 136.3, 132.3, 130.1, 127.8, 114.3, 114.1, 25.8, 21.8	466 M ²⁺ (10), 428 M ²⁺ -Cl(15), 393 M ²⁺ -2Cl (15), 357 M ²⁺ -3Cl (20), 319
43	7.88(s,2H), 7.80(d,2H), 7.51(d,2H), 5.18(s,2H,CH ₂)	149.3, 134.7, 132.6, 129.8, 125.9, 116.5, 114.9, 26.9	506 M ²⁺ (10), 470 M ²⁺ -Cl (20), 434 M ²⁺ -2Cl (15), 397 M ²⁺ -3Cl (10), 316 M ²⁺ -TiCl ₄ (100)
44	8.02(d,2H), 7.99(d,2H), 7.44-7.35(m,4H), 3.68(s,4H,2CH ₂)	170.6, 153.3, 135.3, 126.9, 125.8, 123.1, 122.9, 33.1	486 M ²⁺ (10), 450 M ²⁺ -Cl (15), 415 M ²⁺ -2Cl (10), 296 M ²⁺ -TiCl ₄ (75)
45	7.59(t,2H), 7.26(t,2H), 7.16(d,2H), 7.09(d,2H), 3.47(s,4H,2CH ₂)	166.1, 150.9, 141.4, 125.5, 124.9, 112.0, 111.2, 25.3	454 M ²⁺ (20), 418 M ²⁺ -Cl (15), 381 M ²⁺ -2Cl (20), 312 ⁺ -4Cl (25), 264 M ²⁺ -TiCl ₄ (100)
46	7.53(s,2H), 7.48(d,2H), 7.24(d,2H), 3.76(s,4H,2CH ₂), 2.39(s,6H,2CH ₃)	167.2, 149.7, 142.3, 136.0, 127.6, 119.5, 111.2, 25.6, 21.4	486 M ²⁺ (20), 419 M ²⁺ -Cl-2CH ₃ (10), 414 M ²⁺ -2Cl (15), 378 M ²⁺ -3Cl (30),

