

## Zr(IV) complexes of some heterocyclic ligands: synthesis, characterization, and ethylene polymerization activity

Hamdi Ali ELAGAB<sup>1,2,\*</sup>

<sup>1</sup>Faculty of Science and Arts, Albaha University, Almandaq, Saudi Arabia

<sup>2</sup>Laboratory of Inorganic Chemistry, University of Bayreuth, Bayreuth, Germany

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**Abstract:** Thirty-one complexes of bis-(benzimidazole, benzothiazole, and benzoxazole) compounds with Zr(IV) metal centers were synthesized, characterized, activated with methylaluminumoxane (MAO), and then tested for catalytic ethylene polymerization. The activities of the various catalysts were found to be functions of the heteroatoms in the ligand frameworks and the structure around the active metal center. The highest activity was obtained with **38/MAO** (424 kg E/mol cat. h). The produced polyethylenes showed high molecular weights (**41/MAO**,  $1.9 \times 10^6$  g/mol) and broad molecular weight distributions (**38/MAO**,  $M_w = 9.64 \times 10^5$  g/mol, PD = 23). This could result from different interactions of the MAO counter ion with the heteroatoms of the catalyst ligand generating different active sites.

**Key words:** Synthesis, characterization, heterocycles, zirconium complexes, ethylene polymerization

### 1. 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 reported.<sup>1–6</sup> Moreover, the nickel(II), cobalt(II), and copper(II) coordination chemistry of some tetradentate ligands involving benzothiazole functional groups has been published.<sup>7</sup> In all cases involving benzothiazoles as functional groups the ligands behave as nitrogen donors, except in a few cases involving bridging benzothiazole,<sup>8</sup> 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,<sup>9,10</sup> 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<sup>1,11–23</sup> and 2,6-bis(benzoxazolyl) pyridine<sup>24</sup> derivatives have been reported as ligands for transition metals in order to investigate the complexes for their structures and properties.

In polyolefin chemistry, mononuclear complexes as catalysts for olefin polymerization in homogeneous solution have many advantages because every molecule can act as a catalyst and hence provide high activity.<sup>25–27</sup> In most cases, the molecular weights of the produced resins have narrow molecular weight distributions due to the fact that only one active site is generated in the activation process of the catalyst precursor such as phenoxyimine  $\text{TiCl}_2/\text{MAO}$ . This can be disadvantageous when processing polyolefins and solutions are needed to overcome this problem. So far, special support materials and methods, mixtures of different catalysts, application of dinuclear or multinuclear catalysts, and use of two or more reactors were applied.<sup>28–38</sup> However, the best solution is the

\*Correspondence: hamdieez2000@yahoo.com

design of catalysts that can solve all these problems in one step and in one reactor. In this contribution we report the synthesis and characterization of complexes with heterocyclic ligands that are perfect candidates for this challenge. The vanadium complexes of bis(benzimidazole)amine tridentate ligands [N, N, N], were reported as active ethylene polymerization catalysts after activation with simple alkylaluminum compounds.<sup>39</sup> 2,6-Bis(2-benzimidazolyl)pyridine zirconium dichloride/MAO polymerizes methylacrylate.<sup>40</sup> Recently,<sup>41–48</sup> we reported bis-(benzimidazole, benzoxazole, and benzothiazole) titanium, zirconium, and vanadium complexes that can be activated with methylaluminoxane (MAO) and then be applied successfully for catalytic ethylene polymerization. Herein we report on the effect of heteroatom and the bridging unit on the activity of zirconium complexes of bis(benzimidazolyl, benzothiazolyl, and benzoxazolyl), and their behavior towards ethylene polymerization after activation with MAO.

## 2. Results and discussion

### 2.1. General synthesis of ligand precursors

The condensation reaction of dicarboxylic acids or acid anhydrides and diamine, 2-aminothiophenol or 2-aminophenol in preheated polyphosphoric acid is a well established procedure for the preparation of imidazole-based ligand precursors in high yields.<sup>20,49,50</sup> Scheme 1 shows the synthesis of the benzimidazolyl-based compounds **1–31**.

### 2.2. Synthesis of zirconium complexes **32–62**

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

### 2.3. Characterization

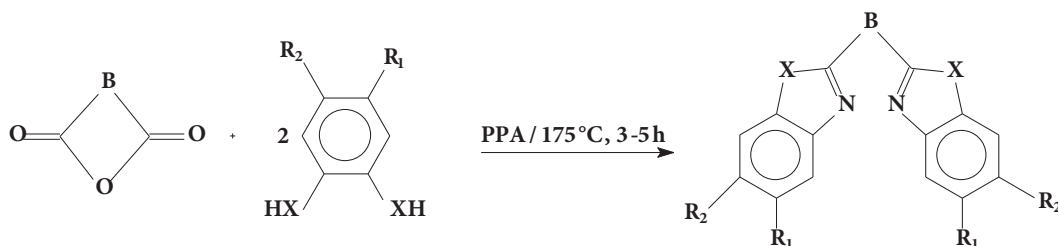
Since all the synthesized complexes were obtained as solids and since they did not crystallize properly, they were characterized by NMR, mass spectroscopy, and elemental analysis. The obtained results agree well with the proposed structures.

#### 2.3.1. NMR spectroscopy

The ligand precursors were characterized by NMR spectroscopy using DMSO as solvent. Table 2 includes the <sup>1</sup>H and <sup>13</sup>C NMR data for compounds **1–31**. For example, the <sup>1</sup>H NMR spectrum of compound **5** (see Figure 1) shows five signals: the singlet at  $\delta = 11.82$  ppm assigned to NH proton, the signal at  $\delta = 6.95$  ppm [d, 2H,  $J_{H,H} = 8.1$  Hz] assigned to aromatic protons H3, the singlet at  $\delta = 6.91$  ppm corresponding to two protons H4, at  $\delta = 6.82$  ppm [d, 2H,  $J_{H,H} = 8.1$  Hz] assigned to H2, and the signal upfield at  $\delta = 2.20$  ppm assigned to the six protons of the methyl groups.

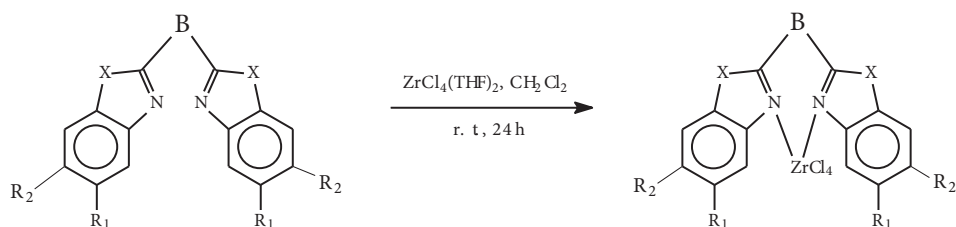
The <sup>13</sup>C NMR spectrum of compound **5** (Figure 2) shows nine signals. The two signals downfield at  $\delta = 155.9$  ppm and at  $\delta = 155.6$  ppm correspond to the carbon atoms 1 and 2, respectively, due to hindered rotation resulting from the N–H–N bond formation. Each of the six signals at  $\delta = 132.9$ , 126.1, 124.4, 123.2, 115.8, and 115.6 ppm corresponds to two carbon atoms (3, 4, 6, 7, 5, and 8, respectively) of the aromatic rings. The methyl group carbon atoms appear upfield at  $\delta = 21.2$  ppm.

Scheme 1. Synthesis of ligand precursors 1–31.



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

The <sup>1</sup>H NMR spectrum of complex **36** (see Figure 3) shows five resonance signals. The broad signal at  $\delta$  11.82 ppm and the signals at  $\delta$  = 7.06 and 6.97 ppm can be assigned to H3 and H4, respectively; at  $\delta$  = 6.82 ppm H2 appears. The methyl group protons can be observed as a singlet at  $\delta$  = 2.17 ppm.

**Scheme 2.** Synthesis of the coordination compounds **32–62**.

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

The <sup>13</sup>C NMR spectrum of complex **36** (Figure 4) shows nine resonance signals each corresponding to two carbon atoms. The signals at  $\delta = 156.1, 155.8, 133.0, 126.2, 124.6, 124.1, 115.9, 115.7,$  and  $21.3$  ppm can be assigned to the carbon atoms C1, C2, C3, C4, C6, C7, C5, C8, and C9, respectively.

**Table 1.** Ethylene polymerization activities of zirconium complexes. All polymerization reactions were carried out in 250 mL of pentane with MAO as cocatalyst (Al: M = 2500:1) at 50 °C, 10 bar ethylene pressure, 1 h reaction time).

No.	Activity [kg/mol cat. h]
<b>32</b>	268
<b>33</b>	60
<b>34</b>	113
<b>35</b>	53
<b>36</b>	49
<b>37</b>	41
<b>38</b>	424
<b>39</b>	145
<b>40</b>	138
<b>41</b>	172
<b>42</b>	43
<b>43</b>	22
<b>44</b>	120
<b>45</b>	123
<b>46</b>	144
<b>47</b>	168
<b>48</b>	130
<b>49</b>	37
<b>50</b>	40
<b>51</b>	132
<b>52</b>	114
<b>53</b>	88
<b>54</b>	74
<b>55</b>	286
<b>56</b>	67
<b>57</b>	123
<b>58</b>	128
<b>59</b>	148
<b>60</b>	132
<b>61</b>	121
<b>62</b>	132

