Zr(IV), Ti(IV), and V(III) complexes of some benzimidazole, benzothiazole, and benzoxazole ligands: characterization and catalyst efficiency in ethylene polymerization

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Abstract: Fifteen complexes of 2, 2-bis- (benzimidazole, benzothiazole, and benzoxazole) compounds with Zr(IV), Ti(IV), and V(III) metal centers were synthesized, characterized, activated with methyalumoxane (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 activity of the catalyst system **6**/MAO was found to be 1372 kg PE/mol cat. h. The polyethylene produced with the catalyst system **6**/MAO showed high molecular weights (1.84×10^6 g/mol) and broad molecular weight distributions (PD = 11). This could result from different interactions of the MAO counter ion with the heteroatoms of the catalyst ligand generating different active sites. The effect of the polymerization temperature of the polymers produced with catalyst **6**/MAO was also investigated.

Key words: Bis-benzimidazole, bis-benzoxazole, bis-benzothiazole, complexes, homogeneous ethylene polymerization

1. Introduction

In polyolefin chemistry, mononuclear complexes (α-diimine nickel bromide or Cp_2ZrCl_2/MAO) as catalysts for olefin polymerization in homogeneous solution have many advantages because every molecule can act as a catalyst and hence provide high activity.[1−3] 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 $TiCl_2$/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, the application of dinuclear or multinuclear catalysts, and the use of two or more reactors have been examined.[4−14] However, the best solution is the design of catalysts that can solve all these problems in one step and in one reactor. In this contribution we report on the synthesis and characterization of complexes with heterocyclic ligands that are perfect candidates for this challenge. So far, for ethylene polymerization, bis (benzimidazolyl) copper complexes were reported as catalysts for ethylene polymerization.[15] Recently,[16−22] we reported bis-(benzimidazole, benzoxazole, and benzothiazole) titanium, zirconium, and vanadium complexes that can be activated with methyalumoxane (MAO) and then be applied successfully for catalytic ethylene polymerization. The vanadium complexes of bis (benzimidazole) amine tridentate ligands [N, N, and N] are active ethylene polymerization catalysts after activation with

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alkylaluminum compounds.[23] Herein we report on the titanium, zirconium, and vanadium complexes of 2, 2-bis (benzimidazole, benzothiazole, and benzoxazole). Their behavior towards ethylene polymerization after activation with methylaluminoxane (MAO) was investigated.

2. Results and discussion

2.1. Synthesis of the ligand precursors 1–5

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 the imidazole-based ligand precursors in high yields.[24,25] Scheme 1 shows the synthesis of the benzimidazolyl-based compounds 1–5.
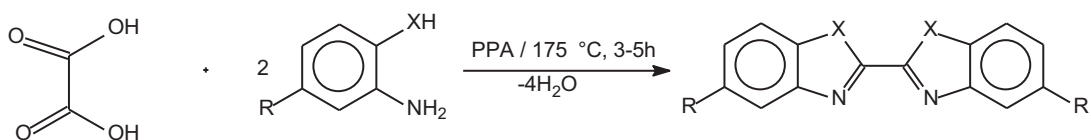
Compound no.	X	R^1
1	NH	H
2	NH	CH$_3$
3	O	H
4	O	CH$_3$
5	S	H

Scheme 1. Synthesis of ligand precursors 1–5.

2.2. Syntheses of the transition metal complexes

2.2.1. Synthesis of the titanium and zirconium complexes

The complexes were synthesized according to Scheme 2 and characterized with different spectroscopic techniques. Table 1 summarizes the spectroscopic data of the synthesized complexes. The titanium and zirconium complexes were prepared by ligand displacement reactions. The tetrahydrofuran adducts of zirconium and titanium tetrachloride were dissolved in the appropriate solvent. When a solid free ligand was added, an immediate color change was observed. The complexes could be isolated in high yields (70%–80%).

2.2.2. Synthesis of the vanadium complexes

The vanadium complexes were synthesized by dissolving vanadium trichloride in diethyl ether followed by the addition of the ligand precursor with constant stirring overnight. The products were obtained in good yields (60%–70%) (see Scheme 2).

2.3. Characterization

Since all of the synthesized complexes were obtained as solids and since they did not crystallize properly, they were characterized spectroscopically.
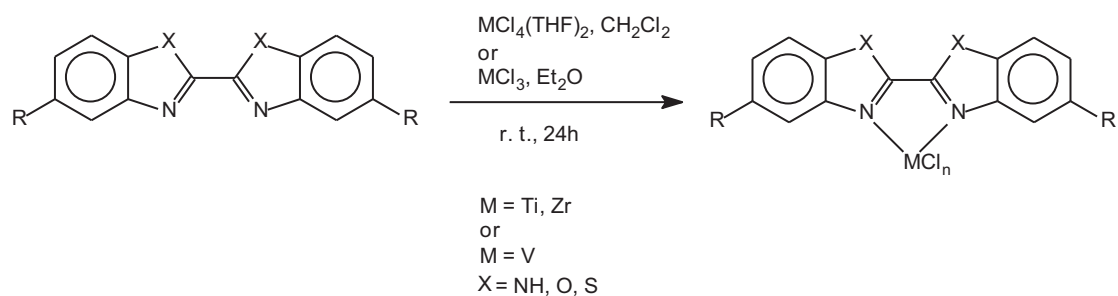
Complex no.	X	R	M
6	NH	H	Ti
7	NH	H	Zr
8	NH	H	V
9	NH	CH_3	Ti
10	NH	CH_3	Zr
11	NH	CH_3	V
12	O	H	Ti
13	O	H	Zr
14	O	H	V
15	O	CH_3	Ti
16	O	CH_3	Zr
17	O	CH_3	V
18	S	H	Ti
19	S	H	Zr
20	S	H	V

Scheme 2. Synthesis of the transition metal complexes **6**–**20**.

