

Bis (benzothiazolyl) benzene and Bis (benzothiazolyl)-4-methyl benzene) Transition Metal Complexes as Catalysts for Ethylene Polymerization: Synthesis, Characterization and Polymerization Activity

Hamdi Ali Elagab^{a,b}

^aLaboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany.

^bDepartment of Chemistry, Faculty of Science and Arts- Almandaq, Albaha University, Saudi Arabia

Article history: Received: 14 January 2017; revised: 24 March 2017; accepted: 27 March 2017. Available online: 31 March 2017. DOI: <http://dx.doi.org/10.17807/orbital.v9i1.945>

Abstract: A series of 16 complexes of 1,2-bis(benzothiazolyl) benzene and 1,2-bis(benzothiazolyl)-4-methyl benzene compounds with Ti(IV), Zr(IV), V(III), Fe(III), Fe(II), Co(II), Ni(II) and Cu(II) were synthesized and characterized. After activation with methylalumoxane (MAO), these complexes showed variable activities towards ethylene polymerization. The polymerization activities of the catalyst system **3**, **5**, **7** and **15** /MAO were investigated under different polymerization conditions. The highest activity 625 [Kg PE / mol Cat. H] is obtained by the catalyst system **5**/MAO at 50 °C and cocatalyst concentration of 1000 equivalents. The produced resins showed high molecular weights associated with broad or even bimodal molecular weight distributions for all catalysts systems except the polymers produced with nickel catalysts **9** and **17**/MAO.

Keywords: synthesis; heterocycles; benzothiazoles; metal complexes; homogeneous ethylene polymerization

1. INTRODUCTION

Benzothiazole contains a heterocyclic sulphur atom and a pseudo-imidazole functional group. 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 complexes with late transition metals are reported [1-6]. Also, the nickel (II), cobalt (II) and copper (II) coordination chemistry of some tetradentate ligands involving benzothiazole functional groups has been published [7]. In all cases involving benzothiazoles as functional groups, the ligands behave as nitrogen donors, except in a few cases involving bridging benzothiazole [8] in which it is assumed to behave as a bidentate ligand involving both N and S donation. 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 polyethylene [9-11]. For ethylene polymerization catalysis, only 1, 2-bis (benzimidazolyl) benzene copper (II) complexes were

reported [12]. Recently [13-19] we reported on the catalytic activities of complexes derived from benzimidazolyl, benzoxazolyl and benzothiazolyl ligand systems and their activities were found to depend on the individual metal centers and the structure of the ligand. Herein we report on the activities of transition metal complexes derived from the ligands 1, 2- bis (benzothiazolyl) benzene and 1, 2 -bis (benzothiazolyl) -4-methyl- benzene towards ethylene polymerization after activation with methylaluminoxane (MAO).

2. MATERIAL AND METHODS

All experimental work was routinely carried out using 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 aluminium hydride. Methylene chloride was dried over phosphorus pentoxide and calcium hydride.

*Corresponding author. E-mail: hali@bu.edu.sa

Methanol and ethanol were dried over magnesium. Deuterated solvents (CDCl_3 , DMSO) for NMR spectroscopy were stored over molecular sieves (3\AA).

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 tetrachloride and zirconium tetrachloride adducts were synthesized via published procedures [20]. 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 ^1H 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). 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. GPC measurements were routinely performed by SABIC Company (Riyadh, Saudi Arabia).

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

2.1. General procedures for the syntheses of the complexes

2.1.1. Syntheses of organic compounds 1-2

2-Aminothiophenol (0.05 mol) was mixed with a dicarboxylic acid or an acid anhydride (0.025 mol) 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 in 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 spectroscopy (Table 1), mass spectroscopy (Table 2) and elemental analysis (Table 3).

Table 1. ^1H NMR, ^{13}C NMR ligands (**1**, **2**) and titanium (**3,11**) zirconium(**4,12**) complexes.

No	^1H NMR δ [ppm]	^{13}C NMR δ [ppm]
1	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
2	8.05(d,2H), 7.84 (d,1H), 7.79-7.74(br,3H), 7.46(dd,3H), 7.35(dd,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
3	8.05(d,2H), 7.97-7.94(m,4H), 7.77-7.74(dd,2H), 7.50(t,2H), 7.44(t,2H)	166.4, 153.4, 136.6, 133.5, 131.7, 131.6, 127.3, 126.4, 123.8, 123.0
4	8.01(d,2H), 7.92-7.90(m,4H), 7.72-7.70(dd,2H), 7.45(t,2H), 7.38(t,2H)	166.4, 153.4, 136.6, 133.5, 131.6, 131.5, 127.2, 126.3, 123.8, 122.9
11	8.02(t,2H), 7.92(dd,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
12	8.00(t,2H), 7.92(t,2H), 7.81(d,1H), 7.72(s,1H), 7.53(d,1H), 7.46(d,2H), 7.38(d,2H), 2.44(s,3H, CH_3)	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

2.1.2. Titanium complexes

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, filtered and washed several times with the reaction solvent pentane and dried under vacuum and weighed. The products were characterized by (NMR Table 1), mass spectroscopy (Table 2) and elemental analysis (Table 3).

Table 2. Mass spectroscopic data for ligands and complexes.

Complex number	General Formula	Mass m/z (%)
1	C ₂₀ H ₁₂ N ₂ S ₂	344 M ^{o+} (100)
2	C ₂₁ H ₁₄ N ₂ S ₂	358 M ^{o+} (100)
3	C ₂₀ H ₁₂ N ₂ S ₂ TiCl ₄	534 M ^{o+} (10), 498 M ^{o+} -Cl (20), 463 M ^{o+} -2Cl (20), 427 M ^{o+} -3Cl (10), 344 M ^{o+} -TiCl ₄ (100)
4	C ₂₀ H ₁₂ N ₂ S ₂ ZrCl ₄	577 M ^{o+} (1), 506 M ^{o+} -2Cl (3), 470 M ^{o+} -3Cl (2), 433 M ^{o+} -4Cl (5), 344 M ^{o+} -ZrCl ₄ (100)
5	C ₂₀ H ₁₂ N ₂ S ₂ VCl ₃	501 M ^{o+} (10), 465 M ^{o+} -Cl (30), 429 M ^{o+} -2Cl (20), 395 M ^{o+} -3Cl (25), 344 M ^{o+} -VCl ₃ (100)
6	C ₂₀ H ₁₂ N ₂ S ₂ FeCl ₂	471 M ^{o+} (30), 435 M ^{o+} -Cl (20), 399 M ^{o+} -2Cl (30), 344 M ^{o+} -FeCl ₂ (100)
7	C ₂₀ H ₁₂ N ₂ S ₂ FeCl ₃	506 M ^{o+} (15), 470 M ^{o+} -Cl (30), 434 M ^{o+} -2Cl (20), 344 M ^{o+} -FeCl ₃ (100)
8	C ₂₀ H ₁₂ N ₂ S ₂ CoCl ₂	474 M ^{o+} (20), 403 M ^{o+} -2Cl (30), 344 M ^{o+} -CoCl ₂ (100)
9	C ₂₀ H ₁₂ N ₂ S ₂ NiCl ₂	474 M ^{o+} (10), 439 M ^{o+} -Cl (30), 403 M ^{o+} -2Cl (20), 344 M ^{o+} -NiCl ₂ (100)
10	C ₂₀ H ₁₂ N ₂ S ₂ CuCl ₂	479 M ^{o+} (20), 443 M ^{o+} -Cl (20), 408 M ^{o+} -2Cl (30), 344 M ^{o+} -CuCl ₂ (100)
11	C ₂₁ H ₁₄ N ₂ S ₂ TiCl ₄	548 M ^{o+} (10), 512 M ^{o+} -Cl (20), 496 M ^{o+} -Cl-CH ₃ (15), 441 M ^{o+} -3Cl (20), 405 M ^{o+} -4Cl (20), 358 M ^{o+} -TiCl ₄ (100)
12	C ₂₁ H ₁₄ N ₂ S ₂ ZrCl ₄	593 M ^{o+} (10), 558 M ^{o+} -Cl (20), 522 M ^{o+} -2Cl (20), 485 M ^{o+} -3Cl (10), 471 M ^{o+} -3Cl-CH ₃ (20), 450 M ^{o+} -4Cl (25), 358 M ^{o+} -ZrCl ₄ (100)
13	C ₂₁ H ₁₄ N ₂ S ₂ VCl ₃	515 M ^{o+} (10), 479M ^{o+} -Cl (30), 444 M ^{o+} -2Cl (20), 408 M ^{o+} -3Cl (25), 358 M ^{o+} -VCl ₃ (100)
14	C ₂₁ H ₁₄ N ₂ S ₂ FeCl ₂	485 M ^{o+} (20), 449 M ^{o+} -Cl (20), 414 M ^{o+} -2Cl (30), 358 M ^{o+} -FeCl ₂ (100)
15	C ₂₁ H ₁₄ N ₂ S ₂ FeCl ₃	520 M ^{o+} (10), 485 M ^{o+} -Cl (20), 449 M ^{o+} -2Cl (20), 413 M ^{o+} -3Cl (20), 358 M ^{o+} -FeCl ₃ (100)
16	C ₂₁ H ₁₄ N ₂ S ₂ CoCl ₂	488 M ^{o+} (20), 453 M ^{o+} -Cl (20), 417 M ^{o+} -2Cl (30), 358 M ^{o+} -CoCl ₂ (100)
17	C ₂₁ H ₁₄ N ₂ S ₂ NiCl ₂	488 M ^{o+} (10), 453 M ^{o+} -Cl (30), 417 M ^{o+} -2Cl (20), 358 M ^{o+} -NiCl ₂ (100)
18	C ₂₁ H ₁₄ N ₂ S ₂ CuCl ₂	493 M ^{o+} (20), 457 M ^{o+} -Cl (30), 422 M ^{o+} -2Cl (30), 358 M ^{o+} -CuCl ₂ (100)