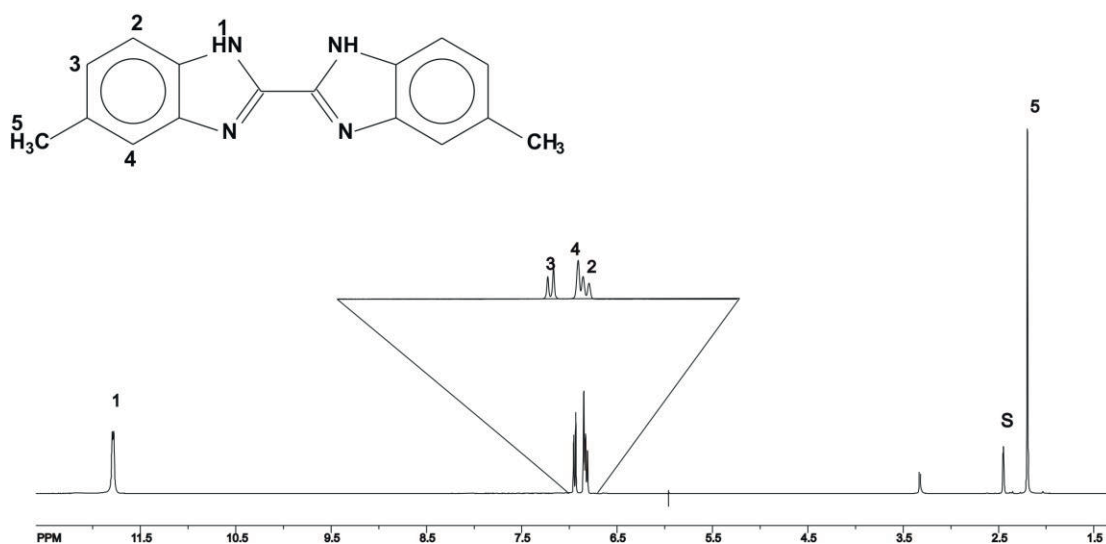
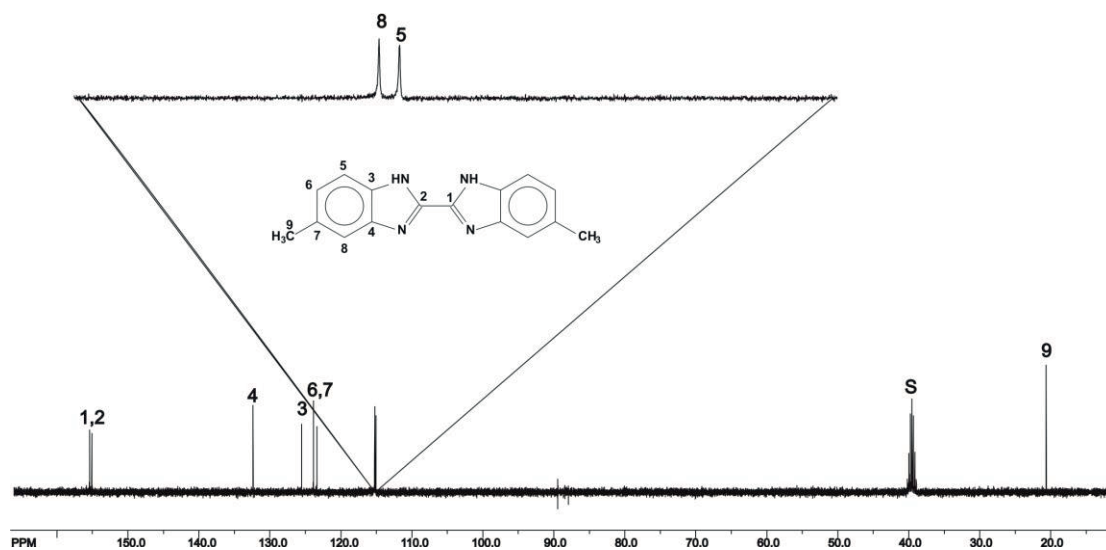
### 2.3.2. Mass spectroscopy

The ligand precursors were also characterized by their mass spectra. The mass spectrum of compound **5** (Figure 4) shows the molecular ion peak  $m/z = 262$  and  $m/z = 170$  ( $M^{\circ+}-CH_3C_6H_4$ ). The ion with the mass  $m/z = 131$  can be explained by the loss of one benzimidazole unit.

The mass spectrum of complex **36** (Figure 6) shows the molecular ion peak at  $m/z = 495$  but an incomplete fragmentation pattern and a peak for the free ligand. Complexes with donor ligands often do not survive the ionization process without decomposition.

### 2.3.3. Elemental analysis

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

Figure 1.  $^1\text{H}$  NMR spectrum of compound 5.Figure 2.  $^{13}\text{C}$  NMR spectrum of compound 5.

#### 2.4. Polymerization results

All coordination compounds were activated with MAO according to the mechanism proposed for the activation of metallocene<sup>51,52</sup> and 2, 6-bis(imino)pyridine iron(II)<sup>53</sup> catalyst precursors.

The complexes of zirconium with ligands derived from bis(benzoimidazolyl), bis(benzoxazolyl), and bis(benzothiazolyl) compounds showed variable activities for ethylene polymerization (Table 2). The activities are greatly influenced by the heteroatoms in addition to the ligand environment.

Ethylene polymerization of zirconium complexes derived from the ligand system bis- benzothiazolyl (Figure 7) shows the following activity order depending on structural variations of the ligand systems 2,2-bis(benzothiazolyl) **32**/MAO > 1,2-bis(benzothiazolyl) benzene **51**/MAO > 1,2-bis(benzothiazolyl)-4-methylbenzene **58**/MAO > 1,2-bis(benzothiazolyl)ethane **44**/MAO > 1,1-bis(benzothiazolyl) methane **41**/MAO.

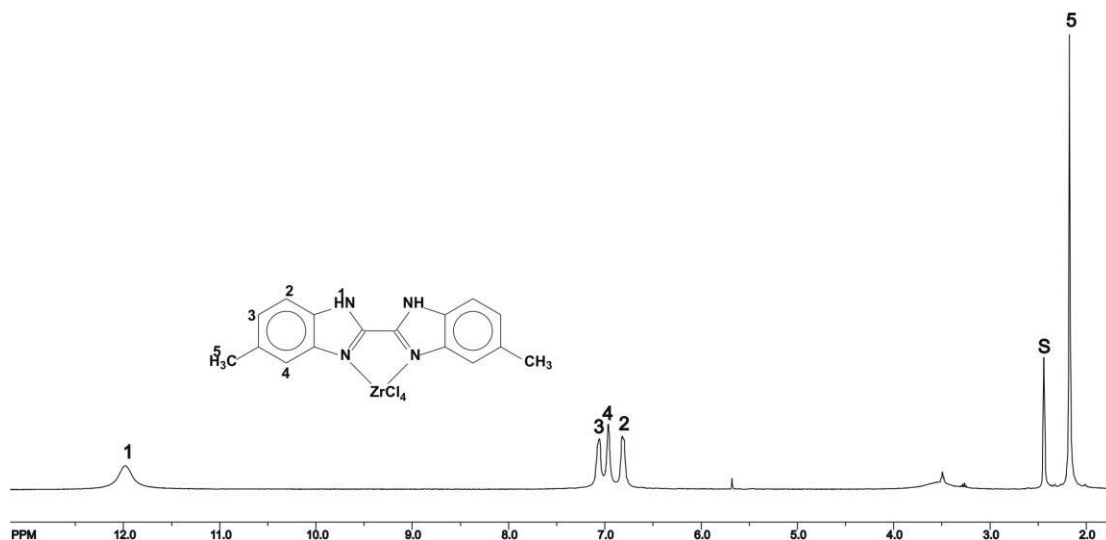


Figure 3.  $^1\text{H}$  NMR spectrum of complex **36**.

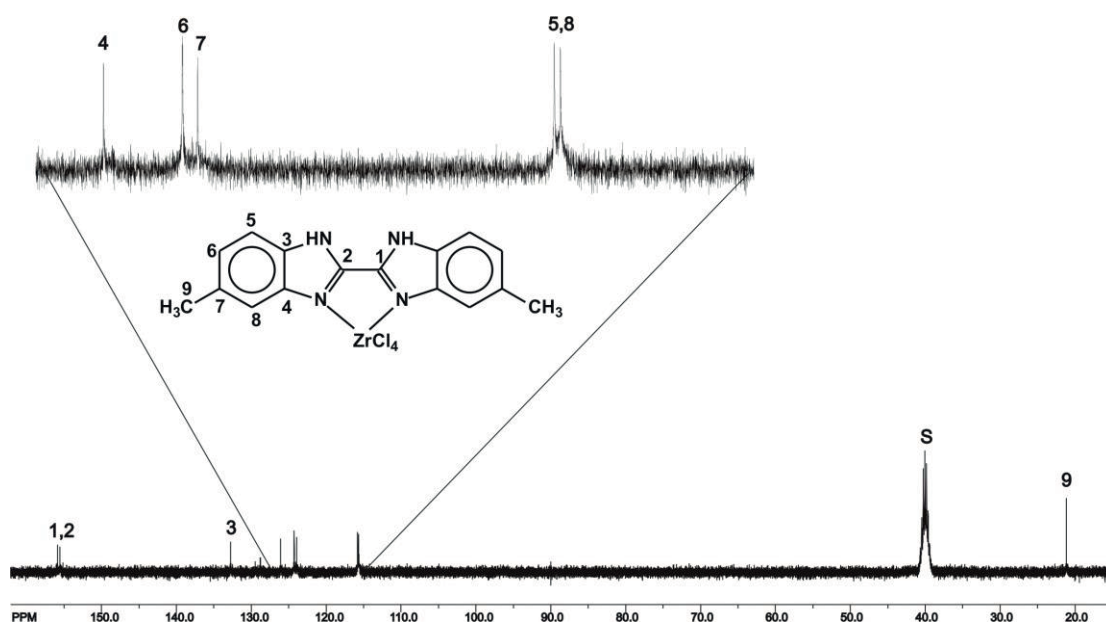


Figure 4.  $^{13}\text{C}$  NMR spectrum of complex **36**.

The complexes of zirconium with ligands derived from 2,2-bis(benzoxazolyl), 1,1-bis-(benzoxazolyl) methane, 1,2-bis-(benzoxazolyl) ethane, 1,2-bis-(benzoxazolyl)benzene, and 1,2-bis-(benzoxazolyl)-4-methylbenzene compounds were activated with MAO in toluene solution. The catalysts showed variable activities for ethylene polymerization. Principally the activities are influenced by the steric conditions of the ligand, the nature of the metal atom, the degree of activation, and the lifetime of the active sites.

1,1-Bis(benzoxazolyl) methane complex **38/MAO** shows higher activity compared to the 4-methyl benzene complex **59/MAO**. The activities of the other complexes show the following order: 1,2-bis(benzoxazolyl) ethane **45/MAO** > 1,2-bis(benzoxazolyl)benzene **52/MAO** > 2,2-bis(benzoxazolyl) **33/MAO** complex (Figure 8).

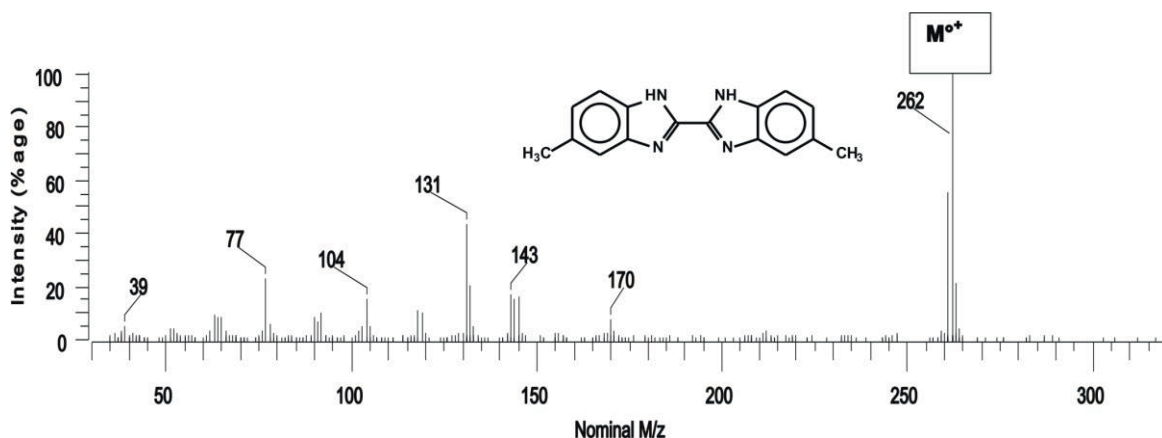


Figure 5. Mass spectrum of compound 5.