Table 1. Elemental analysis data for ligands and their complexes.

Compound no.	General formula	Calculated			Found		
		C	H	N	C	H	N
1	$C_{14}H_{10}N_4$	71.8	4.3	23.9	71.6	4.5	24.1
2	$C_{16}H_{14}N_4$	73.3	5.3	21.4	72.9	5.5	21.1
3	$C_{14}H_8N_2O_2$	71.2	3.4	11.9	70.8	3.6	12.1
4	$C_{16}H_{12}N_2O_2$	72.7	4.5	10.6	72.4	4.7	10.8
5	$C_{14}H_8N_2S_2$	62.7	3.0	10.4	62.9	2.8	10.6
6	$C_{14}H_{10}N_4$ $TiCl_4$	39.6	2.4	13.2	39.5	2.6	12.9
7	$C_{14}H_{10}N_4$ $ZrCl_4$	36.0	2.1	12.0	35.6	2.0	12.4
8	$C_{14}H_{10}N_4$ VCl_3	42.9	2.6	14.3	43.1	2.5	14.1
9	$C_{16}H_{14}N_4$ $TiCl_4$	42.5	3.1	12.4	43.0	2.8	12.1
10	$C_{16}H_{14}N_4$ $ZrCl_4$	38.8	2.8	11.4	38.9	2.7	11.2
11	$C_{16}H_{14}N_4$ VCl_3	45.7	3.3	13.3	45.2	3.5	13.7
12	$C_{14}H_8N_2O_2$ $TiCl_4$	39.4	1.9	6.7	39.4	2.1	6.6
13	$C_{14}H_8N_2O_2$ $ZrCl_4$	35.8	1.7	6.0	36.2	1.8	5.7
14	$C_{14}H_8N_2O_2$ VCl_3	42.6	2.0	7.1	42.7	2.2	6.9
15	$C_{16}H_{12}N_2O_2$ $TiCl_4$	42.3	2.6	6.2	42.7	2.3	5.9
16	$C_{16}H_{12}N_2O_2$ $ZrCl_4$	38.6	2.4	5.6	39.1	2.1	5.9
17	$C_{16}H_{12}N_2O_2$ VCl_3	45.5	2.8	6.6	45.9	3.1	6.2
18	$C_{14}H_8N_2S_2TiCl_4$	36.7	1.7	6.1	36.5	1.8	6.3
19	$C_{14}H_8N_2S_2ZrCl_4$	33.5	1.6	5.6	34.2	1.7	5.4
20	$C_{14}H_8N_2S_2VCl_3$	39.5	1.9	6.6	39.8	2.1	6.4

2.3.1. ^{1}H and ^{13}C NMR spectroscopy

The ligand precursors **1**–**5** and their titanium and zirconium complexes were characterized by NMR spectroscopy. The vanadium complexes, due to their paramagnetism, were characterized by mass spectroscopy and elemental analysis. The ^{1}H NMR spectrum of compound **3** (see Figure 1) shows three sets of resonance signals: a doublet at $\delta = 7.93$ ppm [d, 2H, $J_{H,H} = 7.6$ Hz] can be assigned to the aromatic protons H1, a second doublet at $\delta = 7.74$ ppm [2H, $J_{H,H} = 7.6$ Hz] corresponds to the aromatic protons H4, and a multiplet at $\delta = 7.56$–7.46 ppm counts for the four aromatic protons H2 and H3.
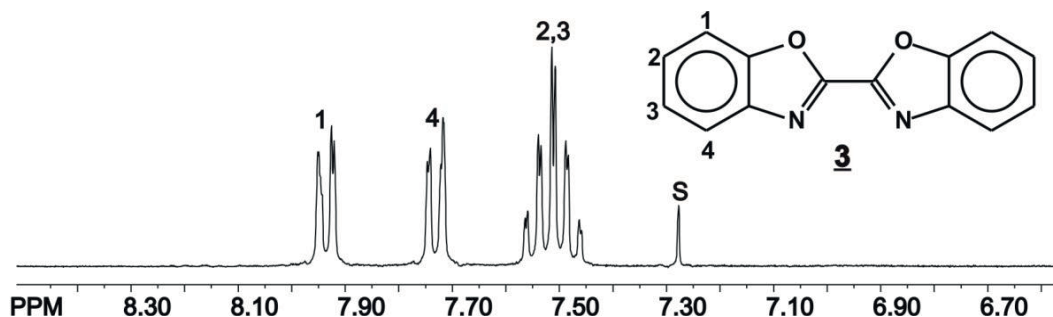

Figure 1. ^{1}H NMR spectrum of compound **3**.