2.1.3. Zirconium complexes

To 0.45g (1.2 mmol) ZrCl₄ (THF) in dichloromethane was added 1.2 mmol of the solid ligand. The reaction mixture was stirred over night at room temperature and then filtered. The residue was washed several times with dichloromethane, then with pentane, dried under vacuum and weighed. The products were characterized by NMR (Table 1), mass spectroscopy (Table 2) and elemental analysis (Table 3).

2.1.4. Vanadium complexes

To 0.41g (2.6 mmol) VCl₃ in ether was added 2.6 mmol of the ligand. The reaction mixture was stirred over night at room temperature. The product was filtered and washed several times with ether and pentane, dried under vacuum and weighed. The products were characterized by mass spectroscopy (Table 2) and elemental analysis (Table 3).

2.1.5. General synthesis of the complexes

Equimolar amounts of Iron (II) chloride

(FeCl₂), iron (III) chloride (FeCl₃), cobalt (II) chloride (CoCl₂), nickel (II) chloride (NiCl₂) and copper (II) chloride (CuCl₂) and the ligands (**1**, **2**) dissolved in dichloromethane were mixed. The mixture was stirred over night at room temperature. The volume of the solvent was reduced in vacuo and the resulting solid were washed several times with dichloromethane and with n-pentane, filtered and dried in vacuo. The complexes were obtained as powders. All complexes were characterized by elemental analysis (Table 3) and mass spectroscopy (Table 2).

2.2. Polymerization of ethylene

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 added to a 1 L Schlenk flask filled with 250 mL 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 one hour. The polymer was filtered over a frit, washed with diluted hydrochloric acid, water, and acetone, and finally dried in vacuo.

Table 3. Elemental analysis data for ligands and complexes.

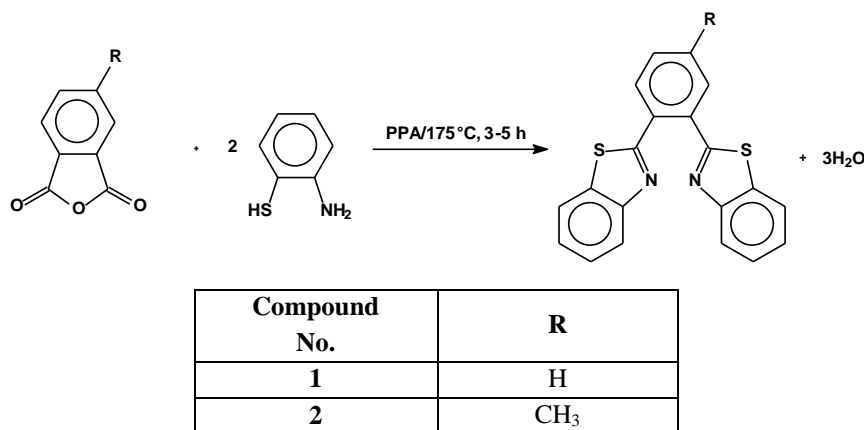
Compound No.	General Formula	Calculated			Found		
		C	H	N	C	H	N
1	C ₂₀ H ₁₂ N ₂ S ₂	68.8	3.5	8.1	69.7	3.5	8.2
2	C ₂₁ H ₁₄ N ₂ S ₂	70.4	3.9	7.8	71.1	3.5	7.6
3	C ₂₀ H ₁₂ N ₂ S ₂ TiCl ₄	44.9	2.2	5.2	45.3	1.9	4.9
4	C ₂₀ H ₁₂ N ₂ S ₂ ZrCl ₄	41.6	2.1	4.6	42.0	2.0	4.7
5	C ₂₀ H ₁₂ N ₂ S ₂ VCl ₃	47.9	2.4	5.6	48.8	2.6	5.4
6	C ₂₀ H ₁₂ N ₂ S ₂ FeCl ₂	51.0	2.5	5.9	50.8	2.2	6.2
7	C ₂₀ H ₁₂ N ₂ S ₂ FeCl ₃	47.5	2.4	5.5	48.2	2.9	5.3
8	C ₂₀ H ₁₂ N ₂ S ₂ CoCl ₂	50.1	2.5	5.8	50.6	2.7	6.1
9	C ₂₀ H ₁₂ N ₂ S ₂ NiCl ₂	50.6	2.5	5.9	50.3	2.8	6.2
10	C ₂₀ H ₁₂ N ₂ S ₂ CuCl ₂	50.6	2.5	5.9	50.7	2.4	6.1
11	C ₂₁ H ₁₄ N ₂ S ₂ TiCl ₄	46.0	2.6	5.1	46.3	2.9	4.8
12	C ₂₁ H ₁₄ N ₂ S ₂ ZrCl ₄	42.6	2.4	4.7	43.0	2.7	4.3
13	C ₂₁ H ₁₄ N ₂ S ₂ VCl ₃	48.3	2.7	5.4	48.0	2.9	5.8
14	C ₂₁ H ₁₄ N ₂ S ₂ FeCl ₂	52.0	2.9	5.8	51.8	3.2	6.1
15	C ₂₁ H ₁₄ N ₂ S ₂ FeCl ₃	48.5	2.7	5.4	49.0	2.6	5.8
16	C ₂₁ H ₁₄ N ₂ S ₂ CoCl ₂	51.6	2.9	5.7	51.8	2.6	5.3
17	C ₂₁ H ₁₄ N ₂ S ₂ NiCl ₂	51.6	2.9	5.7	51.1	3.2	5.9
18	C ₂₁ H ₁₄ N ₂ S ₂ CuCl ₂	51.1	2.8	5.7	51.7	3.0	5.4

3. RESULTS AND DISCUSSION

3.1. General synthesis of the ligand precursors

The condensation reaction of a dicarboxylic acid or an acid anhydride with 2-aminothiophenol in preheated polyphosphoric acid is a well established

procedure for the synthesis of the benzothiazole based ligand precursors [21, 22] in moderate to high yields (Scheme 1).