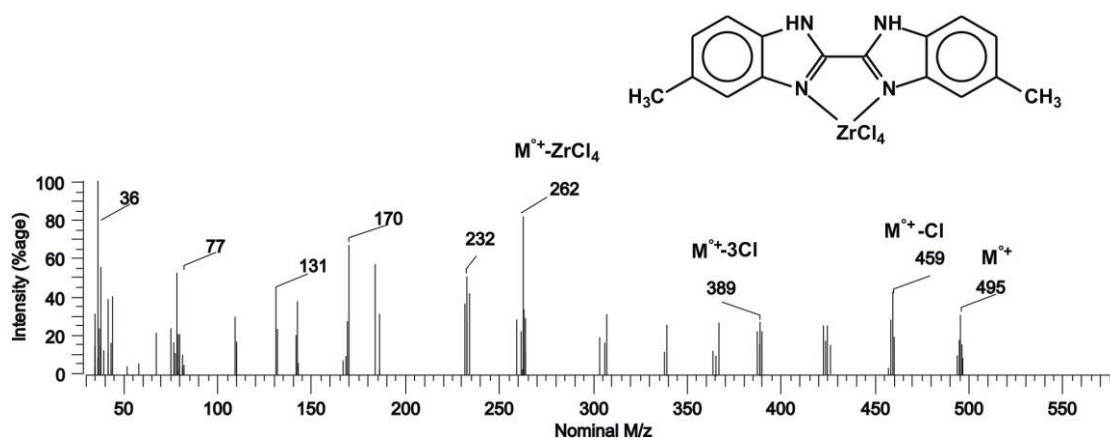


Figure 6. Mass spectrum of complex 36.

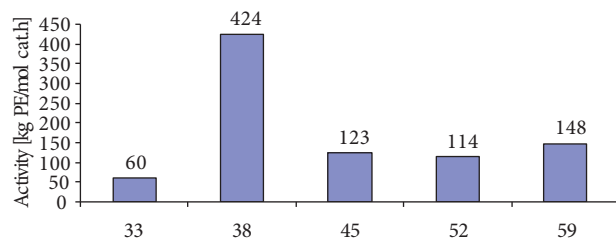


Figure 7. Effect of bridging unit on the activity of bis-(benzothiazole) zirconium complexes.

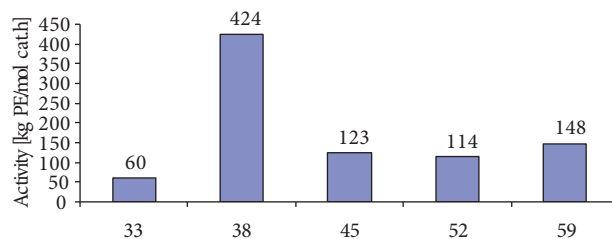


Figure 8. Effect of bridging unit on the activity of bis-(benzoxazole) zirconium complexes.

Bis-benzimidazolyl zirconium complexes show the following activity order:

1,2-bis(benzimidazolyl) benzene **55/MAO** > 1,1-bis(benzimidazolyl) methane **41/MAO** > 1,2-bis(benzimidazolyl)-4-methylbenzene **60/MAO** > 1,2-bis(benzimidazolyl) ethane **48/MAO** > 2,2-bis(benzimidazolyl) **35/MAO** (Figure 9).

Generally, bis-(benzoxazolyl) zirconium complexes show higher activities than those obtained from bis-(benzimidazolyl) ligand of the same type. For example, the catalyst system **38/MAO** shows activity of 424



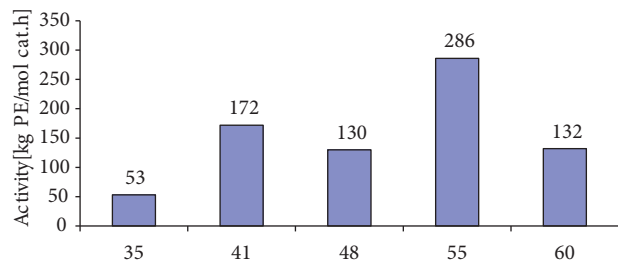
**Table 2.** Elemental analysis data for ligands and zirconium complexes.

Compound no.	General formula	Calculated			Found		
		C	H	N	C	H	N
1	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>	62.7	3.0	10.4	62.9	2.8	10.6
2	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	71.2	3.4	11.9	70.8	3.6	12.1
3	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	72.7	4.5	10.6	72.4	4.7	10.8
4	C <sub>14</sub> H <sub>10</sub> N <sub>4</sub>	71.8	4.3	23.9	71.6	4.5	24.1
5	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub>	73.3	5.3	21.4	72.9	5.5	21.1
6	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> S <sub>2</sub>	63.8	3.5	9.9	63.6	3.4	10.2
7	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	72.0	4.0	11.2	71.8	4.2	11.4
8	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	73.4	5.0	10.1	73.6	5.1	9.8
9	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	73.4	5.0	10.1	73.6	5.1	9.8
10	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub>	72.6	4.8	22.6	71.8	4.6	22.4
11	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub>	73.9	5.8	20.3	73.7	6.0	20.1
12	C <sub>15</sub> H <sub>10</sub> N <sub>4</sub> Cl <sub>2</sub>	64.9	4.1	9.5	65.2	4.4	9.1
13	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> S <sub>2</sub>	64.9	4.1	9.5	65.2	3.9	9.6
14	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	72.7	4.6	10.6	72.9	4.5	10.5
15	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	74.0	5.5	9.6	73.7	5.8	9.9
16	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	74.0	5.5	9.6	73.8	5.7	9.6
17	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub>	73.3	5.3	21.4	72.9	5.4	21.4
18	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub>	74.5	6.2	19.3	74.8	5.9	19.6
19	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub> Cl <sub>2</sub>	58.0	3.6	16.9	58.2	3.7	17.1
20	C <sub>20</sub> H <sub>12</sub> N <sub>2</sub> S <sub>2</sub>	68.8	3.5	8.1	69.7	3.5	8.2
21	C <sub>20</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	76.9	3.9	9.0	77.1	3.7	8.8
22	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	77.7	4.7	8.2	77.7	4.7	8.4
23	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	77.7	4.7	8.2	77.7	4.7	8.4
24	C <sub>20</sub> H <sub>14</sub> N <sub>4</sub>	77.4	4.5	18.1	77.4	4.5	18.1
25	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub>	78.1	5.3	16.6	78.6	5.2	17.1
26	C <sub>20</sub> H <sub>12</sub> N <sub>4</sub> Cl <sub>2</sub>	63.3	3.2	14.8	64.1	3.5	15.2
27	C <sub>21</sub> H <sub>14</sub> N <sub>2</sub> S <sub>2</sub>	70.4	3.9	7.8	69.8	4.1	7.5
28	C <sub>21</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	77.3	4.3	8.6	76.9	4.6	8.9
29	C <sub>21</sub> H <sub>16</sub> N <sub>4</sub>	77.8	4.9	17.3	78.1	5.2	17.6
30	C <sub>23</sub> H <sub>20</sub> N <sub>4</sub>	78.4	5.7	15.9	78.1	5.5	16.2
31	C <sub>21</sub> H <sub>14</sub> N <sub>4</sub> Cl <sub>2</sub>	64.1	3.6	14.2	64.5	3.9	13.9
32	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub> ZrCl <sub>4</sub>	33.5	1.6	5.6	34.2	1.7	5.4
33	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	35.8	1.7	6.0	36.2	1.8	5.7
34	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	38.6	2.4	5.6	39.1	2.1	5.9
35	C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> ZrCl <sub>4</sub>	36.0	2.1	12.0	35.6	2.0	12.4
36	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> ZrCl <sub>4</sub>	38.8	2.8	11.4	38.9	2.7	11.2
37	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> S <sub>2</sub> ZrCl <sub>4</sub>	35.0	1.9	5.4	35.4	2.1	5.6
38	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	37.3	2.1	5.8	36.8	2.0	5.4
39	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	39.9	2.7	5.5	40.3	3.0	5.2
40	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	39.9	2.7	5.5	39.6	2.5	5.8
41	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> ZrCl <sub>4</sub>	35.0	1.9	5.4	35.0	2.0	5.4
42	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub> ZrCl <sub>4</sub>	40.1	3.1	11.0	39.8	3.5	10.7
43	C <sub>15</sub> H <sub>10</sub> N <sub>4</sub> Cl <sub>2</sub> ZrCl <sub>4</sub>	32.7	2.9	10.2	33.2	3.1	10.6
44	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> S <sub>2</sub> ZrCl <sub>4</sub>	36.3	2.3	5.3	37.3	2.5	5.4
45	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	38.6	2.4	5.6	39.2	2.6	5.2
46	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	41.1	3.0	5.3	40.7	3.4	5.8
47	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	41.1	3.0	5.3	41.4	2.8	5.6
48	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> ZrCl <sub>4</sub>	38.8	2.8	11.3	39.3	3.1	10.8

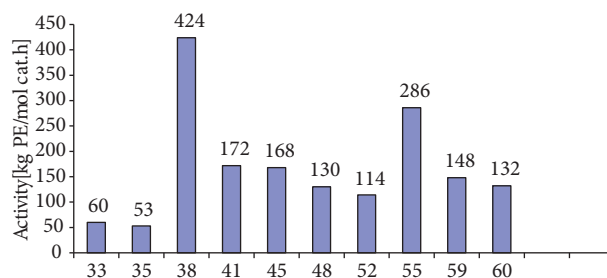
Table 2. Continued.

Compound no.	General formula	Calculated			Found		
		C	H	N	C	H	N
<b>49</b>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> ZrCl <sub>4</sub>	41.3	3.4	10.7	41.6	3.7	10.4
<b>50</b>	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub> Cl <sub>2</sub> ZrCl <sub>4</sub>	34.0	2.1	9.9	33.8	2.5	10.2
<b>51</b>	C <sub>20</sub> H <sub>12</sub> N <sub>2</sub> S <sub>2</sub> ZrCl <sub>4</sub>	41.6	2.1	4.6	42.0	2.0	4.7
<b>52</b>	C <sub>20</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	44.0	2.2	5.1	44.5	2.5	4.8
<b>53</b>	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	46.1	2.8	4.9	45.7	3.1	5.3
<b>54</b>	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	46.1	2.8	4.9	46.4	3.0	4.6
<b>55</b>	C <sub>20</sub> H <sub>14</sub> N <sub>4</sub> ZrCl <sub>4</sub>	44.2	2.6	10.3	44.6	2.2	10.5
<b>56</b>	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> ZrCl <sub>4</sub>	46.2	3.2	9.8	47.1	3.2	9.0
<b>57</b>	C <sub>20</sub> H <sub>12</sub> N <sub>4</sub> Cl <sub>2</sub> ZrCl <sub>4</sub>	39.2	2.0	9.2	39.5	1.8	9.4
<b>58</b>	C <sub>21</sub> H <sub>14</sub> N <sub>2</sub> S <sub>2</sub> ZrCl <sub>4</sub>	42.6	2.4	4.7	43.0	2.7	4.3
<b>59</b>	C <sub>21</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> ZrCl <sub>4</sub>	46.2	3.2	9.8	47.1	3.2	9.0
<b>60</b>	C <sub>21</sub> H <sub>16</sub> N <sub>4</sub> ZrCl <sub>4</sub>	45.2	2.9	10.1	45.7	3.2	9.7
<b>61</b>	C <sub>23</sub> H <sub>20</sub> N <sub>4</sub> ZrCl <sub>4</sub>	47.2	3.4	9.6	46.8	3.7	10.1
<b>62</b>	C <sub>21</sub> H <sub>14</sub> N <sub>4</sub> Cl <sub>2</sub> ZrCl <sub>4</sub>	40.3	2.2	8.9	40.7	2.6	9.4

(kg PE/mol cat. h) compared to 172 (g PE/mol cat. h) for the catalyst system **41/MAO** (Figure 10). 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.