The ^{13}C NMR spectrum for compound **3** (Figure 2) shows seven resonance signals at 152.1 ppm (C7), 151.2 (C5), 141.4 (C6), 127.8 (C3), 126.0 (C2), and 121.8 (C4) and the signal at $\delta = 111.7$ ppm is assigned to C1.
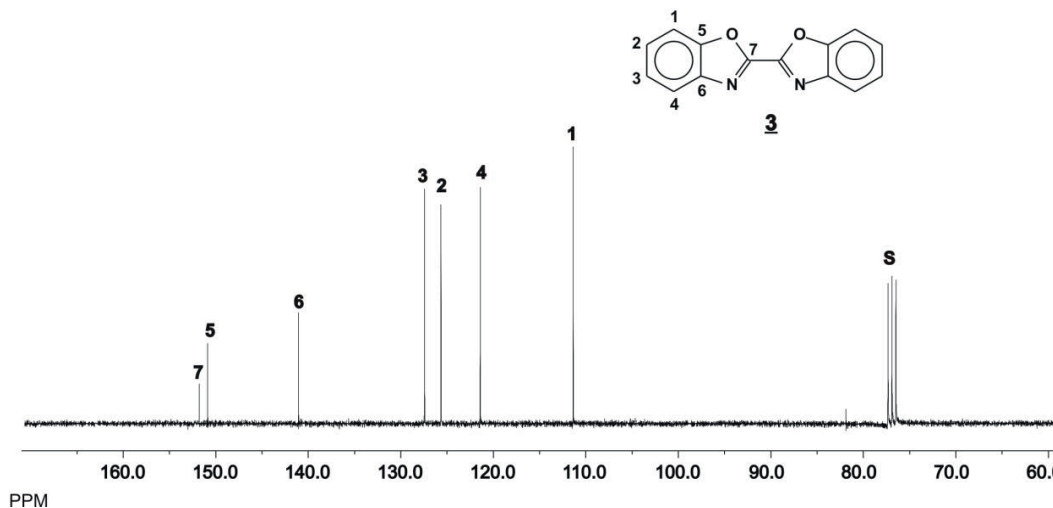

Figure 2. ^{13}C NMR spectrum of compound **3**.

The ^{1}H NMR spectrum of complex **12** (Figure 3) shows two sets of resonance signals. The double doublet at $\delta = 7.95$ ppm can be assigned to the protons H1 and H4. The multiplet at $\delta = 7.56$ ppm can be assigned to the protons H2 and H3.

The ^{13}C NMR spectrum of complex **12** (Figure 4) shows seven resonance signals each corresponding to two carbon atoms. The signal at $\delta = 152.2$ ppm can be assigned to the quaternary carbon atom C7. At $\delta = 150.9$ ppm C5 appears. C6 gives the signal at $\delta = 141.3$ ppm. The signals corresponding to C3 and C2 appear

at $\delta = 128.5$ and 126.7 ppm. At $\delta = 121.8$ ppm, C4 can be detected. The signal at 112.4 ppm is assigned to C1.
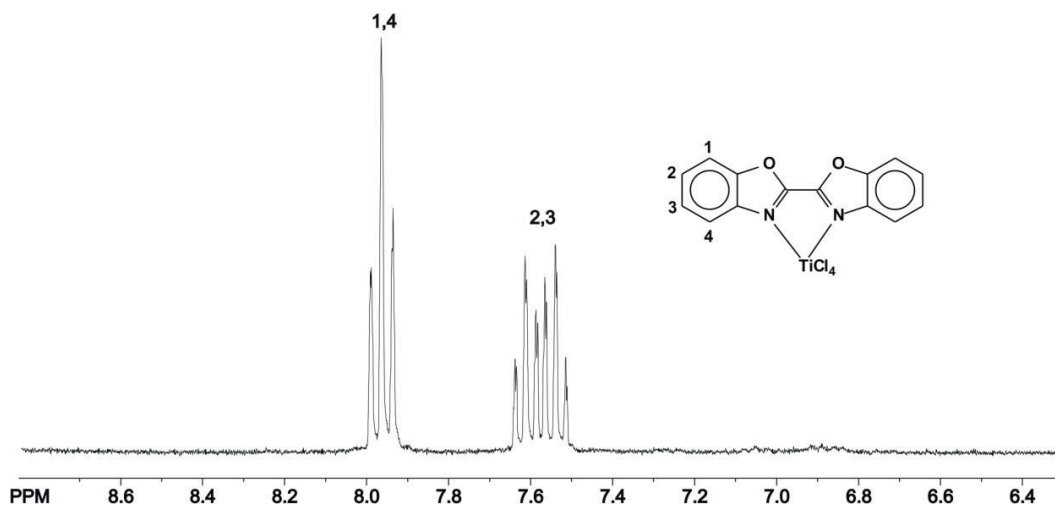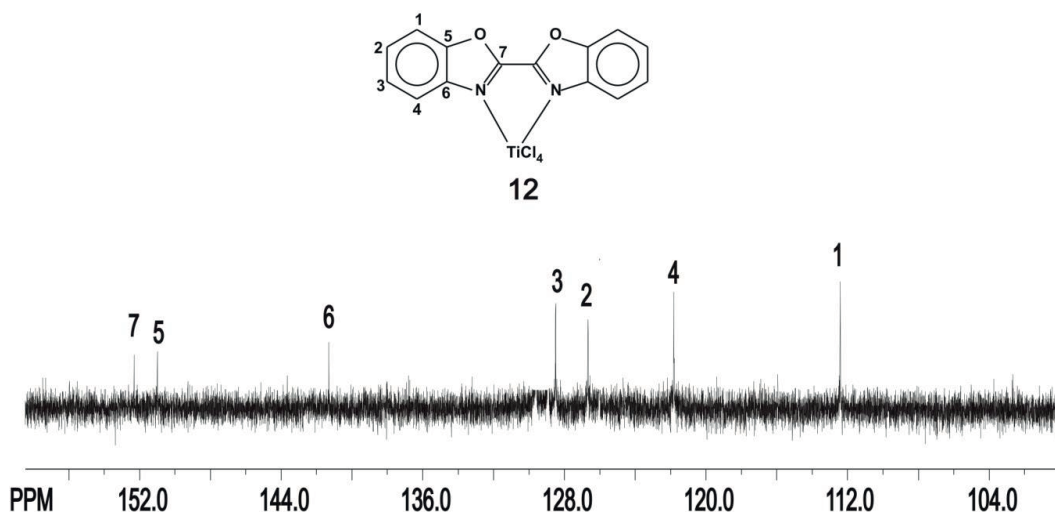

Figure 3. ^{1}H NMR spectrum of complex **12**.