Scheme 1. Synthesis of the ligands precursors 1-2.

3.2. Synthesis of coordination compounds

3.2.1. Synthesis of titanium and zirconium complexes

The complexes were synthesized according to Scheme 2. The reaction of the tetrahydrofuran adducts of zirconium and titanium tetrachloride with the corresponding ligand precursor in methylene chloride results in an immediate colour change and the complexes could be isolated in very high yields (70-

85%). The complexes were characterized by NMR, mass spectrometry and elemental analysis.

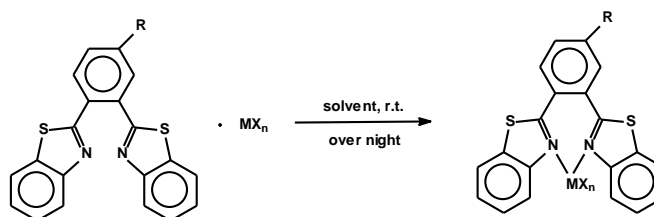
3.2.2. Synthesis of the vanadium complexes

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 product yields range within 60-78%.

3.2.3. Synthesis of the iron (II) and iron (III), cobalt (II), nickel (II) and copper (II) complexes

The complexes were synthesized by dissolving

metal chloride in dichloromethane followed by the addition of the ligand precursor with constant stirring overnight. The product yields range within 65-80 %.



Complex No.	R	M
3	H	Ti
4	H	Zr
5	H	V
6	H	Fe (II)
7	H	Fe (III)
8	H	Co
9	H	Ni
10	H	Cu
11	CH ₃	Ti
12	CH ₃	Zr
13	CH ₃	V
14	CH ₃	Fe (II)
15	CH ₃	Fe (III)
16	CH ₃	Co
17	CH ₃	Ni
18	CH ₃	Cu

Scheme 2. Synthesis of the coordination compounds **3-18**.

3.3. Characterization

3.3.1. ¹H and ¹³C NMR spectroscopy

The ligand precursors **1**, **2** and their titanium and zirconium complexes were characterized by ¹H and ¹³C NMR spectroscopy. The vanadium, iron, nickel, cobalt, and copper complexes, due to their paramagnetism, were characterized by mass spectroscopy and elemental analysis. The ¹H NMR spectrum of compound **2** (see Figure 1) shows six resonance signals. The double doublet at $\delta = 8.05$ ppm [$J_{H,H} = 8.1$ Hz] can be assigned to two protons of the benzothiazole phenyl ring (H6). The doublet at $\delta = 7.84$ ppm [$J_{H,H} = 8.1$ Hz] represent the protons in the position 2. The broad signal at $\delta = 7.79$ - 7.74 ppm is assigned to three protons H3 and H7. The double doublets at $\delta = 7.41$ and 7.31 ppm [$J_{H,H} = 8.1$ and 5.4 Hz] can be assigned to H1, H4 and H5 respectively. The methyl protons appear as singlet at $\delta = 2.50$ ppm.

The ¹³C NMR spectrum of complex **2** (Figure 2) shows 21 resonance signals each corresponding to one carbon atoms. The two signals at $\delta = 166.7$ and 166.5 ppm can be assigned to C4 and C13. The signals appearing at $\delta = 153.5$ and 153.4 ppm corresponds to C10 and C19. At $\delta = 141.0$ ppm C20 was observed. The signals for C5 and C14 are found at $\delta = 136.9$ and 136.8 ppm. At $\delta = 133.6$ ppm C11 appears. At $\delta = 131.7$ ppm, a signal assigned to C12 is observed. The signals at $\delta = 131.3$ and 131.1 ppm can be assigned to C8 and C17. The signal at $\delta = 130.0$ ppm corresponds to C3. The signals at $\delta = 126.4$ and 126.3 ppm can be assigned to C7 and C16. At $\delta = 125.5$ and 125.4 ppm C9 and C18 can be detected, the signals assigned to C1, C2, C6 and C15 were observed at $\delta = 123.8$, 123.7 , 121.7 and 121.6 ppm respectively. The signal at $\delta = 21.5$ ppm corresponds to C21.

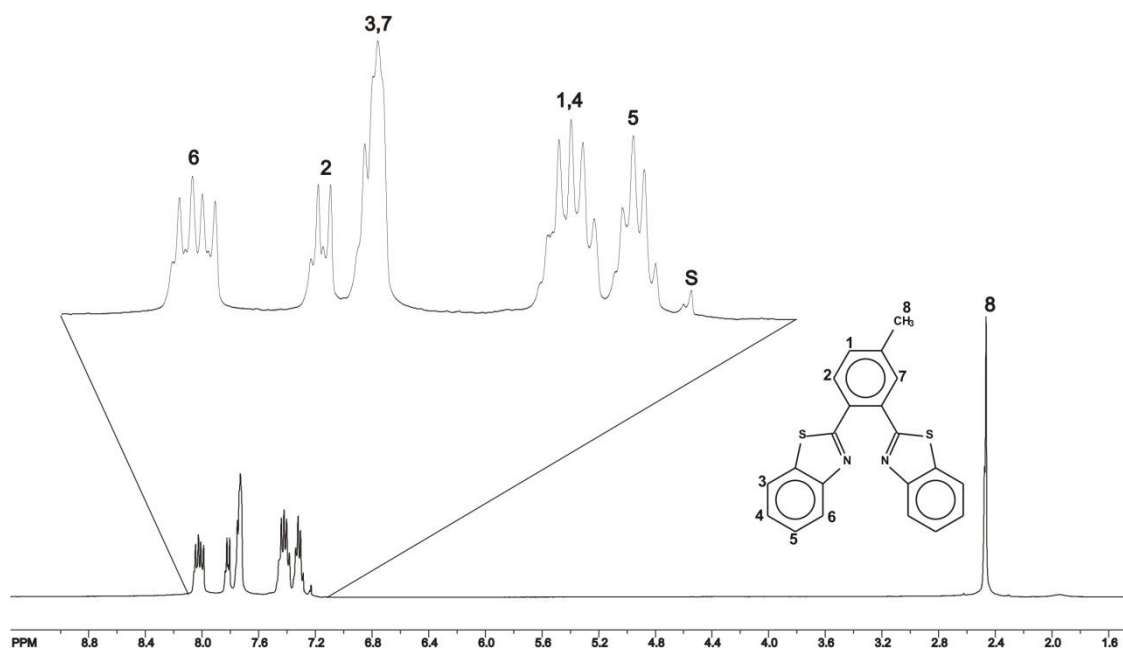


Figure 1. ¹H NMR spectrum of compound 2.