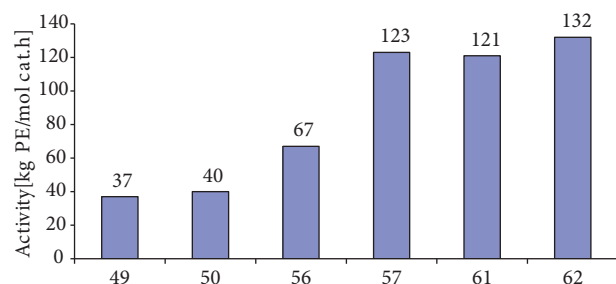
**Figure 9.** Effect of bridging unit on the activity of bis-(benzimidazole) zirconium complexes.



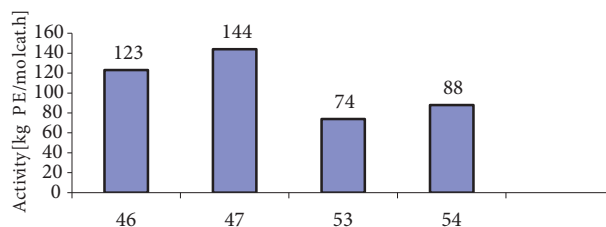
**Figure 10.** Activities of unsubstituted bis-benzoxazole and bis-benzimidazole zirconium complexes.

The activities of bis-benzimidazolyl zirconium complexes are greatly affected by the substituent type. Chloro substituent increases the catalytic activity of the complexes more than the methyl group. For example, the catalyst system **57/MAO** shows activity of 123 (kg PE/mol cat. h), while a catalyst system derived from the same ligand with a methyl substituent **56/MAO** produces 67 (kg PE/mol cat. h), most probably because (Figure 11) the chloro substituent increases the electrophilicity of the metal active center.

The position of the methyl group greatly influences the catalytic activities of zirconium complexes derived from bis-benzoxazole ligands; a methyl substituent para to the imino nitrogen atom reduces the activity of the catalyst compared to a methyl group meta to the imino nitrogen, mostly because the methyl group in para position increases the electron density on the active metal center, for example, the catalyst system 39/MAO (145 kg PE/mol cat. h) compared to 138 kg PE/mol cat. h for 40/MAO; similarly the catalyst pair derived from bis-benzoxazolyl benzene 53/MAO and 54/MAO shows activities of 88 and 74 (kg PE/mol cat. h), respectively (Figure 12).



**Figure11.** The effect of substituent type on the activities of benzimidazole zirconium complexes.

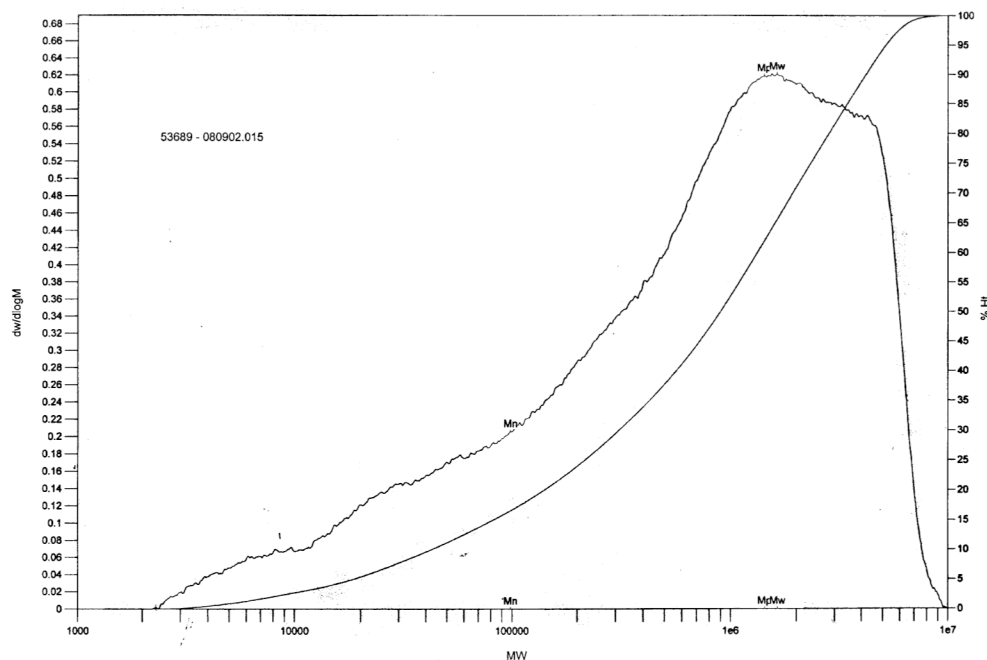


**Figure12.** Effect of methyl group position on the activity of benzoxazole complexes.

GPC analysis of the polyethylenes produced by benzimidazole-based complexes revealed that the symmetric catalyst systems were capable of producing 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 process.<sup>54</sup>

The molecular weight  $M_w$  of the polymer produced with **55/MAO** was determined to be  $1.64 \times 10^6$  g/mol (PD = 16) (see Figure 13).

The molecular weight  $M_w$  of the polymer produced with **41/MAO** was determined to be  $1.91 \times 10^6$  g/mol (PD = 5) (see Figure 14).



**Figure 13.** GPC profile for polyethylene produced with catalyst **55/MAO**.

The molecular weight  $M_w$  and polydispersity of the polymer produced with the catalyst systems **35/MAO**, **38/MAO**, **51/MAO**, and **60/MAO** was found to be  $1.64 \times 10^6$  g/mol (PD = 11),  $9.64 \times 10^5$  g/mol (PD = 23),  $1.37 \times 10^6$  g/mol (PD = 9), and  $1.6 \times 10^6$  g/mol (PD = 11), respectively.

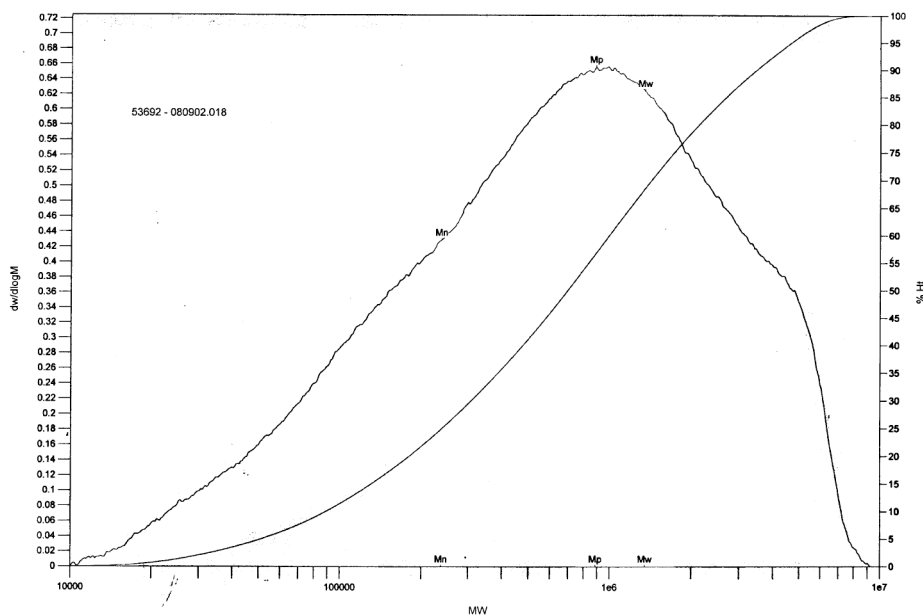


Figure 14. GPC profile for polyethylene produced with catalyst 41/MAO.

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 of producing high density polyethylenes with melting temperatures  $> 135$  °C. The crystallization temperatures of the polymers range from 118 to 120 °C and the polymers have high degrees of crystallinities. For example, DSC curves for polyethylene produced with the catalysts 41/MAO (see Figures 15) show melting temperatures of 135.4 °C and crystallization temperatures of 119.7 °C.

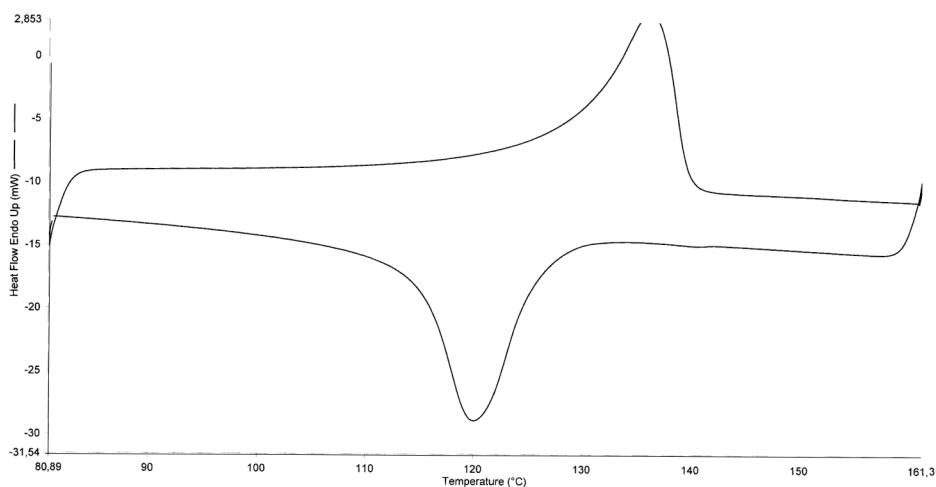


Figure 15. DSC curve for the polyethylene produced with the catalyst 41/MAO.

### 3. Experimental

All experimental work was routinely carried out using the 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 aluminum hydride. Methylene chloride was dried with phosphorus pentoxide and additionally with calcium hydride. Methanol and ethanol were dried over magnesium. Deuterated solvents ( $\text{CDCl}_3$ ,  $\text{DMSO-d}_6$ ) for NMR spectroscopy were stored over molecular sieves (3 Å). Methylalumoxane (30% in toluene) was purchased from Crompton (Bergkamen) and Albemarle (Baton Rouge, LA, USA/Louvain – La Neuve, Belgium). Ethylene (3.0) and argon (4.8/5.0) were supplied by the Rießner Company (Lichtenfels). All other starting materials were commercially available and were used without further purification. The titanium and zirconium adducts were synthesized via published procedures.<sup>55</sup>

### 3.1. NMR spectroscopy

A Bruker ARX 250 spectrometer was used for recording the NMR spectra. The samples were prepared under inert atmosphere (argon) and routinely recorded at 25 °C. The chemical shifts in the  $^1\text{H}$  NMR spectra are referred to the residual proton signal of the solvent ( $\delta = 7.24$  ppm for  $\text{CDCl}_3$ ,  $\delta = 2.50$  ppm for  $\text{DMSO-d}_6$ ) and in  $^{13}\text{C}$  NMR spectra to the solvent signal ( $\delta = 77.0$  ppm for  $\text{CDCl}_3$ ,  $\delta = 39.5$  ppm for  $\text{DMSO-d}_6$ ).