Figure 4. ^{13}C NMR spectrum of complex **12**.

2.3.2. Mass spectroscopy

The mass spectrum of compound **3** (Figure 5) shows a peak with m/z = 236 corresponding to the molecular ion. The peak with m/z = 118 corresponds to the benzoxazole unit C_7H_4NO.

The mass spectrum of complex **12** (Figure 6) shows the molecular ion peak at m/z = 425 but an incomplete fragmentation pattern and a peak for the free ligand appeared at m/z = 236. 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.
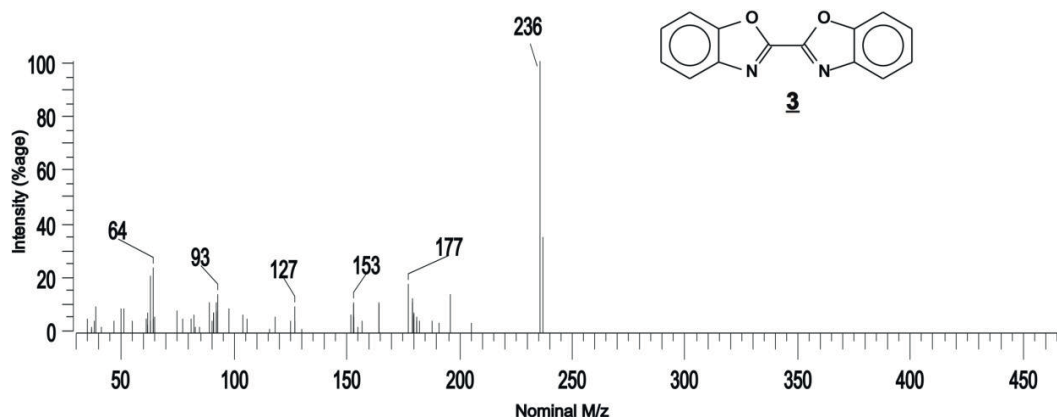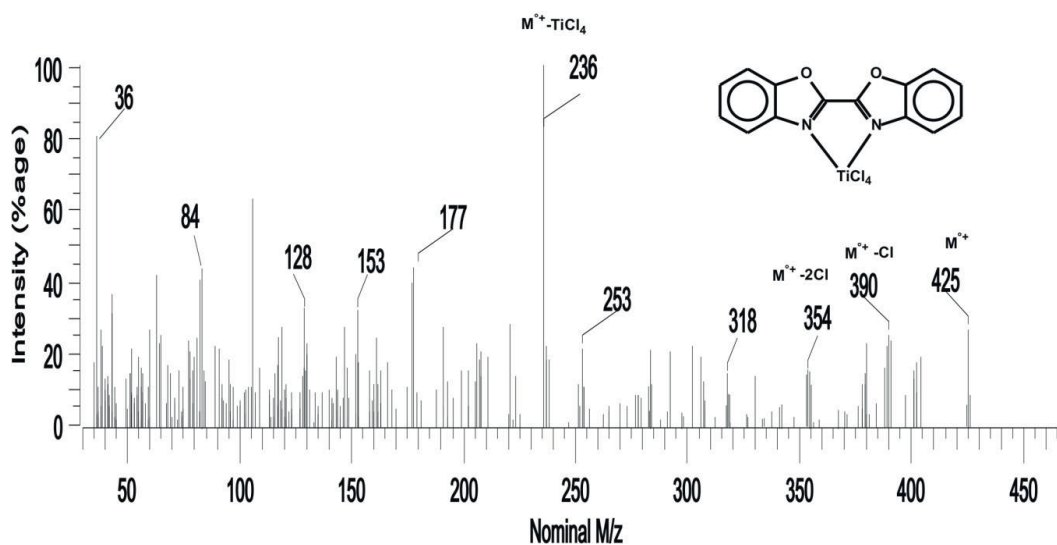
Figure 5. Mass spectrum of compound **3**.

Figure 6. Mass spectrum of complex **12**.

2.4. Polymerization results

All coordination compounds were activated with MAO according to the mechanism proposed for the activation of metallocene and 2,6-bis(imino)pyridine iron(II) compounds.[26−28]

The titanium, zirconium, and vanadium complexes with ligands derived from bis (benzimidazolyl), bis (benzothiazolyl), and bis (benzoxazolyl) compounds were activated with methylalumoxane (MAO) in toluene solution. The homogeneous catalyst solution was used for ethylene polymerization. The activities (Table 2) are greatly influenced by the hetero atoms in addition to the ligand environment and the nature of the metal center. The catalysts generally showed moderate to good activities compared to the benchmark Cp_2ZrCl_2.[29]

The polymerization activities of the catalyst systems derived from bis (benzimidazolyl) (**6**–**8**/MAO) and methyl substituted bis (benzimidazolyl) **9**–**11**/MAO show the following order: titanium > vanadium > zirconium (Figure 7), while the activities of the catalyst systems derived from bis (benzoxazolyl) ligand precursors (**12**–**17**/MAO) show the following activity order: vanadium > titanium > zirconium (Figure 8).