			296 M ²⁺ -TiCl ₄ (100)
47	7.52(s,2H), 7.49(d,2H), 7.14(d,2H), 3.49(s,4H,2CH ₂), 7.44(t,2H)	165.5, 151.2, 139.3, 135.4, 126.0, 119.4, 111.3, 25.3, 21.9 123.0	486 M ²⁺ (20), 449 M ²⁺ -Cl (15) 421 M ²⁺ -Cl-2CH ₃ (15), M ²⁺ -3Cl (10), 344 M ²⁺ -TiCl ₄ (100)
48	7.76-7.70(m,4H), 7.50- 7.43(m,4H), 3.95(s,4H,2CH ₂)	152.5, 132.6, 125.6, 114.6, 24.5	452 M ²⁺ (10), 416M ²⁺ -Cl (20), 380 M ²⁺ -2Cl (15), 343 M ²⁺ -3Cl (10), 310 M ²⁺ -4Cl (20), 262 M ²⁺ -TiCl ₄ (10)
49	7.62(d,2H), 7.53(s,2H), 7.30(d,2H), 3.87(s,4H,2CH ₂), 2.46(s,6H,2CH ₃)	151.1, 136.3, 133.0, 130.0, 126.7, 114.7, 114.4, 24.7, 21.9	480 M ²⁺ (20), 443 M ²⁺ -Cl (20), 408 M ²⁺ -2Cl 1(5), 372 M ²⁺ -3Cl (15), 336 M ²⁺ -4Cl (20), 290 M ²⁺ -TiCl ₄ (100)
50	7.84(s,2H), 7.78(d,2H), 7.50(d,2H), 3.78(s,4H,2CH ₂) 2.42(s,6H,2CH ₃)	154.3, 135.5, 133.6, 130.3, 125.0, 116.2, 115.0, 25.7	518 M ²⁺ (10), 485 M ²⁺ -Cl (15), 450 M ²⁺ -2Cl (10), 413 M ²⁺ -3Cl (10),377 M ²⁺ -4Cl (20) 330 M ²⁺ -TiCl ₄ (100) 414 M ²⁺ -2Cl (20), 378 M ²⁺ -3Cl (20),296 M ²⁺ -TiCl ₄ (100)
51	8.05(d,2H), 7.97- 7.94(m,4H), 7.77- 7.74(dd,2H), 7.50(t,2H),	166.4, 153.4, 136.6, 133.5, 131.7, 131.6, 127.3, 126.4, 123.8,	534 M ²⁺ (10), 498 M ²⁺ -Cl (20), 463 M ²⁺ -2Cl (20), 427
52	8.11-8.09(dd,2H), 7.83- 7.81(dd,2H), 7.68(t,2H), 7.53(t,2H), 7.35-7.33(m,4H)	162.2, 151.0, 141.9, 132.5, 131.7, 127.4, 126.5, 125.5, 120.7, 111.5	545 M ²⁺ (10), 509 M ²⁺ -Cl (20), 472 M ²⁺ -2Cl (15), 312 M ²⁺ -ZrCl ₄ (100)
53	8.12(d,2H), 7.85(t,2H), 7.53(s,2H), 7.46(d,2H), 7.21(d,2H), 2.42(s,6H,2CH ₃)	162.3, 149.3, 142.2, 134.9, 132.4, 131.6, 127.5, 127.4, 120.5, 110.9, 21.6	530 M ²⁺ (10), 464 M ²⁺ -Cl-2CH ₃ (20), 459 M ²⁺ -2Cl (15), 423 M ²⁺ -3Cl (15), 388 M ²⁺ -4Cl (10), 340 M ²⁺ - TiCl ₄ (100)
54	8.14-8.11(dd,2H), 7.87- 7.84(dd,2H), 7.62(d,2H), 7.41(s,2H), 7.22(d,2H), 2.43(s,6H,2CH ₃)	161.8, 151.4, 139.8, 136.6, 132.4, 131.7, 127.5, 126.7, 120.2, 111.5, 21.9	530 M ²⁺ (15), 494 M ²⁺ -Cl (20), 430 M ²⁺ -2Cl-2CH ₃ (15), 423 M ²⁺ -3Cl (10), 389 M ²⁺ -4Cl (20), 340 M ²⁺ - TiCl ₄ (100)