### 3.2. 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.

### 3.3. Gel permeation chromatography (GPC)

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

### 3.4. Elemental analysis

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

### 3.5. General procedures for the syntheses of the complexes

#### 3.5.1. Syntheses of organic compounds 1–31

A diamine compound (0.05 mol) was mixed with a dicarboxylic acid or an acid anhydride (0.025 mol) and the mixture was poured into 50 mL of preheated (100 °C) polyphosphoric acid. The mixture was stirred and heated at 175 °C for 3–5 h. The reaction mixture was then poured into ice cold water and left 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 elemental analyses (Table 2), NMR, and mass spectrometry (Table 3).

#### 3.5.2. Zirconium complexes

To 0.45 g (1.2 mmol) of  $\text{ZrCl}_4(\text{THF})_2$  in dichloromethane was added 1.2 mmol of the organic compound. The reaction mixture was stirred overnight at room temperature, filtered, washed several times with dichloromethane and then with pentane, dried in vacuo, and weighed. The products were characterized by elemental analyses (Table 2), NMR, and mass spectroscopy (Table 3).

**Table 3.**  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and mass spectroscopic data of ligand precursors and complexes.

No.	$^1\text{H}$ NMR $\delta$ [ppm]	$^{13}\text{C}$ NMR $\delta$ [ppm]	Mass m/z (%)
1	8.15 (d, 2H, $J = 7.8$ Hz), 7.96 (d, 2H, $J = 7.8$ Hz), 7.54 (t, 2H, $J = 7.8$ Hz), 7.47 (t, 2H, $J = 7.8$ Hz)	152.6, 151.8, 134.8, 127.7, 127.3, 122.4, 121.7	268 $\text{M}^{\circ+}$ (100)
2	7.93 [d, 2H, $J = 7.6$ Hz] 7.73 [d, 2H, $J = 7.6$ Hz], 7.51 [t, 4H, $J = 7.6$ Hz]	152.1, 151.2, 141.4, 127.8, 126.0, 121.8, 111.7	236 $\text{M}^{\circ+}$ (100)
3	7.63 (s, 2H), 7.11 [d, 2H, $J = 7.8$ Hz], 6.98 [d, 2H, $J = 7.8$ Hz] 2.37 (s, 6H)	155.4, 147.5, 141.3, 132.7, 127.7, 123.2, 108.6, 20.9	264 $\text{M}^{\circ+}$ (100)
4	12.22 (br, 2H, NH), 7.11–6.99 (m, 8H)	156.0, 126.4, 123.8, 116.0	234 $\text{M}^{\circ+}$ (100)
5	11.82 (br, 2H, NH), 6.95 (d, 2H, $J = 8.1$ Hz), 6.91 (s, 2H) 6.82 (d, 2H, $J = 8.1$ Hz), 2.23 (s, 6H, $\text{CH}_3$ )	156.0, 155.6, 132.9, 126.1, 124.4, 123.2, 115.8, 115.6, 21.2	262 $\text{M}^{\circ+}$ (100)
6	8.04 (d, 2H, $J = 7.6$ Hz), 7.95 (d, 2H, $J = 7.6$ Hz), 7.47 (t, 2H, $J = 7.6$ Hz), 7.43 (t, 2H, $J = 7.68$ Hz), 5.05 (s, 2H, $\text{CH}_2$ )	167.0, 153.2, 135.9, 127.0, 125.9, 123.2, 122.9, 38.5	282 $\text{M}^{\circ+}$ (100)
7	7.70 (d, 2H, $J = 7.8$ Hz), 7.50 (d, 2H, $J = 7.8$ Hz), 7.31 (t, 4H, $J = 7.8$ Hz), 4.62 (s, 2H, $\text{CH}_2$ )	159.5, 151.5, 141.3, 125.5, 124.8, 120.4, 110.9, 29.6	250 $\text{M}^{\circ+}$ (100)
8	7.60 (d, 2H, $J = 7.8$ Hz), 7.52 (s, 2H), 7.21 (d, 2H, $J = 7.8$ Hz), 4.84 (s, 2H, $\text{CH}_2$ ), 2.41 (s, 6H, $2\text{CH}_3$ )	161.4, 149.5, 141.5, 134.7, 126.9, 120.2, 110.9, 29.4, 21.6	278 $\text{M}^{\circ+}$ (100)
9	7.59 (d, 2H, $J = 7.8$ Hz), 7.52 (s, 2H), 7.19 (d, 2H, $J = 7.8$ Hz), 4.82 (s, 2H, $\text{CH}_2$ ), 2.46 (s, 6H, $2\text{CH}_3$ )	160.8, 151.5, 139.2, 136.0, 126.4, 119.7, 111.5, 29.3, 21.9	278 $\text{M}^{\circ+}$ (100)
10	12.41 (s, 2H, NH), 7.46 (dd, 4H, $J = 6.8, 3.2$ Hz), 7.11 (dd, 4H, $J = 6.8$ Hz), 4.43 (s, 2H, $\text{CH}_2$ )	150.8, 138.4 122.9, 115.4, 29.8	248 $\text{M}^{\circ+}$ (100)
11	12.33 (s, 2H, NH), 7.32 (d, 2H, $J = 7.8$ Hz), 7.23 (s, 2H), 6.91 (d, 2H, $J = 7.8$ Hz), 4.35 (s, 2H, $\text{CH}_2$ ), 2.33 (s, 6H, $\text{CH}_3$ )	150.6, 139.2 137.9, 131.2, 123.5, 115.3, 114.7, 30.0, 21.9	276 $\text{M}^{\circ+}$ (100)
12	12.69 (s, 2H, NH), 7.54 (s, 2H), 7.48 (d, 2H, $J = 7.8$ Hz), 7.14 (d, 2H, $J = 7.8$ Hz), 4.46 (s, 2H, $\text{CH}_2$ )	149.3, 134.7, 132.5, 129.6, 125.9, 116.6, 115.1, 26.8	317 $\text{M}^{\circ+}$ (100)
13	7.98 (d, 2H, $J = 7.8$ Hz), 7.82 (d, 2H, $J = 7.8$ Hz), 7.44 (t, 2H, $J = 8.2$ Hz), 7.37 (t, 2H, $J = 8.2$ Hz), 3.74 (s, 4H, $2\text{CH}_2$ )	169.6, 153.5, 135.5, 126.4, 125.3, 123.0, 121.9, 33.6	296 $\text{M}^{\circ+}$ (100)
14	7.65 (t, 2H, $J = 7.8$ Hz), 7.46 (t, 2H, $J = 7.8$ Hz), 7.28 (d, 4H, $J = 7.8$ Hz), 3.56 (s, 4H)	165.2, 151.2, 141.6, 125.2, 124.7, 120.2, 110.9, 25.7	264 $\text{M}^{\circ+}$ (100)
15	7.46 (s, 2H), 7.41 (d, 2H, $J = 7.8$ Hz), 7.16 (d, 2H, $J = 7.8$ Hz), 3.55 (s, 4H, $2\text{CH}_2$ ), 2.47 (s, 6H, $2\text{CH}_3$ )	165.5, 149.4, 141.8, 134.3, 125.9, 119.7, 109.9, 25.7, 21.3	292 $\text{M}^{\circ+}$ (100)
No.	$^1\text{H}$ NMR $\delta$ [ppm]	$^{13}\text{C}$ NMR $\delta$ [ppm]	Mass m/z (%)
16	7.53 (d, 2H, $J = 7.6$ Hz), 7.35 (s, 2H), 7.16 (d, 2H, $J = 7.6$ Hz), 3.54 (s, 4H, $2\text{CH}_2$ ), 2.50 (s, 6H, $2\text{CH}_3$ )	164.8, 151.5, 139.3, 135.4, 125.5, 119.1, 110.7, 25.6, 21.6	292 $\text{M}^{\circ+}$ (100)
17	12.41 (s, 2H, NH), 7.57 (d, 4H, $J = 7.8$ Hz), 7.26 (t, 4H, $J = 8.2$ Hz), 3.56 (s, 4H, $2\text{CH}_2$ )	153.8, 135.4, 124.3, 114.6, 25.4	262 $\text{M}^{\circ+}$ (100)
18	12.75 (s, 2H, NH), 7.31 (d, 2H, $J = 7.8$ Hz), 7.22 (s, 2H), 6.90 (d, 2H, $J = 7.8$ Hz), 3.51 (s, 4H, $\text{CH}_2$ ), 2.33 (s, 6H, $\text{CH}_3$ )	154.2, 138.7, 137.4, 131.2, 123.5, 115.0, 114.5, 27.0, 21.9	290 $\text{M}^{\circ+}$ (100)
19	12.56 (s, 2H, NH), 7.50 (s, 2H), 7.44 (d, 2H, $J = 7.8$ Hz), 7.09 (d, 2H), 3.36 (s, 4H, $2\text{CH}_2$ )	156.2, 140.6, 138.0, 126.3, 122.1, 116.2, 115.1 27.0	331 $\text{M}^{\circ+}$ (100)
20	8.01 (d, 2H, $J = 7.6$ Hz), 7.93–7.90 (dd, 2H, $J = 6.5, 3.2$ Hz), 7.77 (d, 2H, $J = 7.6$ Hz), 7.61–7.58 (dd, 2H, $J = 6.5, 3.2$ Hz), 7.44 (t, 2H, $J = 7.6$ Hz), 7.33 (t, 2H, $J = 7.6$ Hz)	166.4, 153.4, 136.6, 133.5, 131.6, 131.5, 127.2, 126.3, 123.8, 121.9	344 $\text{M}^{\circ+}$ (100)
21	8.07 (t, 2H, $J = 7.8$ Hz), 7.81 (t, 2H, $J = 7.8$ Hz), 7.72 (t, 2H, $J = 7.8$ Hz), 7.53 (d, 2H, $J = 7.8$ Hz), 7.35 (d, 4H, $J = 7.8$ Hz)	162.2, 151.0, 141.9, 132.5, 131.7, 127.4, 126.5, 125.5, 120.7, 111.5	312 $\text{M}^{\circ+}$ (100)

Table 3. Continued.