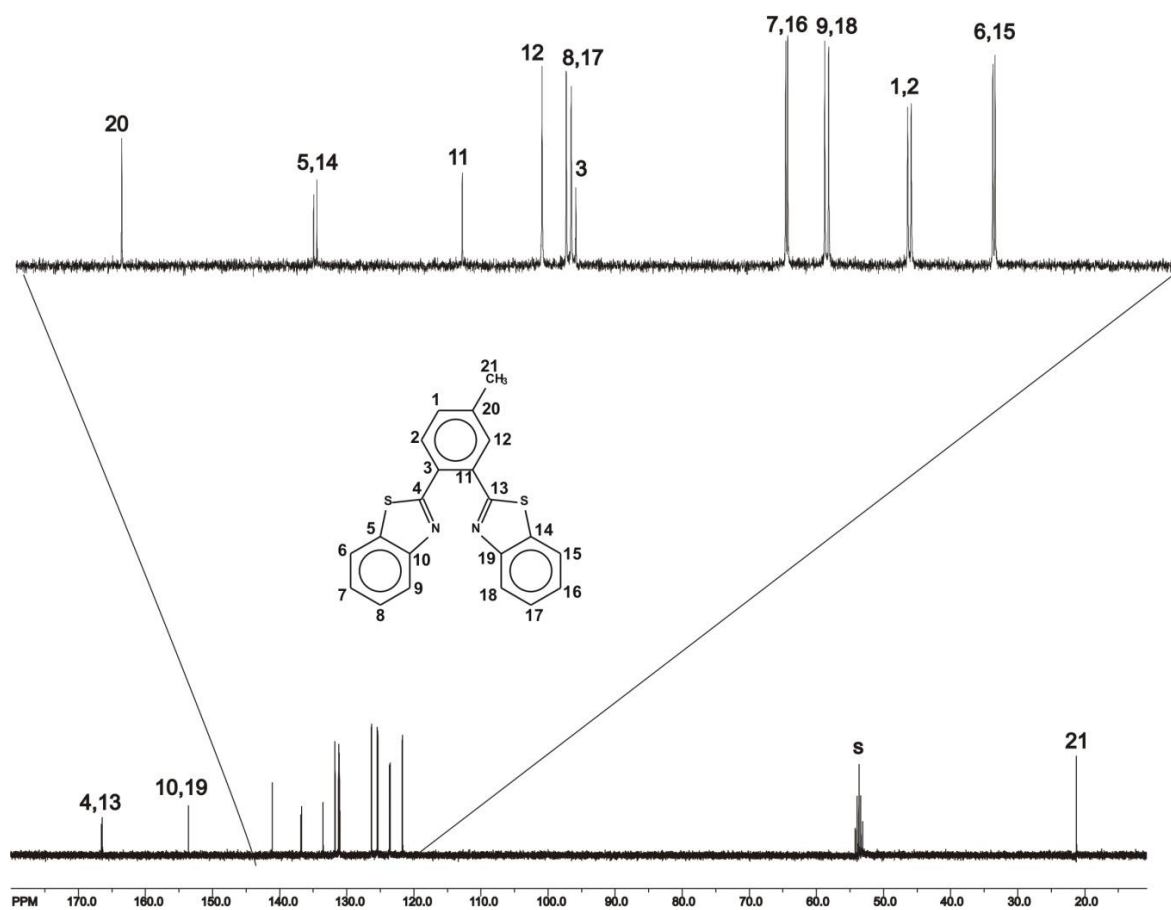


Figure 2. ¹³C NMR spectrum of compound 2.

The ¹H NMR spectrum of complex **11** (Figure 3) shows eight sets of resonance signals. The triplet at

$\delta = 8.02$ ppm [2H, $J_{H,H} = 8.2$ Hz] can be assigned to the protons H6 and the double doublet at $\delta = 7.92$

ppm [2H, $J_{H,H} = 8.2$ Hz] can be assigned to the protons H3, H2 appears as doublet at $\delta = 7.82$ ppm [1H, $J_{H,H} = 8.2$ Hz]. The singlet at $\delta = 7.73$ ppm is assigned to the protons H7. The doublet at $\delta = 7.53$

[2H, $J_{H,H} = 7.8$ Hz] is assigned to H1. The double doublets at $\delta = 7.49-7.43$ ppm [2H, $J_{H,H} = 7.8$ Hz] and $\delta = 7.41-7.35$ ppm [2H, $J_{H,H} = 7.8$ Hz] can be assigned to the protons H4 and H5 respectively.

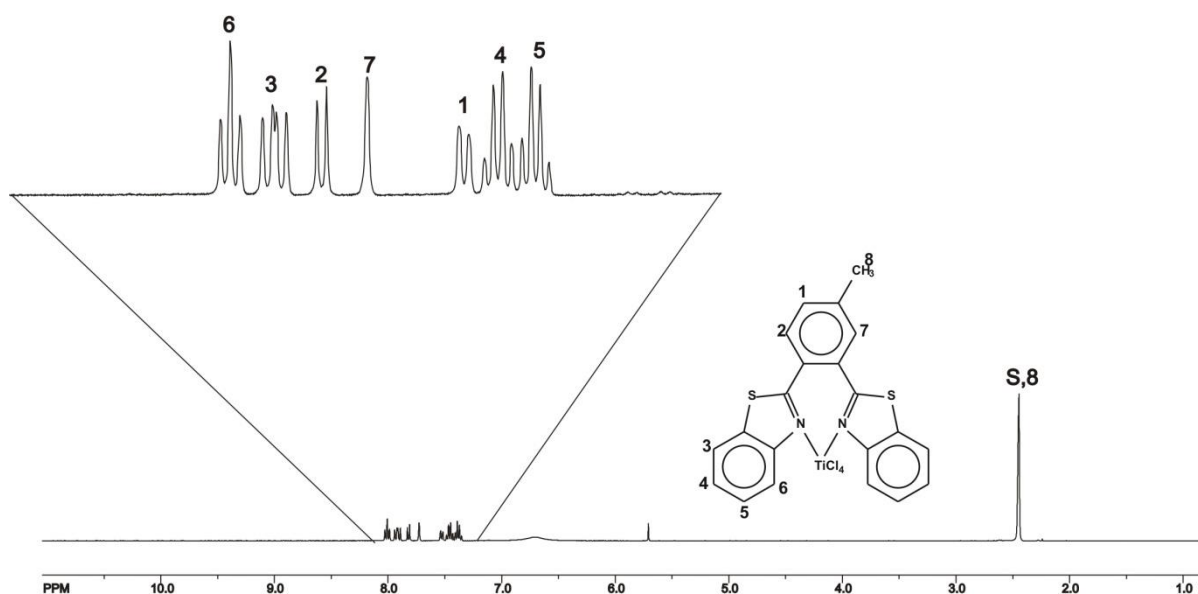


Figure 3. ^1H NMR spectrum of complex **11**.

The ^{13}C NMR spectrum of complex **11** (Figure 4) shows 21 resonance signals each corresponding to one carbon atoms. The two signals at $\delta = 166.5$ and 166.4 ppm can be assigned to C4 and C13. The signals appearing at $\delta = 153.4$ and 153.3 ppm corresponds to C10 and C19. At $\delta = 141.6$ ppm C20 was observed. The signals for C5 and C4 are found at $\delta = 136.6$ and 136.5 ppm. At $\delta = 133.4$ ppm C11 appears. The signals at $\delta = 132.2$ and 132.1 ppm can be assigned to C8 and C17. At $\delta = 131.6$ ppm, a signal assigned to C12 is observed and the signal at $\delta = 130.8$ ppm corresponds to C3. The signals at $\delta = 127.2$ and 127.1 ppm can be assigned to C7 and C16. At $\delta = 126.3$ and 126.2 ppm C9 and C18 can be detected, the signals assigned to C1, C2, C6 and C15 were observed at $\delta = 123.8$, 123.7 , 122.9 and 122.8 ppm respectively. The signal at $\delta = 21.5$ ppm corresponds to C21.