Table 2. Ethylene polymerization activities of complexes **6**–**20**. All polymerization reactions were carried out in 250 mL of pentane with MAO as cocatalyst (10 bar ethylene pressure).

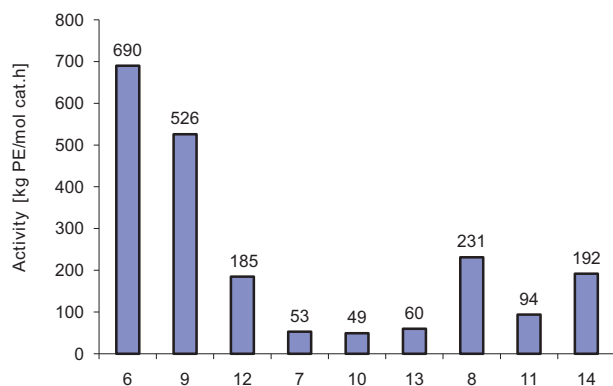| Complex no.	Polymerization condition	Activity [kg/mol cat. h]	Complex no.	Polymerization condition	Activity [kg/mol cat. h]
6	20 °C Al:Ti (2500:1)	525	9	50 °C Al:Ti (2500:1)	526
6	40 °C Al:Ti (2500:1)	783	10	50 °C Al:Zr (2500:1)	49
6	50 °C Al:Ti (2500:1)	690	11	50 °C Al:V (2500:1)	94
6	20 °C Al:Ti (1100: 1)	500	12	50 °C Al:Ti (2500:1)	185
6	40 °C Al:Ti (1100:1)	388	13	50 °C Al:Zr (2500:1)	60
6	50 °C Al:Ti (1100:1)	371	14	50 °C Al:V (2500:1)	192
6	40 °C Al:Ti (1500:1)	480	15	50 °C Al:Ti (2500:1)	261
6	40 °C Al:Ti (1750:1)	670	16	50 °C Al:Zr (2500:1)	113
6	40 °C Al:Ti (2000:1)	1372	17	50 °C Al:V (2500:1)	307
6	40 °C Al:Ti (2250:1)	866	18	50 °C Al:Ti (2500:1)	140
6	40 °C Al:Ti (2500:1)	783	19	50 °C Al:Zr (2500:1)	268
7	50 °C Al:Zr (2500:1)	53	20	50 °C Al:V (2500:1)	148
8	50 °C Al:V (2500:1)	231			

Figure 7. Polymerization activities of the bis-(benzimidazolyl) (**6**–**8**), bis-(4-methyl benzimidazolyl) (**9**–**11**), and bis-(benzoxazolyl) complexes (**12**–**14**).
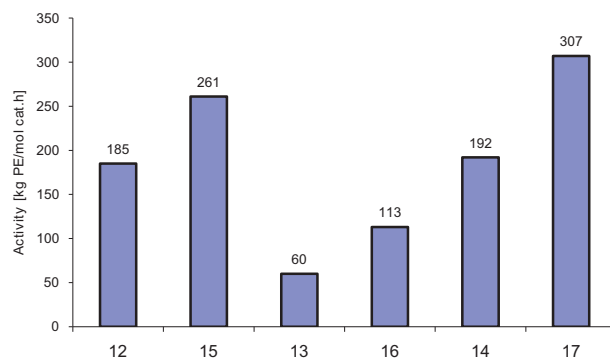
Figure 8. Effect of substituent on the activities of bis-benzoxazole complexes (**12**–**17**).

The catalytic activities of catalysts derived from bis (benzothiazolyl) complexes (**18**–**20**/MAO) (Figure 9) were found to be in the following order: Zr > V > Ti.
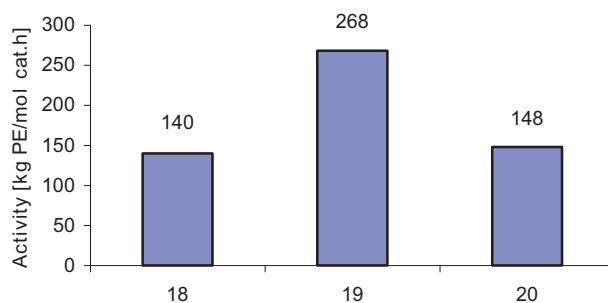

Figure 9. Polymerization activities of bis-benzothiazolyl) complexes (**18**–**20**).

The differences in catalytic activities can be accounted for by the hetero atom effect (N > O > S). The activities of the titanium complexes **6**, **12**, and **18** revealed that the nitrogen-containing complex **6** showed a higher activity than the oxygen-containing complex **12**, which is more active than the sulfur-containing complex **18**. The same trend of activity was observed for the vanadium complexes (**8** > **14** > **20**). The similarities between titanium and vanadium atoms and the comparable electronegativities of oxygen and nitrogen may account for the activities of these complexes. The atomic radius of zirconium and the size of the chelate rings (shorter distance) lead to an increased electron density on the metal atom and hence to lower activities for the zirconium complexes compared to the vanadium and titanium complexes. The lower activities of the zirconium derivatives could be the consequence of thermodynamically stronger metal carbon bonds slowing down the kinetics of the various polymerization steps.[30]

Among the catalyst systems derived from bis (benzimidazolyl) a substituent in *meta* position to the imino nitrogen atom influences the catalytic activities of the system compared to the unsubstituted one. The methyl substituted bis (benzimidazolyl) complexes **9**–**11** showed lower activities than the unsubstituted complexes **6**–**8** (see Figure 7).