No.	<sup>1</sup> H NMR $\delta$ [ppm]	<sup>13</sup> C NMR $\delta$ [ppm]	Mass m/z (%)
22	8.13 (t, 2H, $J = 7.8$ Hz), 7.84 (d, 2H, $J = 7.8$ Hz), 7.52 (s, 2H), 7.44 (d, 2H, $J = 7.8$ Hz), 7.19 (d, 2H, $J = 7.8$ Hz), 2.40 (s, 6H, 2CH <sub>3</sub> )	162.3, 149.4, 142.2, 134.9, 132.4, 131.6, 127.6, 127.4, 120.5, 110.9, 21.6	340 M <sup>o+</sup> (100)
23	8.12–8.09 (m, 2H), 7.85–7.82 (m, 2H), 7.60 (d, 2H, $J = 7.8$ Hz), 7.37 (s, 2H), 7.20 (d, 2H, $J = 7.8$ Hz), 2.41 (s, 6H, 2CH <sub>3</sub> )	161.8, 151.4, 139.8, 136.5, 132.3, 131.7, 127.5, 126.7, 120.2, 111.4, 21.9	340 M <sup>o+</sup> (100)
24	12.64 (s, 2H, N–H), 7.88 (d, 1H, $J = 7.8$ Hz), 7.80 (d, 1H, $J = 7.8$ Hz), 7.69 (t, 2H), 7.61 (m, 4H), 7.26 (m, 4H),	151.6, 137.9, 133.5, 131.9, 129.4, 123.5, 115.5	310 M <sup>o+</sup> (100)
25	12.41 (s, 2H, NH), 8.05 (s, 2H), 7.78 (s, 2H, N–H), 7.63 (s, 2H), 7.56 (d, 2H, $J = 7.8$ Hz), 7.35 (s, 2H), 7.00 (d, 2H, $J = 7.8$ Hz), 2.37 (s, 6H, CH <sub>3</sub> )	151.6, 139.0, 137.8, 132.2, 132.0, 130.4, 129.9, 115.9, 115.1, 22.0	338 M <sup>o+</sup> (100)
26	12.41 (s, 2H, NH), 8.14 (s, 2H), 7.61 (br, 4H), 7.55 (d, 2H, $J = 7.8$ Hz), 7.12 (d, 2H, $J = 7.8$ Hz)	154.3, 141.4, 138.9, 132.1, 130.4, 130.3, 126.6, 122.4, 117.1, 115.8	378 M <sup>o+</sup> (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 <sub>3</sub> )	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 <sup>o+</sup> (100)
28	7.97 (d, 1H, $J = 7.8$ Hz), 7.89 (s, 1H, $J = 7.8$ Hz), 7.64 (d, 2H), 7.59 (d, 1H, $J = 7.8$ Hz), 7.49 (d, 2H, $J = 7.8$ Hz), 7.31 (t, 4H, $J = 7.8$ Hz), 2.37 (s, 3H, CH <sub>3</sub> )	162.7, 162.6, 151.2, 151.1, 142.2, 142.1, 142.1, 132.1, 131.9, 131.19, 127.5, 125.5, 125.4, 124.9, 124.6, 124.5, 120.4, 120.2, 110.7, 110.6, 21.4	326 M <sup>o+</sup> (100)
29	12.40 (s, 2H, NH), 9.67 (s, 2H, N–H), 7.97 (d, 1H, $J = 7.8$ Hz), 7.92 (s, 1H), 7.56–7.51 (m, 4H), 7.48–7.46 (d, 1H, $J = 7.8$ Hz), 7.18–7.15 (m, 4H), 2.40 (s, 3H, CH <sub>2</sub> )	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 <sup>o+</sup> (100)
30	12.76 (s, 2H, NH), 7.96 (d, 1H, $J = 7.8$ Hz), 7.91 (s, 1H), 7.44–7.43 (m, 3H), 7.35 (s, 2H), 6.98 (d, 2H, $J = 7.8$ Hz), 2.42 (s, 3H, CH <sub>3</sub> ), 2.36 (s, 6H, 2CH <sub>3</sub> )	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 <sup>o+</sup> (100)
31	12.84 (s, 2H, NH), 8.09 (d, 1H, $J = 7.8$ Hz), 8.04 (s, 1H), 7.62 (d, 2H, $J = 7.8$ Hz), 7.56–7.53 (m, 2H), 7.36 (d, 1H, $J = 7.8$ Hz), 7.10 (d, 2H, $J = 7.8$ Hz), 2.38 (s, 3H, CH <sub>3</sub> )	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 <sup>o+</sup> (100)
32	8.21 [d, 2H, $J = 7.8$ Hz], 7.98 [d, 2H, $J = 7.8$ Hz], 7.56 [t, 2H, $J = 7.8$ Hz], 7.49 [t, 2H, $J = 7.8$ Hz]	nd.	501 M <sup>o+</sup> (20), 465 M <sup>o+</sup> –Cl (20), 429 M <sup>o+</sup> –2Cl (25), 358 M <sup>o+</sup> –4Cl (30), 268 M <sup>o+</sup> –ZrCl <sub>4</sub> (100)
33	7.96 (dd, 4H, $J = 8.1, 3.2$ Hz), 7.62–7.55 (m, 4H)	152.2, 150.9, 141.3, 128.6, 126.8, 121.8, 111.9	469 M <sup>o+</sup> (10), 433 M <sup>o+</sup> –Cl (5), 397 M <sup>o+</sup> –2Cl (20), 361 M <sup>o+</sup> –3Cl (5), 236 M <sup>o+</sup> –ZrCl <sub>4</sub> (100)

Table 3. Continued.

No.	$^1\text{H}$ NMR $\delta$ [ppm]	$^{13}\text{C}$ NMR $\delta$ [ppm]	Mass $m/z$ (%)
34	7.67 (s, 2H), 7.16 (d, 2H, $J = 7.8$ Hz), 7.02 (d, 2H, $J = 7.8$ Hz), 2.38 (s, 6H)	155.3, 147.8, 141.0, 132.4, 127.5, 123.1, 108.8, 21.2	498 $\text{M}^{\circ+}$ (15), 461 $\text{M}^{\circ+}-\text{Cl}$ (20), 425 $\text{M}^{\circ+}-2\text{Cl}$ (10), 354 $\text{M}^{\circ+}-4\text{Cl}$ (20), 264 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
35	12.43 (br, 2H, NH), 7.18 [d, 4H, $J = 7.6$ Hz] 7.04 [t, 4H, $J = 7.6$ Hz]	156.2, 126.6, 124.0, 116.2	467 $^{\circ+}$ (20), 397 $\text{M}^{\circ+}-2\text{Cl}$ (20), 361 $\text{M}^{\circ+}-3\text{Cl}$ (10), 234 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
36	12.12 (br, 2H, NH), 7.06 [d, 2H, $J = 7.6$ Hz], 6.97 (s, 2H), 6.82 [d, 2H, $J = 7.6$ Hz], 2.17 (s, 6H, 2CH <sub>3</sub> )	156.1, 155.8, 133.0, 126.2, 124.6, 124.1, 115.9, 115.7, 21.3	495 $\text{M}^{\circ+}$ (10), 478 $\text{M}^{\circ+}-\text{CH}_3$ (15), 423 $\text{M}^{\circ+}-2\text{Cl}$ (20), 389 $\text{M}^{\circ+}-3\text{Cl}$ (20), 352 $\text{M}^{\circ+}-4\text{Cl}$ (20) 262 $\text{M}^{\circ+}-\text{ZrCl}_4$ (50)
37	8.10 (d, 2H, $J = 7.6$ Hz), 8.01 (d, 2H, $J = 7.6$ Hz), 7.53 (t, 2H, $J = 7.6$ Hz), 7.45 (t, 2H, $J = 7.6$ Hz), 5.10 (s, 2H, CH <sub>2</sub> )	167.1, 153.4, 135.9, 127.0, 126.0, 123.3, 123.0, 38.5	517 $\text{M}^{\circ+}$ (10), 478 $\text{M}^{\circ+}-\text{Cl}$ (10), 444 $\text{M}^{\circ+}-2\text{Cl}$ (20), 406 $\text{M}^{\circ+}-3\text{Cl}$ (5), 282 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
38	7.76 (d, 4H, $J = 7.8$ Hz), 7.47 (t, 4H, $J = 7.8$ Hz), 4.99 (s, 2H, CH <sub>2</sub> )	161.78, 151.4, 151.2, 141.5, 141.1, 126.6, 126.4, 125.7, 125.6, 120.7, 120.6, 111.8, 29.6	483 $\text{M}^{\circ+}$ (20), 447 $\text{M}^{\circ+}-\text{Cl}$ (25), 411 $\text{M}^{\circ+}-2\text{Cl}$ (15), 375 $\text{M}^{\circ+}-3\text{Cl}$ (10), 250 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
39	7.57 (d, 2H, $J = 7.8$ Hz), 7.51 (s, 2H), 7.20 (d, 2H, $J = 7.8$ Hz), 4.82 (s, 2H, CH <sub>2</sub> ), 2.40 (s, 6H, 2CH <sub>3</sub> )	161.4, 149.4, 141.5, 134.7, 127.0, 120.2, 110.9, 29.4, 21.6	511 $\text{M}^{\circ+}$ (30), 474 $\text{M}^{\circ+}-\text{Cl}$ (20), 404 $\text{M}^{\circ+}-3\text{Cl}$ (10), 340 $\text{M}^{\circ+}-4\text{Cl}-2\text{CH}_3$ (30), 278 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
40	7.58 (d, 2H, $J = 7.8$ Hz), 7.52 (s, 2H), 7.19 (d, 2H, $J = 7.8$ Hz), 4.81 (s, 2H, CH <sub>2</sub> ), 2.42 (s, 6H, 2CH <sub>3</sub> )	160.8, 151.5, 139.1, 136.0, 126.4, 119.7, 111.5, 29.3, 21.9	511 $\text{M}^{\circ+}$ (15), 474 $\text{M}^{\circ+}-\text{Cl}$ (20), 404 $\text{M}^{\circ+}-3\text{Cl}$ (30), 340 $\text{M}^{\circ+}-4\text{Cl}-2\text{CH}_3$ (30), 278 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
41	7.63–7.62 (m, 4H), 7.33–7.30 (m, 4H), 4.91 (s, 2H, CH <sub>2</sub> )	150.6, 138.7, 122.6, 115.3, 29.6	481 $\text{M}^{\circ+}$ (10), 444 $\text{M}^{\circ+}-\text{Cl}$ (20), 407 $\text{M}^{\circ+}-2\text{Cl}$ (10), 370 $\text{M}^{\circ+}-3\text{Cl}$ (20), 336 $\text{M}^{\circ+}-4\text{Cl}$ (15), 248 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
42	7.55 (d, 2H, $J = 7.8$ Hz), 7.47 (s, 2H), 7.21 (d, 2H, $J = 7.8$ Hz), 5.05 (s, 2H, CH <sub>2</sub> ), 2.40 (s, 6H, 2CH <sub>3</sub> )	147.5, 135.0, 134.0, 132.2, 126.7, 114.6, 114.3, 26.6, 21.8	510 $\text{M}^{\circ+}$ (20), 477 $\text{M}^{\circ+}-\text{Cl}$ (20), 440 $\text{M}^{\circ+}-2\text{Cl}$ (25), 405 $\text{M}^{\circ+}-3\text{Cl}$ (20), 276 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
43	7.89 (s, 2H), 7.80 (d, 2H, $J = 7.8$ Hz), 7.52 (d, 2H, $J = 7.8$ Hz), 5.23 (s, 2H, CH <sub>2</sub> )	149.1, 134.3, 132.2, 130.1, 126.1, 116.5, 114.8, 26.7	549 $\text{M}^{\circ+}$ (25), 513 $\text{M}^{\circ+}-\text{Cl}$ (15), 476 $\text{M}^{\circ+}-2\text{Cl}$ (10), 440 $\text{M}^{\circ+}-3\text{Cl}$ (25), 316 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
44	8.03 (d, 2H, $J = 7.8$ Hz), 7.92 (d, 2H, $J = 7.8$ Hz), 7.49–7.35 (m, 4H), 3.71 (s, 4H, 2CH <sub>2</sub> )	170.7, 152.8, 135.3, 126.7, 125.7, 122.9, 122.7, 33.0	530 $\text{M}^{\circ+}$ (10), 493 $\text{M}^{\circ+}-\text{Cl}$ (25), 456 $\text{M}^{\circ+}-2\text{Cl}$ (15), 389 $\text{M}^{\circ+}-4\text{Cl}$ (20), 296 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)
45	7.68–7.64 (m, 4H), 7.35–7.31 (m, 4H), 3.55 (s, 4H, 2CH <sub>2</sub> )	166.2, 150.9, 141.4, 125.5, 125.0, 120.0, 111.3, 25.3	497 $\text{M}^{\circ+}$ (20), 462 $\text{M}^{\circ+}-\text{Cl}$ (20), 426 $\text{M}^{\circ+}-2\text{Cl}$ (25), 354 $\text{M}^{\circ+}-4\text{Cl}$ (10), 264 $\text{M}^{\circ+}-\text{ZrCl}_4$ (100)



Table 3. Continued.