3.3.2. Mass spectroscopy

The mass spectrum of compound **2** is shown in Figure 5. The molecular ion peak is detected at $m/z = 358$; the loss of one sulphur atom results in an ion at $m/z = 326$. The peak with $m/z = 223$ is assigned to ($\text{M}^{2+} - \text{C}_6\text{H}_4\text{NS}$). The ion with $m/z = 108$ can be

assigned to ($\text{C}_6\text{H}_4\text{S}$).

The mass spectrum of complex **11** (see Figure 6) shows the molecular ion peak at $m/z = 548$. The ion resulting from the loss of one and two chlorine atoms can be found at $m/z = 512$ and $m/z = 476$ respectively. The base peak appears at $m/z = 358$ representing the mass of the free ligand. Generally, it can be observed that the weak dative bonds involved in the formation of the complexes is responsible for relatively low intensities of the fragmentation pattern.

3.4. Polymerization results

All coordination compounds were activated with MAO assuming the mechanism proposed for the activation of metallocene [23, 24] and 2,6-bis(imino)pyridine iron (II) [25] compounds.

The complexes of transition metals with ligands derived from 1, 2-bis (benzothiazolyl) benzene compounds were activated with methylalumoxane (MAO) in toluene solution. The homogeneous catalyst solutions were used for ethylene polymerization reactions. They showed variable activities for ethylene polymerization under different polymerization conditions (co-catalyst concentration, polymerization temperature). The

activities are greatly influenced by the ligand environment and the nature of the metal atom.

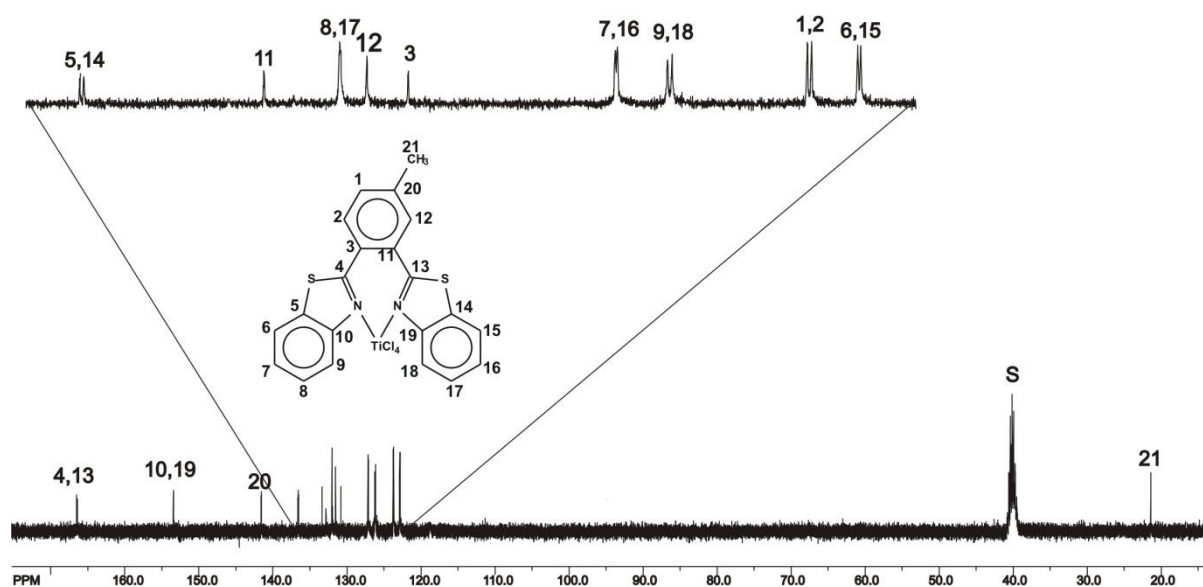


Figure 4. ^{13}C NMR spectrum of complex 11.

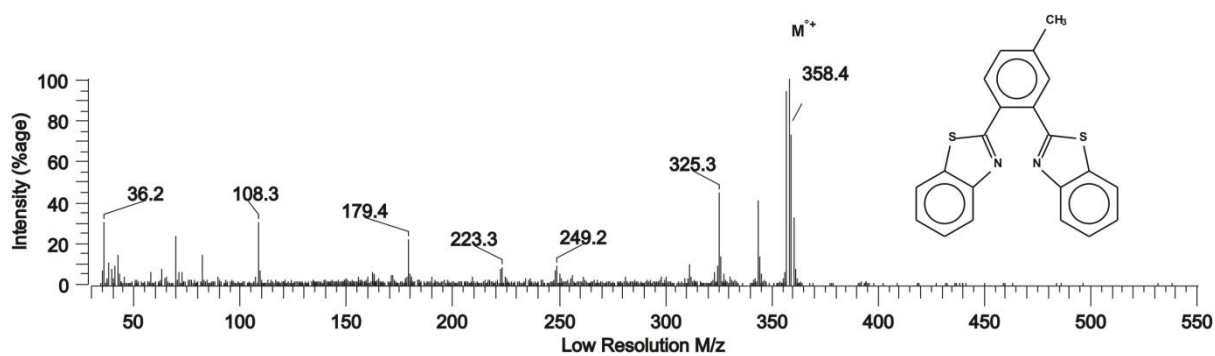


Figure 5. Mass spectrum of compound 2.

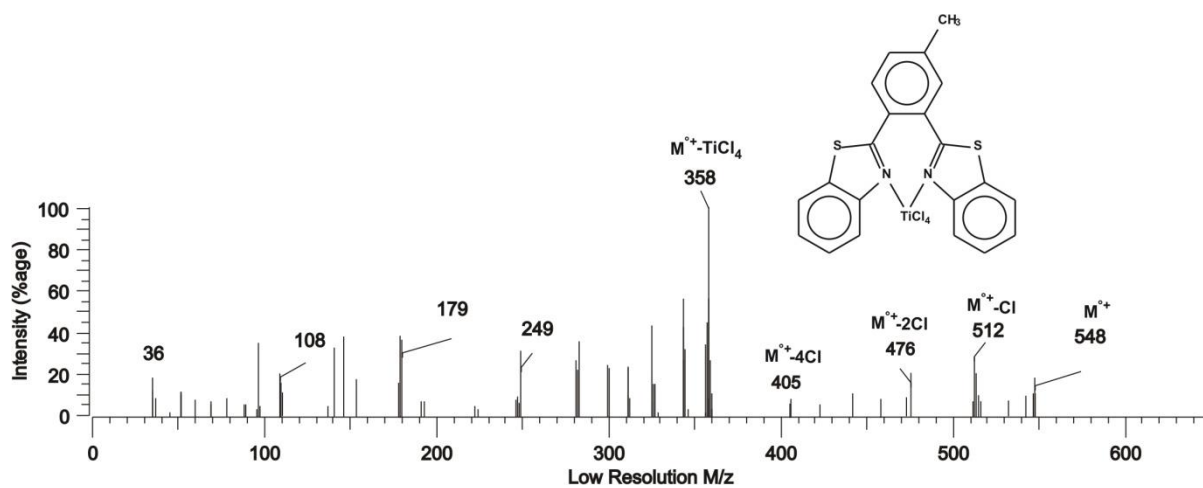


Figure 6. Mass spectrum of complex 11.