55	8.37(d,2H), 8.08(t,2H), 7.924-7.835(m,4H), 7.637- 7.625(m,4H)	148.2, 134.0, 133.8, 133.6, 126.5, 125.1, 115.4	500 M ⁺ (10), 463 M ⁺ -Cl (20), 428 M ⁺ -2Cl (15), 394 M ⁺ -3Cl (15), 357 M ⁺ -4Cl (20), 310 M ⁺ -TiCl ₄ (100)
56	8.18-8.16(dd,2H), 7.92- 7.90(dd,2H), 7.54(d,2H), 7.44(s,2H), 7.24(d,2H), 2.40(s,6H,2CH ₃)	147.7, 137.6, 133.2, 131.9, 129.6, 128.9, 127.6, 126.1, 114.8, 114.5, 21.8	530 M ⁺ (20), 492 M ⁺ -Cl (10), 454 M ⁺ -2Cl (15), 418 M ⁺ -3Cl (20), 338 M ⁺ -TiCl ₄ (50)
57	8.22(d,2H), 7.92(t,2H), 7.74(s,2H), 7.69(d,2H), 7.43(d,2H)	151.0, 136.6, 134.5, 132.4, 132.1, 129.3, 126.6, 125.3, 116.8, 115.1	568 M ⁺ (10), 481 M ⁺ -2Cl-NH (20), 462 M ⁺ -3Cl (10), 426 M ⁺ -4Cl (20), 378 M ⁺ -TiCl ₄ (100)
58	8.02(t,2H), 7.92(t,2H), 7.82(d,1H), 7.73(s,1H), 7.53(d,1H), 7.49-7.43(dd,2H), 7.41-7.35(dd,2H), 2.47(s,3H,CH ₃)-	166.5, 166.4, 153.4, 153.4, 141.6, 136.6, 136.5, 133.5, 132.1, 132.0, 131.6, 130.8, 127.1, 127.2, 126.3, 126.2, 123.8, 123.7, 122.9, 122.8, 21.5	548 M ⁺ (10), 512 M ⁺ -Cl (20), 496 M ⁺ -Cl-CH ₃ (15), 441 M ⁺ -3Cl (20), 405 M ⁺ -4Cl (20), 358 M ⁺ -TiCl ₄ (100)
59	7.98(d,1H), 7.91(s,1H), 7.68- 7.64(m,2H), 7.61(d,1H), 7.53-7.49(dd,2H), 7.32(t,4H), 2.45(s,3H,CH ₃)	162.3, 162.3, 151.0, 150.9, 142.8, 141.9, 141.8, 133.0, 132.1, 131.6, 127.3, 126.4, 126.3, 125.5, 125.4, 124.6, 120.7, 120.6, 111.5, 111.4, 21.5	516 M ⁺ (10), 480 M ⁺ -Cl (10), 444 M ⁺ -2Cl (20), 408 M ⁺ -2Cl(10), 372 M ⁺ -4Cl (20), 326 M ⁺ - TiCl ₄ (100)
60	8.13(d,1H), 7.70- 7.67(m,4H), 7.45- 7.44(m,6H), 2.51(s,3H,CH ₃)	149.2, 143.1, 135.1, 134.5, 133.1, 132.7, 126.0, 125.5, 125.3, 122.9, 115.3, 115.2, 21.6	516 M ⁺ (20), 443 M ⁺ -2Cl (20), 409 M ⁺ -3Cl (20), 372 M ⁺ -4Cl (20), 324 M ⁺ -TiCl ₄ (50)
61	8.27(d,2H), 7.92(d,1H), 7.74(d,2H), 7.63(s,2H), 7.45(d,2H), 2.65(s,6H,2CH ₃), 2.61(s,3H,CH ₃)	147.0, 146.9, 144.3, 136.6, 136.5, 134.7, 134.1, 133.6, 133.5, 131.6, 131.4, 129.9, 129.2, 128.1, 126.3, 124.2, 121.5, 114.8, 114.7, 114.5, 22.1, 21.9	542 M ⁺ (20), 468 M ⁺ -2Cl (20), 433 M ⁺ -3Cl (15), 371 M ⁺ -4Cl -2CH ₃ (20), 352 M ⁺ - TiCl ₄ (100)
62	8.06(s,1H), 8.04 (s,2H) 7.70- 7.61(m,4H), 7.39- 7.34(m,2H), 2.45(s,3H,CH ₃)	151.2, 142.7, 137.0, 136.3, 134.8, 134.1, 132.7, 132.5, 132.1, 132.1, 126.8, 125.9, 125.3, 125.1, 123.5, 116.7, 116.6, 115.2, 115.0, 21.5	582 M ⁺ (20), 565 M ⁺ -CH ₃ (15), 545 M ⁺ -Cl (20), 508 M ⁺ -2Cl (20), 472 M ⁺ -3Cl (25), 458 M ⁺ -4Cl-CH ₃ (15), 393 M ⁺ -TiCl ₄ (100)

active than bis (benzimidazolyl) - 4-methyl benzene titanium complexes (**61**, **62**).

GPC analysis of the polyethylenes produced by benzimidazole based complexes revealed that the symmetric catalysts systems were capable to produce resins with high to very high molecular weights associated with broad or even bimodal molecular weight distributions. The bimodality may arise from the fact that the **MAO** counterion induces the necessary dissymmetry of the active sites in the activation process⁴⁶.

The molecular weight M_w of the polymer produced with **55** / **MAO** was determined to be 1.3×10^6 g / mol, (PD = 19.2) (see Figure 13).

The molecular weight M_w and polydispersity of the polymer produced with catalyst systems 35 / **MAO**, 41 / **MAO**, 49/**MAO** and 58 / **MAO** was determined to be 1.3×10^6 g / mol, (PD = 16.3), 1.1×10^6 g / mol, (PD = 8.4), $4.4.37 \times 10^5$ g / mol, (PD = 9.1), and 3.3×10^6 g / mol, (PD = 10.2) respectively.