The catalytic activities of complexes derived from 2, 2-bis-(benzoxazole) were affected by the nature and the position of the corresponding substituent. The introduction of a methyl substituent in *meta* position to the

imino nitrogen atoms increased the activities of the titanium complex **15**, the zirconium complex **16**, and the vanadium complex **17** compared to the unsubstituted complexes **12**–**14**.

The effects of polymerization temperature and the concentration of the cocatalyst (see Figure 10) were studied using the catalyst system **6**/MAO. It was observed that the activity increased with increasing temperature. For instance, at 20 °C the catalyst showed an activity of 524.7 kg PE/mol cat. h while the activity at 40 °C was 782.9 kg PE/mol cat. h and the activity at 50 °C was 690 kg PE/mol cat. h the drop on the catalyst activity at higher temperature is due to decomposition of the active sites. The highest activity was observed at 40 °C. Applying the catalyst system **6**/MAO, the variation in catalytic activities with the concentration of the cocatalyst was also studied and the highest activity was found to be 1372 kg PE/mol cat. h when the Al: Ti ratio was 2000:1 (see Figure 11).
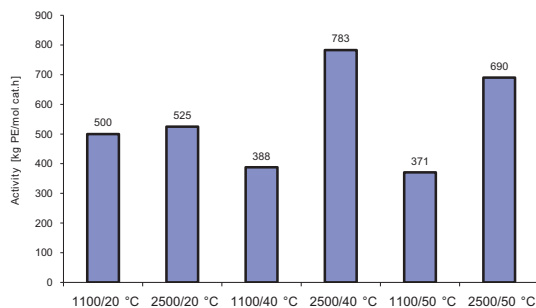

Figure 10. Effect of temperature and cocatalyst concentration on polymerization activity of the catalyst **6**/MAO.
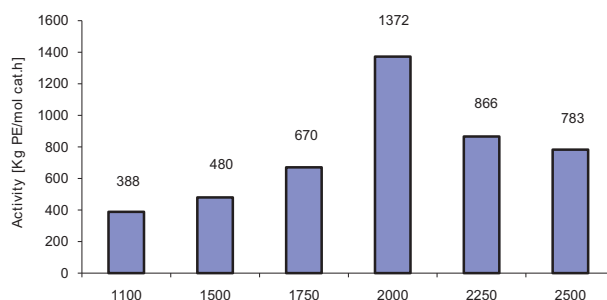
Figure 11. Variation in catalyst (**6**/MAO, 40 °C) activity with cocatalyst concentration.

GPC analyses of the polyethylenes produced with bis (benzimidazolyl), bis (benzothiazolyl), and bis (benzoxazolyl) complexes revealed that the symmetric catalyst systems were capable of producing resins with moderate to very high molecular weights associated with narrow or broad molecular weight distributions. Moreover, the substitution pattern affects both the molecular weights and the molecular weight distributions. The broadness may arise from the fact that the MAO counterion induces the necessary dissymmetry of the active sites in the activation process.[31] For example, the catalyst system **6**/MAO produce polyethylene with a molecular weight $M_w = 1.76 \times 10^6$ g/mol and a polydispersity (PD) = 10.8, and the resin obtained with the catalyst system **8**/MAO shows molecular weight of 1.7×10^6 g/mol and a PD = 5.7 (see Figure 12). The molecular weight and polydispersity of polyethylene obtained with the catalyst derived from the *meta* methyl substituted bis(benzimidazolyl) titanium complex **9** (see Figure 13) was found to be 1.81×10^6 g/mol and PD = 5.3.