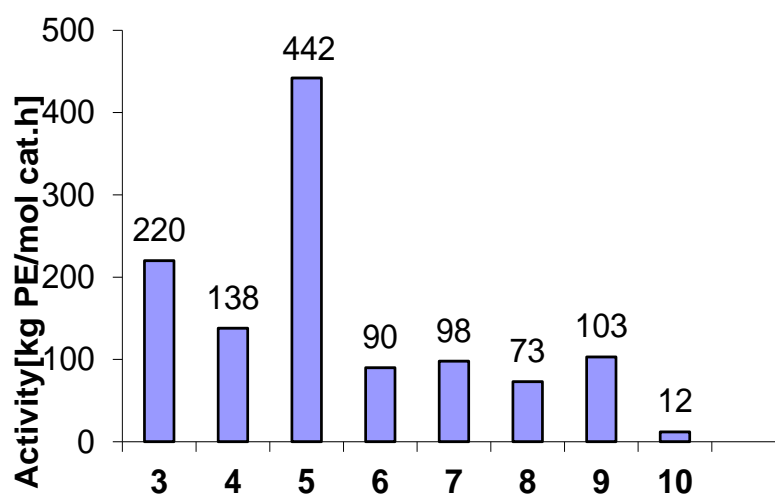
Table 4. Polymerization activities of complexes 3 - 18.

Complex No.	Polymerization temperature °C	Cocatalyst concentration M:Al	Activity [kg/mol cat. h]	Mw [g/mol]	PD
3	50	(Ti : Al = 1: 1000)	356	1.5×10^6	4.2
3	50	(Ti : Al = 1: 2500)	220	1.3×10^6	5.6
4	50	(Zr : Al = 1:2500)	138	4.6×10^5	6.6
5	50	(V : Al = 1:2500)	442	2.1×10^6	4.5
5	50	(V : Al = 1:1000)	625	1.6×10^6	7.9
5	65	(V : Al = 1:2500)	178	7.2×10^5	6.3
6	50	(Fe(II) : Al = 1:2500)	90	5.8×10^5	3.9
7	50	(Fe(III) : Al = 1:2500)	98	6.7×10^5	4.7
7	50	(Fe(III) : Al = 1:2000)	117	7.2×10^5	4.2
7	50	(Fe(III) : Al = 1:1500)	182	9.2×10^5	5.4
7	50	(Fe(III) : Al = 1:1000)	102	5.2×10^5	4.4
8	50	(Co : Al = 1:2500)	73	n.d.	n.d.
9	50	(Ni : Al = 1:2500)	103	6.3×10^4	1.7
10	50	(Cu : Al = 1:2500)	12	n.d.	n.d.
11	50	(Ti : Al = 1:2500)	260	3.3×10^6	10.2
12	50	(Zr : Al = 1:2500)	128	1.6×10^6	11.0
13	50	(V : Al = 1:2500)	241	1.6×10^6	6.0
14	50	(Fe(II) : Al = 1:2500)	63	4.8×10^5	3.3
15	50	(Fe(III) : Al = 1:2500)	78	5.7×10^5	4.4
15	50	(Fe(III) : Al = 1:2000)	97	7.3×10^5	4.0
15	50	(Fe(III) : Al = 1:1500)	133	8.4×10^5	5.8
15	50	(Fe(III) : Al = 1:1000)	85	5.6×10^5	3.4
16	50	(Co : Al = 1:2500)	55	n.d.	n.d.
17	50	(Ni : Al = 1:2500)	81	5.6×10^4	2.1
18	50	(Cu : Al = 1:2500)	8	n.d.	n.d.

n.d. = not determined. (All polymerization reactions were carried out in 250 ml pentane with MAO as cocatalyst (Al: M, 2500:1) at 50 °C and 10 bar ethylene pressure, 1 hour).

The activities of complexes derived from 1, 2-bis(benzothiazolyl) benzene (Figure 7) were found to follow the order V > Ti > Zr > Ni > Fe (III) > Fe (II) >

Co > Cu. This order of activities may be accounted for by the nature of the active metal centres.

**Figure 7.** Polymerization activities of 1, 2-bis (benzothiazolyl) benzene complexes 3-10.

Similarly, complexes obtained from the ligand 1, 2-bis (benzothiazolyl)-4-methyl- benzene (Figure 8) were found to follow the same activity order,

however, the catalyst generally showed lower activities compared to the unsubstituted complexes.

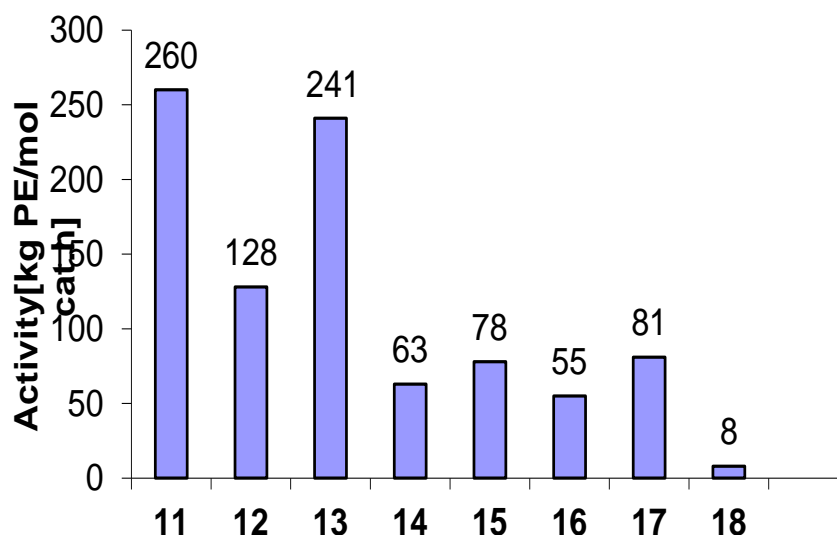


Figure 8. Polymerization activities of 1, 2- bis (benzothiazolyl) - 4-methyl benzene complexes 11- 18.

The vanadium complexes (Figure 9) showed the highest activity among the catalyst series. **5/MAO** showed higher activity than **13/MAO** derived from the 1, 2-bis (benzothiazolyl) -4-methyl- benzene ligand. The higher activity of **5/MAO** (442 kg PE/mol cat.h) compared to **13MAO** (241 kg PE/mol cat.h). The methyl group due to its electronic effect cuts the activity of the catalyst system to half the value obtained with the unsubstituted complex.

The lower activities of the late transition metal complexes (iron, cobalt, nickel and copper) compared

to that of the early transition metals (V, Ti and Zr) may result from the high nucleophilicity of the former metals.

The activity of the catalysts **3/MAO** and **5/MAO** was tested with different MAO concentrations. At 50°C with aluminum to titanium ratio of 1000: 1, the catalyst **3/MAO** shows an activity of 356 [kg PE/mol cat.h]. Increasing the cocatalyst concentration to 2500 equivalents results in an activity decrease to 220 [kg PE/mol cat.h] (see Figure 9).

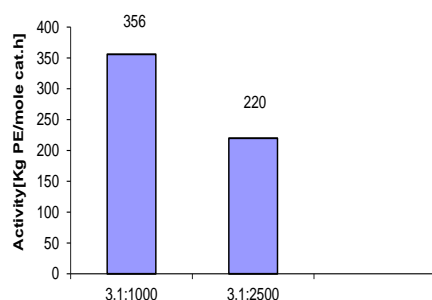


Figure 9. effect of cocatalyst concentration on the activity of **3/MAO**.

Similarly, **5/MAO** At 50°C with aluminum to vanadium ratio of 1000:1 (see Figure 10) shows an activity of 625 [kg PE/mol cat.h]. Increasing the cocatalyst concentration to 2500 equivalents results in an activity decrease to 442 [kg PE/mol cat.h]. The decrease of activity with increasing cocatalyst concentration may be explained by the steric effect of

the cocatalyst around the active metal centre slowing down the coordination of the monomer to the metal [23].

Applying complex **5/MAO**, the temperature dependence of the polymerization activities was investigated (Figure 11). Under the same cocatalyst concentration and at a reaction temperature of 50°C

the catalyst system **5/MAO** shows an activity of 442 [kg PE/mol cat·h]. Increasing the temperature to 65°C lead to an activity of 178 [kg PE/mol cat·h]. This

behaviour is in agreement with the fact that kinetics is accelerated with rising temperatures.