Differential scanning calorimetric (DSC) measurements for representative samples of polyethylenes produced with bis-(benzimidazolyl, benzothiazolyl, and benzoxazolyl) zirconium complexes revealed that the catalyst systems were capable to produce high density polyethylenes with melting temperatures > 135 °C. The crystallization temperatures of the polymers range from 118 - 125 °C and the polymers have high degrees of crystallinities. For example, DSC curves for polyethylene produced with the catalysts **55** / **MAO** (see Figures 14) show melting temperatures 137.5 °C and crystallization temperatures of 120.3 °C.

EXPERIMENTAL

All experimental work was routinely carried out using Schlenk technique unless otherwise stated. Anhydrous and purified argon was used as inert gas. n-Pentane, diethyl ether, toluene and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminium hydride. Methylene chloride was dried with phosphorus pentoxide and additionally with calcium hydride. Methanol and ethanol were dried over magnesium. Deuterated solvents (CDCl_3 ,

DMSO-d_6) for NMR spectroscopy were stored over molecular sieves (3ú). Methylalumoxane (30 % in toluene) was purchased from Crompton (Bergkamen) and Albemarle (Baton Rouge, USA / Louvain – La Neuve, Belgium). Ethylene (3.0) and argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). All other starting materials were commercially available and were used without further purification. The titanium adducts were synthesized via published procedures⁴⁷.

NMR spectroscopy

The spectrometer Bruker ARX 250 was available for recording the NMR spectra. The samples were prepared under inert atmosphere (argon) and routinely recorded at 25 °C. The chemical shifts in the ^1H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for CDCl_3 , $\delta = 2.50$ ppm for DMSO-d_6) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for CDCl_3 , $\delta = 39.5$ ppm for DMSO-d_6).

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.

Gel permeation chromatography (GPC)

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

Elemental analysis

Elemental analyses were performed with a VarioEl III CHN instrument. The raw values of the carbon, hydrogen, and nitrogen contents were multiplied with calibration factors (calibration compound: acetamide).

General procedures for the syntheses of the complexes

Syntheses of organic compounds 1-31

A diamine compound (0.05mol) was mixed with a dicarboxylic acid or an acid anhydride (0.025mol) and the mixture was poured in 50 ml of preheated (100°C) polyphosphoric acid. The mixture was stirred and heated at 175°C for 3-5 hours. The reaction mixture was then poured into ice cold water and allowed to stand overnight. The precipitate was

removed by filtration and washed several times with diluted sodium hydrogen carbonate solution and finally with water. The reaction product was then air dried and weighed. The products were characterized by NMR and mass spectrometry (Table 3) and elemental analyses (Table 32).

Titanium complexes 32-62

To 0.87g, (2.6 mmol) TiCl_4 (THF)₂ in dichloromethane was added 2.6 mmol of the solid ligand. The reaction mixture was stirred over night at room temperature; the solid formed was collected by filtration under reduced pressure and washed several times with dichloromethane, then with pentane, dried in vacuo and weighed. The products were characterized by NMR and mass spectroscopy (Table 3), and by elemental analyses (Table 1).

Polymerization of ethylene

An amount of 2 – 5 mg of the desired complex was suspended in 5 ml of toluene. Methylaluminoxane (30% in toluene) was added resulting in an immediate color change. The mixture was added to a 1l Schlenk flask filled with 250 ml n-pentane. This mixture was transferred to a 1l Büchi laboratory autoclave under inert atmosphere and thermostated. An ethylene pressure of 10 bar was

applied for one hour. The polymer was filtered over a frit, washed with diluted hydrochloric acid, water, and acetone, and finally dried in vacuo.

CONCLUSIONS

Mononuclear transition metal complexes with hetero atoms in the ligand system can offer a big advantage. After activation with MAO, more than one active center can be generated and as a consequence bimodal or multimodal resins are produced in catalytic ethylene polymerization reactions. Obviously the hetero atoms of the activated catalysts undergo different interactions with the Lewis acidic moieties of MAO. Structure-property-relationship studies indicate that the nature of the hetero atom and steric and electronic conditions in the coordination sphere are strongly influence the performance of such catalysts.

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