No.	$^1\text{H}$ NMR $\delta$ [ppm]	$^{13}\text{C}$ NMR $\delta$ [ppm]	Mass $m/z$ (%)
46	7.53 (d, 2H, $J = 7.8$ Hz), 7.44 (s, 2H), 7.15 (d, 2H, $J = 7.8$ Hz), 3.50 (s, 4H, 2CH <sub>2</sub> ), 2.38 (s, 6H, 2CH <sub>3</sub> )	166.2, 149.4, 141.3, 134.3, 126.4, 119.9, 110.7, 25.4, 21.6	526 M <sup>o+</sup> (30), 460 M <sup>o+</sup> -Cl-2CH <sub>3</sub> (25), 453 M <sup>o+</sup> -2Cl (1), 417 M <sup>o+</sup> -3Cl (20), 381 M <sup>o+</sup> -4Cl (10), 296 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
47	7.51 (s, 2H), 7.46 (d, 2H, $J = 7.8$ Hz), 7.12 (d, 2H, $J = 7.8$ Hz), 3.48 (s, 4H, 2CH <sub>2</sub> ), 2.40 (s, 6H, 2CH <sub>3</sub> )	165.5, 151.2, 139.2, 135.4, 126.0, 119.4, 111.3, 25.3, 21.8	526 M <sup>o+</sup> (30), 460 M <sup>o+</sup> -Cl-2CH <sub>3</sub> (20), 453 M <sup>o+</sup> -2Cl (30), 417 M <sup>o+</sup> -3Cl (20), 381 M <sup>o+</sup> -4Cl (10), 296 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
48	7.73–7.71 (m, 4H), 7.45–7.42 (m, 4H), 3.84 (s, 4H, 2CH <sub>2</sub> )	152.7, 133.3, 125.3, 114.7, 24.7	495 M <sup>o+</sup> (20), 458 M <sup>o+</sup> -Cl (20), 422 M <sup>o+</sup> -2Cl (25), 387 M <sup>o+</sup> -3Cl (30), 351 M <sup>o+</sup> -4Cl (20), 262 M <sup>o+</sup> -ZrCl <sub>4</sub> (50)
49	7.66 (d, 2H, $J = 7.8$ Hz), 7.57 (s, 2H), 7.35 (d, 2H, $J = 7.8$ Hz), 3.85 (s, 4H, 2CH <sub>2</sub> ), 2.48 (s, 6H, 2CH <sub>3</sub> )	151.6, 136.0, 132.3, 130.0, 127.5, 114.1, 114.0, 24.4, 21.8	523 M <sup>o+</sup> (20), 487 M <sup>o+</sup> -Cl (20), 451 M <sup>o+</sup> -2Cl (25), 414 M <sup>o+</sup> -3Cl (30), 377 M <sup>o+</sup> -4Cl (20), 290 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
50	7.83 (s, 2H), 7.75 (d, 2H, $J = 7.8$ Hz), 7.48 (d, 2H, $J = 7.8$ Hz), 3.76 (s, 4H, 2CH <sub>2</sub> )	154.4, 134.6, 132.5, 129.7, 125.5, 116.2, 114.7, 24.9	564 M <sup>o+</sup> (10), 528 M <sup>o+</sup> -Cl (25), 493 M <sup>o+</sup> -2Cl (20), 456 M <sup>o+</sup> -3Cl (30), 419 M <sup>o+</sup> -4Cl (20), 331 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
51	8.01 (d, 2H, $J = 7.8, 3.2$ Hz), 7.92–7.90 (m, 4H), 7.72–7.70 (dd, 2H, $J = 7.8, 3.2$ Hz), 7.45 (t, 2H, $J = 7.8$ Hz), 7.38 (t, 2H, $J = 7.8$ Hz)	166.4, 153.4, 136.6, 133.5, 131.6, 131.5, 127.2, 126.3, 123.8, 122.9	577 M <sup>o+</sup> (10), 506 M <sup>o+</sup> -2Cl (30), 470 M <sup>o+</sup> -3Cl (20), 433 M <sup>o+</sup> -4Cl (25), 344 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
52	8.11–8.09 (dd, 2H, $J = 7.8, 3.2$ Hz), 7.83–7.81 (dd, 2H, $J = 7.8, 3.2$ Hz), 7.68 (t, 2H, $J = 7.8, 3.2$ Hz), 7.53 (t, 2H, $J = 7.8$ Hz), 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 <sup>o+</sup> (20), 509 M <sup>o+</sup> -Cl (20), 472 M <sup>o+</sup> -2Cl (15), 312 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
53	8.24–8.21 (dd, 2H, $J = 7.8, 3.2$ Hz), 7.97 (t, 2H, $J = 7.8$ Hz), 7.63 (s, 2H), 7.57 (d, 2H, $J = 7.8$ Hz), 7.31 (d, 2H, $J = 7.8$ Hz), 2.52 (s, 6H, 2CH <sub>3</sub> )	162.6, 149.6, 142.4, 135.2, 132.7, 131.9, 127.8, 127.7, 120.8, 111.2, 21.9	573 M <sup>o+</sup> (15), 506 M <sup>o+</sup> -Cl-2CH <sub>3</sub> (10), 501 M <sup>o+</sup> -2Cl (30), 465 M <sup>o+</sup> -3Cl (30), 431 M <sup>o+</sup> -4Cl (20), 340 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
54	8.13–8.10 (dd, 2H, $J = 7.8, 3.2$ Hz), 7.86–7.83 (dd, 2H, $J = 7.8, 3.2$ Hz), 7.61 (d, 2H, $J = 7.8$ Hz), 7.40 (s, 2H), 7.21 (d, 2H, $J = 7.8$ Hz), 2.42 (s, 6H, 2CH <sub>3</sub> )	161.8, 151.4, 139.8, 136.5, 132.4, 131.7, 127.5, 126.7, 120.2, 111.5, 21.9	573 M <sup>o+</sup> (30), 537 M <sup>o+</sup> -Cl (20), 472 M <sup>o+</sup> -2Cl-2CH <sub>3</sub> (30), 467 M <sup>o+</sup> -3Cl (20), 431 M <sup>o+</sup> -4Cl (20), 340 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
55	8.28–8.25 (dd, 2H, $J = 7.8, 3.2$ Hz), 7.94 (t, 2H, $J = 7.8$ Hz), 7.71–7.67 (m, 4H), 7.45–7.42 (m, 4H)	149.1, 135.0, 132.5, 126.2, 125.4, 115.3, 114.8	543 M <sup>o+</sup> (15), 506 M <sup>o+</sup> -Cl (20), 437 M <sup>o+</sup> -3Cl (30), 400 M <sup>o+</sup> -4Cl (15), 310 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
56	8.27 (t, 2H, $J = 7.8$ Hz), 8.03 (d, 2H, $J = 7.8$ Hz), 7.64 (d, 2H, $J = 7.8$ Hz), 7.54 (s, 2H), 7.36 (d, 2H, $J = 7.8$ Hz), 2.49 (s, 6H, 2CH <sub>3</sub> )	147.2, 136.2, 133.8, 133.5, 133.3, 131.8, 127.8, 124.7, 114.7, 114.43, 21.9	571 M <sup>o+</sup> (15), 498 M <sup>o+</sup> -2Cl (10), 464 M <sup>o+</sup> -3Cl (20), 429 M <sup>o+</sup> -4Cl (20), 338 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
57	8.08 (d, 2H, $J = 7.8$ Hz), 7.76 (t, 2H, $J = 7.8$ Hz), 7.67 (s, 2H), 7.61 (d, 2H, $J = 7.8$ Hz), 7.25 (d, 2H, $J = 7.8$ Hz)	151.7, 137.7, 135.4, 131.9, 128.7, 127.7, 124.6, 123.4, 116.8, 115.3	611 M <sup>o+</sup> (20), 541 M <sup>o+</sup> -2Cl (30), 503 M <sup>o+</sup> -3Cl (20), 467 M <sup>o+</sup> -4Cl (15), 378 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)

Table 3. Continued.