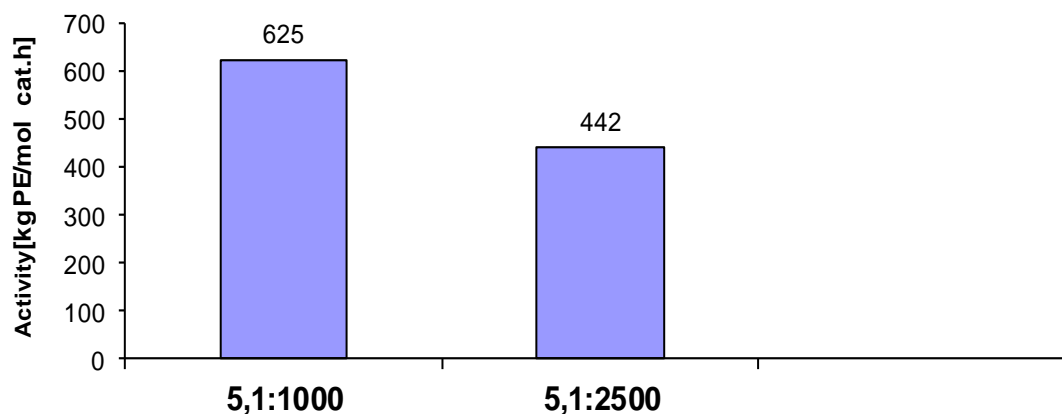


Figure 10. Effect of cocatalyst concentration on the activity of **5/MAO**.

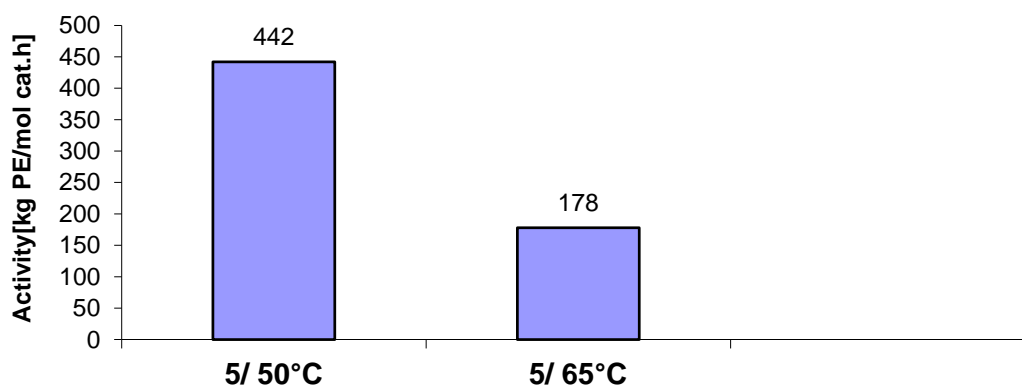


Figure 11. Effect of polymerization temperature on the activity of **5/MAO**.

The effect of oxidation state (Figure 12) was also investigated applying the iron (II) complexes (6, 14) and Iron (III) complexes (7, 15) Fe (III) catalyst after activation with MAO under the same polymerization conditions showed higher activity than those of Fe(II) complexes. For instance, **6/MAO** shows an activity of 90 [kg PE/mol cat·h] while **7/MAO** shows an activity of 98 [kg PE/mol cat·h]. This difference of catalytic activities can be accounted for by the higher electrophilic character of Fe (III) complexes compared to Fe (II) complexes.

The activity of the catalysts **7/MAO** and **15/MAO** was tested with different MAO concentrations. At 50°C with aluminum to iron (III) ratio of 1000: 1, the catalyst **7/MAO** shows an

activity of 102[kg PE/mol cat·h]. Increasing the cocatalyst concentration to 1500 equivalents results in an activity of 182 [kg PE/mol cat·h] further increase in MAO concentration results in an activity decrease to 117 [kg PE/mol cat·h] (see Figure 13).

Similarly, catalyst **15/MAO** shows an activity of 85 [kg PE/mol cat·h] at 50°C with aluminum to iron (III) ratio of 1000: 1. Increasing the cocatalyst concentration to 1500 equivalents results in an activity of 133 [kg PE/mol cat·h]. Increasing the concentration of MAO to 2500 equivalent results in an activity decrease to 78 [kg PE/mol cat·h] (see Figure 14). The higher cocatalyst concentration may also block some of the active sites leading to an overall decrease in catalyst activity [23].

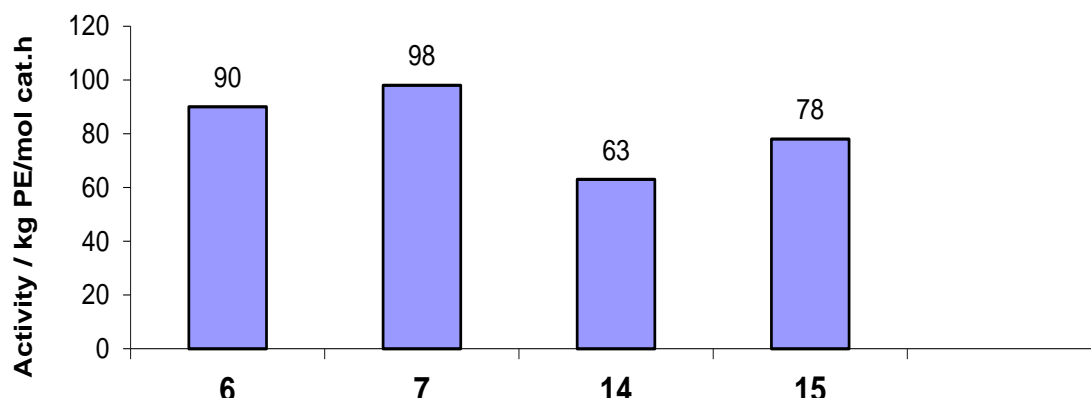


Figure 12. effect of oxidation state on the activities of Fe (III) and Fe (II) complexes.

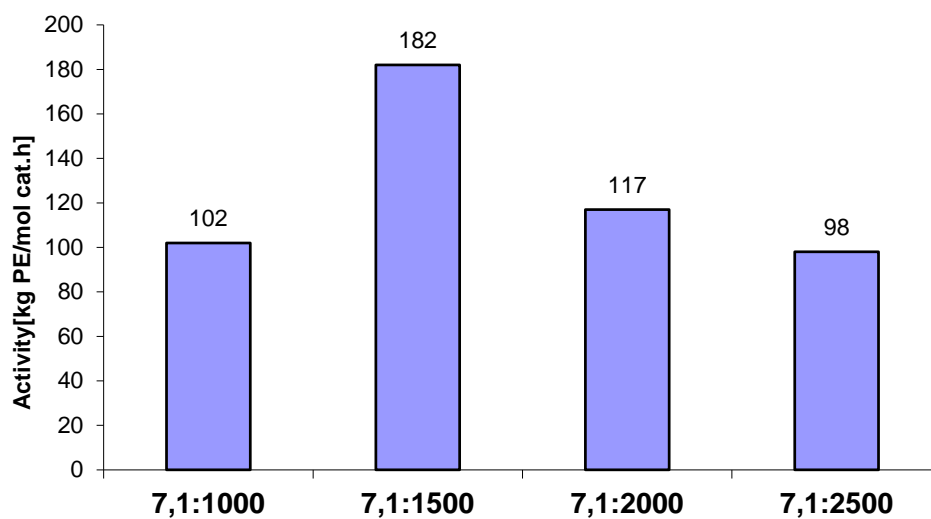


Figure 13. Effect of cocatalyst concentration on the activity of 7/MAO.