Polyethylenes produced with the catalyst systems **14**/MAO, **18**/MAO, and **20**/MAO show the following M_w and PD values: 284,484 g/mol (PD = 3.2), 328,060 g/mol (PD = 5.3) and 422,106 g/mol (PD = 4). The high molecular weight resins suggest that the rates of propagation reactions (the activation barrier for propagation is usually low if existent at all) are much faster than the rates of termination (the termination reactions are subjected to activation barriers).[32,33]
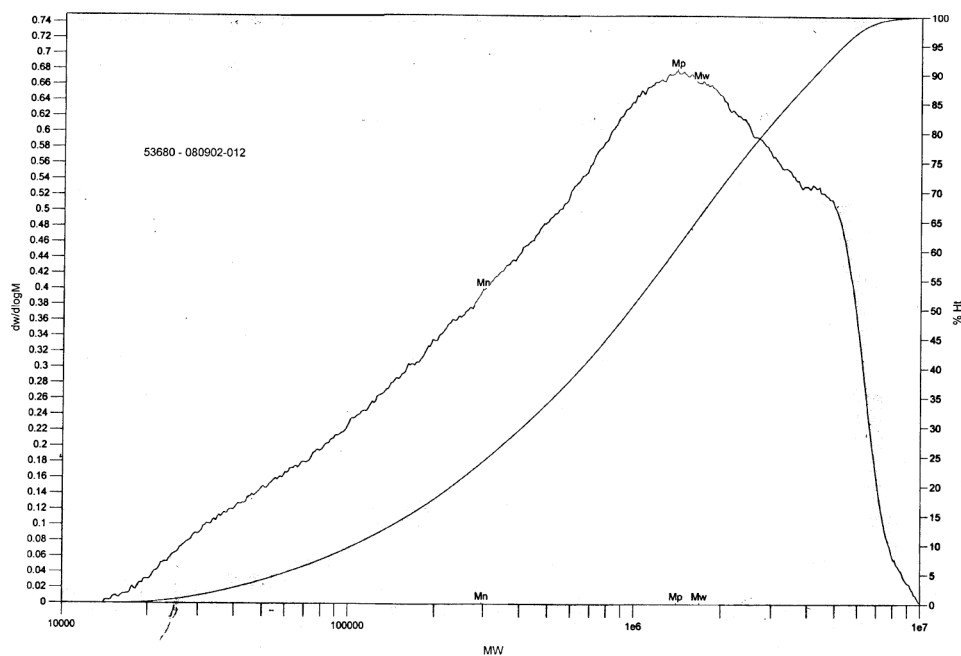
Figure 12. HT-GPC spectrum of the polyethylene produced with the catalyst system **8**/MAO.
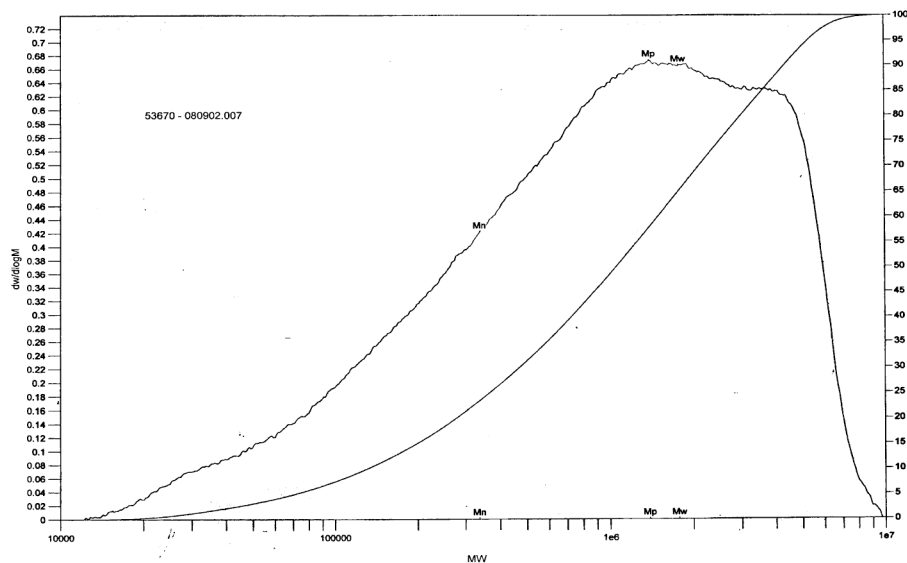
Figure 13. HT-GPC spectrum of the polyethylene produced with the catalyst system **9**/MAO.

3. Experimental

All experimental work was routinely carried out using the Schlenk technique unless otherwise stated. Dried 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 over phosphorus pentoxide and calcium hydride. Methanol and ethanol were dried over magnesium. Deuterated solvents ($CDCl_3$, DMSO) for NMR spectroscopy were stored over molecular sieves (3 Å).

Methylalumoxane (30% in toluene) was purchased from Crompton (Bergkamen, Germany) 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, Germany). All other starting materials were commercially available and were used without further purification. The titanium and zirconium tetrachloride adducts were synthesized by published procedures. [34]

3.1. NMR spectroscopy

The spectrometers Varian Inova 300/400 MHz and Bruker ARX 250 were 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 ^{1}H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for $CDCl_3$, $\delta = 2.5$ ppm for DMSO) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for $CDCl_3$, $\delta = 39.5$ ppm for DMSO).

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 the SABIC Company (Riyadh, Saudi Arabia).

3.4. Elemental analysis

Elemental analyses were performed with a VarioEl III CHN instrument. An amount of 4–6 mg of the complex was weighed into a standard tin pan. The tin pan was carefully closed and introduced into the autosampler of the 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 compounds 1–5

O-phenylene diamine, 4-methyl-o-phenylene diamine, 2-aminophenol, and 2-aminothiophenol (0.05 mol) were mixed with oxalic acid (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 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 spectroscopy (Table 3) and elemental analysis (Table 1).

3.5.2. Titanium complexes

To 0.87 g (2.6 mmol) of $TiCl_4$ $(THF)_2$ in dichloromethane was added 2.6 mmol of the free ligand. The reaction mixture was stirred overnight at room temperature, filtered, and washed several times with pentane. The solid product was dried under vacuum and weighed. The products were characterized by NMR and mass spectroscopy (Table 3) and elemental analysis (Table 1).

Table 3. NMR and mass spectroscopic data of ligands **1–5** and complexes **6–20**.