No.	<sup>1</sup> H NMR $\delta$ [ppm]	<sup>13</sup> C NMR $\delta$ [ppm]	Mass m/z (%)
58	8.00 (t, 2H, $J = 7.8$ Hz), 7.92 (t, 2H, $J = 7.8$ Hz), 7.81 (d, 1H, $J = 7.8$ Hz), 7.72 (s, 1H), 7.53 (d, 1H, $J = 7.8$ Hz), 7.46 (d, 2H, $J = 7.8$ Hz), 7.38 (d, 2H, $J = 7.8$ Hz), 2.44 (s, 3H, CH <sub>3</sub> )	166.5, 166.4, 153.4, 153.4, 141.6, 136.6, 136.5, 133.4, 132.1, 132.0, 131.6, 130.8, 127.2, 127.1, 126.3, 126.2, 123.8, 123.7, 122.9, 122.8, 21.5	593 M <sup>o+</sup> (30), 558 M <sup>o+</sup> -Cl (20), 522 M <sup>o+</sup> -2Cl (15), 485 M <sup>o+</sup> -3Cl (20), 471 M <sup>o+</sup> -3Cl-CH <sub>3</sub> (20), 450 M <sup>o+</sup> -4Cl (50), 358 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
59	8.00 (d, 1H, $J = 7.8$ Hz), 7.92 (s, 1H), 7.69–7.65 (m, 2H), 7.62 (d, 1H, $J = 7.8$ Hz), 7.54–7.50 (m, 2H), 7.34 (t, 4H, $J = 7.8$ Hz), 2.45 (s, 3H, CH <sub>3</sub> )	162.3, 162.2, 151.0, 150.9, 142.8, 141.9, 141.8, 133.0, 132.2, 131.5, 127.3, 126.4, 126.3, 125.5, 125.4, 124.7, 120.7, 120.6, 111.5, 111.4, 21.5	560 M <sup>o+</sup> (15), 524 M <sup>o+</sup> -Cl (20), 474 M <sup>o+</sup> -2Cl-CH <sub>3</sub> (30), 452 M <sup>o+</sup> -3Cl (20), 417 M <sup>o+</sup> -4Cl (20), 326 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
60	8.13 (d, 1H, $J = 7.8$ Hz), 7.69–7.63 (m, 4H), 7.42–7.39 (dd, 4H, $J = 7.8$ Hz), 7.38 (s, 1H), 7.37 (d, 1H, $J = 7.8$ Hz), 2.51 (s, 3H, CH <sub>3</sub> )	149.8, 142.5, 135.9, 135.1, 132.5, 132.2, 127.0, 125.1, 124.8, 123.6, 115.4, 115.2, 21.6	557 M <sup>o+</sup> (10) 542 M <sup>o+</sup> -CH <sub>3</sub> (15), 414 M <sup>o+</sup> -4Cl (20), 324 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
61	8.16 (d, 2H, $J = 7.8$ Hz), 7.82 (d, 1H, $J = 7.6$ Hz), 7.63 (d, 2H, $J = 7.6$ Hz), 7.53 (s, 2H), 7.34 (d, 2H, $J = 7.6$ Hz), 2.47 (s, 6H, 2CH <sub>3</sub> ), 2.30 (s, 3H, CH <sub>3</sub> )	147.6, 147.2 143.5, 135.8, 134.2, 133.7, 133.4, 133.2, 132.2, 131.8, 129.6, 128.9, 127.5, 126.0, 124.9, 122.0, 114.7, 114.6, 114.4, 114.3, 21.9, 21.6	585 M <sup>o+</sup> (20), 514 M <sup>o+</sup> -2Cl (30), 478 M <sup>o+</sup> -3Cl (15), 413 M <sup>o+</sup> -4Cl -2CH <sub>3</sub> (30), 352 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)
62	8.10 (s, 1H), 8.07 (s, 2H), 7.75–7.64 (m, 4H), 7.42–7.37 (m, 2H), 2.51 (s, 3H, CH <sub>3</sub> )	151.6, 142.4, 137.6, 136.9, 135.4, 134.7, 132.4, 132.0, 131.5, 128.9, 128.7, 127.3, 127.1, 124.9, 124.8, 116.8, 116.7, 115.3, 115.1, 21.6	626 M <sup>o+</sup> (20), 611 M <sup>o+</sup> -CH <sub>3</sub> (25), 590 M <sup>o+</sup> -Cl (20), 553 M <sup>o+</sup> -2Cl (20), 517 M <sup>o+</sup> -3Cl (30), 469 M <sup>o+</sup> -4Cl-CH <sub>3</sub> (25), 393 M <sup>o+</sup> -ZrCl <sub>4</sub> (100)

### 3.6. Polymerization of ethylene

2–5 mg of the desired complex was suspended in 5 mL of toluene. Methylaluminoxane (30% in toluene) was then added, resulting in an immediate color change. The mixture was added to a 1-L Schlenk flask filled with 250 mL of n-pentane. This mixture was transferred to a 1-L Büchi laboratory autoclave under inert atmosphere and thermostated. An ethylene pressure of 10 bar was applied for 1 h. The polymer was filtered over a frit; washed with diluted hydrochloric acid, water, and acetone; and finally dried in vacuo.

### 4. Conclusions

Bis-(benzimidazolyl, benzothiazolyl, and benzoxazolyl) form symmetric chelate complexes with Zr(IV) chloride. After activation with MAO the generated catalysts polymerize ethylene in solution with various activities. Structure–property relationships the nature and position of substituents and the hetero atoms determine the performance of such catalysts. The highest activity (424 kg PE/mol cat. h) was obtained with the catalyst **38/MAO**. The high molecular weights of the produced polymers ( $1.9 \times 10^6$  g/mol) indicate low energy barriers for the olefin insertion and high barriers for the termination steps. Relative broad molecular weight distributions of the produced polyethylenes (PD = 1.9–23) could result from the existence of several active sites in the polymerization process. The catalysts generally show moderate to good activities compared to the benchmark catalyst Cp<sub>2</sub>ZrCl<sub>2</sub>.

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## References

1. Lever, A. B. P.; Ramaswamy, B. S.; Simonsen, S. H.; Thompson, L. K. *Can. J. Chem.* **1970**, *48*, 3076-3088.
2. Rendell, J. C.; Thompson, L. K. *Can. J. Chem.* **1979**, *57*, 1-7.
3. Thompson, L. K.; Rendell, J. C.; Wellon, G. C. *Can. J. Chem.* **1982**, *60*, 514-520.
4. Duff, E. J.; Hughes, M. N.; Rutt, K. J. *J. Chem. Soc. A.* **1969**, 2101-2105.
5. Campell, M. J. M.; Card, D. W.; Grzeskowiak, R.; Goldstein, M. *J. Chem. Soc. A.* **1970**, 672-675.
6. Chan, N. N. Y.; Goodgame, M.; Weeks, M. J. *J. Chem. Soc. A.* **1968**, 2499-2501.
7. Thompson, L. K.; Ball, R. G.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1566-1576.
8. Duff, E. J.; Hughes, M. N.; Rutt, K. J. *J. Chem. Soc. A.* **1968**, 2354-2357.
9. Livingstone, S. E; Nolan, J. D. *J. Chem. Soc. Dalton Trans.* **1972**, 218-223.
10. Salameh, A. S.; Tayim, H. A. *Polyhedron* **1982**, *6*, 543-548.
11. Wang, S.; Cui, Y.; Tan, R.; Luo, Q.; Shi, J.; Wu, Q. *Polyhedron* **1994**, *11*, 1661-1668.
12. Wang, J.; Zhu, Y.; Wang, S.; Gao, Y.; Shi, Q. *Polyhedron* **1994**, *13*, 1405-1409.
13. Holz, R. C.; Thomson, L. C. *Inorg. Chem.* **1988**, *27*, 4640-4644.
14. Wang, S. X.; Zhu, Y.; Zhang, F. G.; Wang, Q. Y.; Wang, L. F. *Polyhedron* **1992**, *11*, 1909-1915.
15. Addison, A. D.; Burman, S.; Wahlgren, C. B.; Rajjan, O. A.; Rowe, T. W.; Sinn, E. J. *Chem. Soc. Dalton Trans.* **1987**, 2621-2630.
16. Ruttimann, S.; Moreau, C. M.; Williams, A. F.; Bernardinelli, G.; Addison, A. W. *Polyhedron* **1992**, *11*, 635-646.
17. Nelson, S. M.; Esho, F. S.; Drew, M. G. B. *J. Chem. Soc. Dalton Trans.* **1982**, 407-415.
18. Shashikala, N.; Gayathri, V.; Gowda, N. M. N.; Reddy, G. K. N. *J. Indian Chem. Soc.* **1989**, *66*, 537-540.
19. Sanni, S. B.; Behm, H. J.; Benrskens, P. T.; Albada, G. A. V.; Reedijk, J.; Lenstra, A. T.H.; Addison, A. W.; Palaniandavar, M. J. *J. Chem. Soc. Dalton Trans.* **1988**, 1429-1435.
20. Wellon, G. C.; Bautista, D. V.; Thompson, L. K.; Hartstock, F. W. *Inorg. Chim. Acta.* **1983**, *75*, 271-276.
21. Breslow, R.; Hunt, J. T.; Smiley, R.; Tamowski, T. *J. Am. Chem. Soc.* **1983**, *105*, 5337-5342.
22. Beer, R. H.; Tolmann, W. B.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1989**, *28*, 4557-4558.
23. Winter, J. A.; Caruso, D.; Shepherd, R. E. *Inorg. Chem.* **1988**, *27*, 1086-1089.
24. Jin, G.; Chen, F. CN 101089022A, 2007.
25. Kaminsky, W.; Fernandes, M. *Polyolefins* **2015**, *2*, 1-19.
26. Redshaw, C.; Tang, Y. *Chem. Soc. Rev.* **2012**, *41*, 4484-4510.
27. Baier, M. C.; Zuideveld, M. A.; Mecking, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 9722-9744.
28. Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347-1376.
29. Köppl, A.; Alt, H. G.; Schmidt, R. *J. Organomet. Chem.* **1999**, *577*, 351-357.
30. Alt, H. G. *J. Chem. Soc. Dalton Trans.* **1999**, 1703-1709.
31. Schilling, M.; Bal, R.; Görl, C.; Alt, H. G. *Polymer* **2007**, 7461-7475.
32. Schilling, M.; Görl, C.; Alt, H. G. *Appl. Catal. A General* **2008**, *348*, 79-85.
33. Alt, H. G. *Dalton Trans.* **2005**, 3271-3276.
34. Severn, J. R.; Chadwick, J.C. *Tailor-Made Polymers*; 4th ed. Wiley-VCH: Weinheim, Germany, 2008.
35. Ruhland, M.; Lang, J. R. V.; Alt, H. G.; Müller, A. H. E. *Eur. J. Inorg. Chem.* **2013**, 2146-2153.
36. Alshammari, H.; Alt, H. G. *J. J. C.* **2014**, *9*, 34-49.
37. Alshammari, H.; Alt, H. G. *J. J. C.* **2014**, *9*, 110-126.

38. Alshammari, H.; Alt, H. G. *Polyolefins* **2014**, *1*, 107-116.
39. Tomov, A. K.; Gibson, V. C.; Zaher, D.; Elsegood, M. R. J.; Dale, S. H. *Chem. Commun.* **2004**, 1956-1957.
40. Cho, H. Y.; Tarte, N. H.; Cui, L.; Hong, D. S.; Woo, S. I.; Gong, Y. D. *Macromol. Chem. Phys.* **2006**, *207*, 1965-1971.
41. Elagab, H. A.; Alt, H. G. *Inorg. Chim. Acta.* **2015**, *428*, 100-111.
42. Elagab, H. A.; Alt, H. G. *Eur. Poly. J.* **2015**, *68*, 385-397.
43. Elagab, H. A.; Alt, H. G. *Inorg. Chim. Acta.* **2015**, *431*, 266-275.
44. Elagab, H. A.; Alt, H. G. *J. J. C.* **2015**, *10*, 1-19.
45. Elagab, H. A.; Alt, H. G. *J. J. C.* **2015**, *10*, 41-57.
46. Elagab, H. A.; Alt, H. G. *Eur. Poly. J.* **2015**, *71*, 85-98.
47. Elagab, H. A.; Alt, H. G. *Inorg. Chim. Acta.* **2015**, *437*, 26-37.
48. Elagab, H. A.; Alt, H. G. Zr (IV), Ti (IV), and V (III) complexes of some benzimidazole, benzothiazole, and benzoxazole ligands. Characterization and catalyst efficiency in ethylene polymerization. *Turk. J. Chem.* (in press).
49. Phillips, M. A. *J. Chem. Soc.* **1928**, 2393-2399.
50. Rai, C.; Braunwarth, J. B. *J. Org. Chem.* **961**, *26*, 3434-3436.
51. Bochmann, M.; Wilson, L. M. *J. Chem. Soc. Chem. Commun.* **1986**, *21*, 1610-1611.
52. Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold A. L. *Organometallics* **1987**, *6*, 1041-1051.
53. Seitz, M.; Milius, W.; Alt, H. G. *J. Mol. Cat. A: Chemical* **2007**, *261*, 246-253.
54. Yang, M; Yan, W. D.; Shen, X. I.; Mu, B.; Wang, B. Q. *Chinese J. Poly. Sci.* **2008**, *26*, 415-423.
55. Manzer, L. E. *Inorganic Synthesis* **1982**, *21*, 135-140.