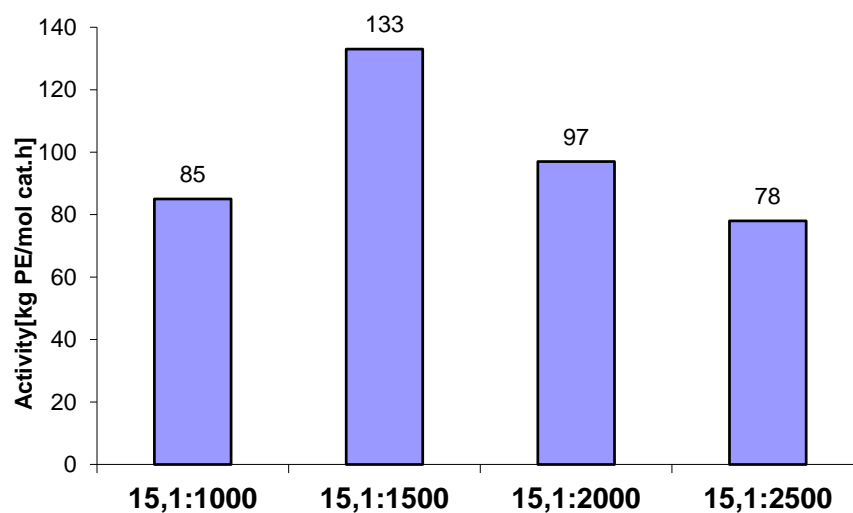


Figure 14. Effect of cocatalyst concentration on the activity of 15/MAO.

GPC analysis of the polyethylenes produced by 1, 2-bis(benzothiazolyl) benzene complexes (**3-10**) and 1, 2-bis (benzothiazolyl) - 4-methyl benzene complexes (**11-18**) revealed that the symmetric catalysts systems were capable to produce resins with high to very high molecular weights associated with narrow to broad molecular weight distributions. The broad molecular weight may arise from the fact that the MAO counterion induces the necessary dissymmetry of the active sites in the activation process [26]. The molecular weight M_w of the polymer produced with **12 / MAO** was determined to be 1.6×10^6 g / mol, (PD = 11.0). The molecular weight M_w of the polymer produced with **3 / MAO** was determined to be 1.5×10^6 g / mol, (PD = 4.2). The molecular weight M_w and polydispersity of the polymer produced with catalyst systems **5 / MAO**, and **11 / MAO** was determined to be 2.1×10^6 g / mol, (PD = 4.5) and 3.3×10^6 g / mol (PD = 10.2) respectively. The polymer produced with nickel complexes **9/MAO** (PD =) and **17 / MAO** (5.6×10^4 g / mol) showed a relatively low molecular weights M_w (6.3×10^4 and 5.6×10^4 g / mol) and narrow molecular weight distributions (polydispersity = 1.7 and 2.1) respectively.

4. CONCLUSION

Transition metal complexes containing benzothiazolyl building blocks are suitable catalyst precursors for ethylene polymerization in spite of the nature of the metals. When two of these heterocycles are connected via a 1, 2-phenylene bridge, the two nitrogen atoms of the heterocycle form a chelating complex with the corresponding metal. These complexes after activation with a suitable cocatalyst (MAO) they show different activities depending on the ligand structure, the nature of the metal atoms and polymerization conditions. The broad molecular weight distributions could have their origin from several different active sites that are formed from different interactions of the cocatalyst anion and the heteroatoms of the catalyst ligands.

5. ACKNOWLEDGMENTS

We thank Saudi Basic Industries Corporation (SABIC) for the financial support.

6. REFERENCES AND NOTES

- [1] Lever, A. B. P.; Ramaswamy, B. S.; Simonsen, S. H.; Thompson, L. K. *Can. J. Chem.* **1970**, *48*, 3076. [\[CrossRef\]](#)
- [2] Rendell, J. C.; Thompson, L. K. *Can. J. Chem.* **1979**, *57*, 1. [\[CrossRef\]](#)
- [3] Thompson, L. K.; Rendell, J. C.; Wellon, G. C. *Can. J. Chem.* **1982**, *60*, 514. [\[CrossRef\]](#)
- [4] Duff, E. J.; Hughes, M. N.; Rutt, K. J. *J. Chem. Soc. A* **1969**, 2101. [\[CrossRef\]](#)
- [5] Campell, M. J. M.; Card, D. W.; Grzeskowiak, R.; Goldstein, M. *J. Chem. Soc. A* **1970**, 672. [\[CrossRef\]](#)
- [6] Chan, N. N. Y.; Goodgame, M.; Weeks, M. J. *J. Chem. Soc. A* **1968**, 2499. [\[CrossRef\]](#)
- [7] Thompson, L. K.; Ball, R. G.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1566. [\[CrossRef\]](#)
- [8] Duff, E. J.; Hughes, M. N.; Rutt, K. J. *J. Chem. Soc. A* **1968**, 2354. [\[CrossRef\]](#)
- [9] Wang, S.; Cui, Y.; Tan, R.; Luo, Q.; Shi, J.; Wu, Q. *Polyhedron*. **1994**, *11*, 1661. [\[CrossRef\]](#)
- [10] Wang J, Zhu Y, Wang S, Gao Y, Shi Q. *Polyhedron*. **1994**, *13*, 1405. [\[CrossRef\]](#)
- [11] Holz, R. C.; Thomson, L. C. *Inorg. Chem.* **1988**, *27*, 4640. [\[CrossRef\]](#)
- [12] Wang, S. X.; Zhu, Y.; Zhang, F. G.; Wang, Q. Y.; Wang, L. F. *Polyhedron*. **1992**, *11*, 1909. [\[CrossRef\]](#)
- [13] Elagab, H. A.; Alt, H. G. *Inorg. Chim. Acta.* **2015**, *428*, 100. [\[CrossRef\]](#)
- [14] Elagab, H. A.; Alt, H. G. *Eur. Poly. J.* **2015**, *68*, 385. [\[CrossRef\]](#)
- [15] Elagab, H. A.; Alt, H. G. *Inorg. Chim. Acta.* **2015**, *431*, 266. [\[CrossRef\]](#)
- [16] Elagab, H. A.; Alt, H. G. *Jordan Journal of Chemistry.* **2015**, *10*, 1.
- [17] Elagab, H. A.; Alt, H. G. *Jordan Journal of Chemistry.* **2015**, *10*, 41.
- [18] Elagab, H. A.; Alt, H. G. *Eur. Poly. J.* **2015**, *71*, 85. [\[CrossRef\]](#)
- [19] Elagab, H. A.; Alt, H. G. *Inorg. Chim. Acta.* **2015**, *437*, 26. [\[CrossRef\]](#)
- [20] Manzer, L. E. *Inorganic Synthesis*, **1982**, *21*, 135. [\[CrossRef\]](#)
- [21] Rai, C.; Braunwarth, J. B. *J. Org. Chem.* **1961**, *26*, 3434. [\[CrossRef\]](#)
- [22] Phillips, M. A-CCCXVII. *J. Chem. Soc.* **1928**, 2393. [\[CrossRef\]](#)
- [23] Bochmann, M.; Wilson, L. M. *J. Chem. Soc. Chem. Commun.* **1986**, *21*, 1610. [\[CrossRef\]](#)
- [24] Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. [\[CrossRef\]](#)
- [25] Seitz, M.; Milius, W.; Alt, H. G. *J. Mol. Catal. A:* **2007**, *261*, 246. [\[CrossRef\]](#)
- [26] Alt H G, Ernst R. *J. Mol. Catal.A:* **2003**, *195*, 11. [\[CrossRef\]](#)