Compound no.	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z [%]
1	12.22 (br, 2H, NH), 7.11–6.99 (m,8H)	156.0, 126.4, 123.8, 116.0	234 M$^{°+}$ (100)
2	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, CH$_3$)	156.0, 155.6, 132.9, 126.1, 124.4, 123.2, 115.8, 115.6, 21.2	262 M$^{°+}$ (100)
3^a	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 M$^{°+}$ (100)
4	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 M$^{°+}$ (100)
5	8.15 [d, 2H, J = 7.8 Hz], 7.96 [d, 2H, J = 7.8 Hz], 7.54 [d, 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 M$^{°+}$ (100)
6	12.50 (br, 2H, NH), 7.40 [d, 4H, J = 7.6 Hz], 7.15 [t, 4H, J = 7.6 Hz]	156.1, 126.6, 123.8, 116.2	425$^{°+}$ (20), 352 M$^{°+}$-2Cl (20), 317 M$^{°+}$-3Cl (10), 234 M$^{°+}$-TiCl$_4$ (100)
7	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$^{°+}$ (20), 397 M$^{°+}$-2Cl (20), 361 M$^{°+}$-3Cl (10), 234 M$^{°+}$-ZrCl$_4$ (100)
8	n.d.	n.d.	392$^{°+}$ (30), 323 M$^{°+}$-2Cl (20), 288 M$^{°+}$-3Cl (10), 234 M$^{°+}$-VCl$_3$ (50)
9	12.34 (br, 2H, NH), 7.01 [d, 2H, J = 7.6 Hz], 6.90 (s, 2H), 6.75 [d, 2H, J = 7.6 Hz], 2.15 (s, 6H, 2CH$_3$)	155.9, 155.6, 132.8, 126.1, 124.3, 123.9, 115.8, 21.2	452 M$^{°+}$ (20), 437 M$^{°+}$-CH$_3$ (10), 381 M$^{°+}$-2Cl (20), 345 M$^{°+}$-3Cl (15), 309 M$^{°+}$-4Cl (20) 262 M$^{°+}$-ZrCl$_4$ (100)
10	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$_3$)	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)
11	n.d.	n.d.	420 M$^{°+}$ (20), 405 M$^{°+}$-CH$_3$ (10), 349 M$^{°+}$-2Cl (20), 312 M$^{°+}$-3Cl (20), 262 M$^{°+}$-VCl$_3$ (100)
12	7.95 [dd, 4H, J = 8.1, 3.2 Hz], 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)
13	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$^{°+}$ (10), 433 M$^{°+}$-Cl (5), 397 M$^{°+}$-2Cl (20), 361 M$^{°+}$-3Cl (5), 236 M$^{°+}$-ZrCl$_4$ (100)
14	n.d.	n.d.	394 M$^{°+}$ (20), 360 M$^{°+}$-Cl (15), 287 M$^{°+}$-3Cl (10), 236 M$^{°+}$-VCl$_3$ (100)
15	7.66 (s, 2H), 7.20 [d, 2H, J = 7.8 Hz], 7.00 (d, 2H, J = 7.8 Hz), 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)
16	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 M$^{°+}$ (15), 461 M$^{°+}$-Cl (20), 425 M$^{°+}$-2Cl (10), 354 M$^{°+}$-4Cl (20), 264 M$^{°+}$-ZrCl$_4$ (100)
17	n.d.	n.d.	422 M$^{°+}$ (20), 386 M$^{°+}$-Cl (15), 315 M$^{°+}$-3Cl (10), 264 M$^{°+}$-VCl$_3$ (100)
18	8.23 [d, 2H, J = 7.8 Hz], 7.97 [d, 2H, J = 7.8 Hz], 7.56 [t, 2H, J = 7.8 Hz], 7.50 [t, 2H, J = 7.8 Hz].	n.d.	458 M$^{°+}$ (20), 422 M$^{°+}$-Cl (10), 387 M$^{°+}$-2Cl (20), 317 M$^{°+}$-4Cl (20), 268 M$^{°+}$-TiCl$_4$ (100)
19	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].	n.d.	501 M$^{°+}$ (20), 465 M$^{°+}$-Cl (20), 429 M$^{°+}$-2Cl (25), 358 M$^{°+}$-4Cl (30), 268 M$^{°+}$-ZrCl$_4$ (100)
20	n.d.	n.d.	425 M$^{°+}$ (25), 390 M$^{°+}$-Cl (40), 355 M$^{°+}$-2Cl (20) 319 M$^{°+}$-3Cl (20), 268 M$^{°+}$-VCl$_3$ (100)

a = solvent CDCl$_3$, n.d. = not determined br = broad

3.5.3. Zirconium complexes

To 0.45 g (1.2 mmol) of $ZrCl_4$ $(THF)_2$ in dichloromethane was added 1.2 mmol of the free ligand. The reaction mixture was stirred overnight at room temperature. After filtration, the solid product obtained was washed several times with dichloromethane and then with pentane, dried under vacuum, and weighed. The products were characterized by NMR and mass spectroscopy (Table 3) and elemental analysis (Table 1).

3.5.4. Vanadium complex

To 0.41 g (2.6 mmol) of VCl_3 in ether was added 2.6 mmol of the free ligand. The reaction mixture was stirred overnight at room temperature. The solid product obtained was filtered and washed several times with ether and pentane, dried under vacuum, and weighed. The products were characterized by mass spectroscopy (Table 3) and elemental analysis (Table 1); due to their paramagnetic nature their NMR spectra are not so informative.

3.6. Polymerization of ethylene in the 1-L Büchi autoclave

An amount of 2–5 mg of the desired complex was suspended in 5 mL of toluene. Methylalumoxane (30% in toluene) was added, resulting in an immediate color change. The mixture was transferred 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 obtained polymer was filtered over a frit, washed with diluted hydrochloric acid, water, and acetone, and finally dried in vacuo.

4. Conclusions

2, 2-bis-(Benzimidazole, benzothiazole, and benzoxazole) form symmetric chelate complexes with Ti, Zr, and V chlorides. After activation with MAO the generated catalysts polymerize ethylene in solution with various activities. Structure–property relationships indicate that the nature of the metal, and the nature and position of substituents and the hetero atoms determine the performance of such catalysts. The highest activity (1372.2 kg PE/mol cat. h) was obtained with the titanium catalyst **6**/MAO. The high molecular weights of the produced polymers (**6**/MAO, 1.84×10^6 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 = 3–11) 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_2ZrCl_2.

Acknowledgment

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