

Polymerization of Ethylene Catalyzed by Vanadium(III) Complexes

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Abstract: Thirty five complexes of 1,2- bis(benzimidazole, benzothiazole and benzoxazole)benzene, 1,2-bis(benzimidazole, benzothiazole and benzoxazole)-4-methyl-benzene, 1,2-bis (benzimidazole, benzothiazole and benzoxazole)4-bromobenzene, 1, 2-bis(benzimidazole, benzothiazole and benzoxazole) 4- chlorobenzene, and 2, 6-bis(benzimidazole, benzothiazole and benzoxazole) pyridine compounds with V (III) metal centers were synthesized, characterized, activated with methylalumoxane (MAO) and then tested for catalytic ethylene polymerization. The catalysts generally show moderate to good activities compared to the benchmark catalyst Cp_2ZrCl_2 . The activities of the various catalysts were found to be function of the hetero atoms in the ligand frameworks and also strongly influenced by the bridging unit of the ligand. The highest activity was obtained with **36** / MAO (442 kg PE / mol cat. h). The produced polyethylenes showed high molecular weights (up to 2.7×10^6 g/mol) and broad molecular weight distributions (PD = 1.4 - 16.6). Thermal analysis of polyethylenes produced with vanadium complexes revealed that the catalyst systems were capable to produce high density polyethylenes with melting temperatures > 135 °C and crystallization temperatures range from 117-120 °C with high degree of crystallinity.

Keywords: synthesis; characterization; heterocycles; vanadium complexes; ethylene polymerization

1. INTRODUCTION

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 [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. The ligand 2, 6-bis (2-benzothiazolyl) pyridine [9, 10], has been shown to behave as an N-3 donor in its complexes with manganese (II), iron (II) and nickel (II). 2, 6-Bis (benzimidazolyl) pyridine [11-23], derivatives have been reported as ligands for transition metals in order to investigate the complexes for their structures and properties.

In polyolefin chemistry, an increasing interest

has been focused on the exploration and development of homogeneous transition metal catalysts, as a result of an increasing demand for polyethylene [24 -32]. A series of (8-(benzimidazol-2-yl) quinoline) dichlorocobalt (II) complexes were reported to be active ethylene polymerization catalysts [33- 34]. 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 [35]. 2, 6-bis (2-benzimidazolyl) pyridine zirconium dichloride / MAO polymerize methylacrylate [36]. Recently, [37-46] we reported the ethylene polymerization activity of benzimidazole, benzothiazole, benzoxazole and 2-(benzimidazolyl)pyridine titanium, zirconium and vanadium complexes. Herein we reported on the effect of heteroatom on the activity of vanadium complexes of 1,2-bis(benzimidazolyl, benzothiazolyl, and benzoxazolyl)benzene and the tridentate 2,6-bis(benzimidazolyl, benzothiazolyl, and benzoxazolyl)pyridine. Their behavior towards ethylene polymerization after activation with

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methylaluminoxane (MAO) was investigated.

2. MATERIAL AND METHODS

All experimental work was routinely carried out using Schlenk technique unless otherwise stated. Anhydrous and purified argon was used as inert gas. n-Pentane, diethyl ether, toluene and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride. Methylene chloride was dried with phosphorus pentoxide and additionally with calcium hydride. Methanol and ethanol were dried over magnesium. Deuterated solvents (CDCl_3 , DMSO-d_6) for NMR spectroscopy were stored over molecular sieves (3Å). 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 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 , $\delta = 2.50$ ppm for DMSO-d_6) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for CDCl_3 , $\delta = 39.5$ ppm for DMSO-d_6). Mass 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. 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 1-35

(O-Phenylenediamine, 2-aminophenol and 2-aminothiophenol) compound (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 (PPA). The mixture was stirred and heated at 175 °C for 3-5 hours. The reaction mixture was then poured into ice cold water and allowed to stand overnight. The precipitate was removed by filtration and washed several times with diluted sodium hydrogen carbonate solution and finally with water. The reaction product was then air dried and quantified. The products were characterized by NMR, mass spectrometry and elemental analyses.

Compound (1) 1,2-bis(benzothiazolyl)benzene: Yield: 85 %; Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{S}_2$: C, 68.8; H, 3.5; N, 8.1%. Found: C, 69.7, H, 3.5, N, 8.2%; ^1H -NMR: 8.01 (*d*, 2H, $J = 7.6$ Hz, aromatic), 7.91 (*dd*, 2H, $J = 7.6$ and 5.4 Hz, aromatic), 7.77 (*d*, 2H, $J = 7.6$ Hz, aromatic), 7.60 (*dd*, 2H, $J = 7.6$ and 5.4 Hz, aromatic), 7.44 (*t*, 2H, $J = 7.6$ Hz, aromatic), 7.33 (*t*, 2H, $J = 7.6$ Hz, aromatic); ^{13}C -NMR: 166.4, 153.4, 136.6, 133.5, 131.6, 131.5, 127.2, 126.3, 123.8, 121.9; MS (*m/z*, (relative abundance, %)): 344 (M^+ , 100).

Compound (2) 1,2-bis(benzothiazolyl)-4-methylbenzene: Yield: 75%; Anal. Calcd. for $\text{C}_{21}\text{H}_{14}\text{N}_2\text{S}_2$: C, 70.4; H, 3.9; N, 7.8%. Found: C, 69.8, H, 4.1, N, 7.5%; ^1H -NMR: 8.01-7.95(*m*, 2H, aromatic), 7.84-7.79(*m*, 3H, aromatic), 7.74(*s*, 1H, aromatic), 7.48-7.44(*m*, 3H, aromatic), 7.38-7.33(*m*, 2H, aromatic), 2.50(*s*, 3H, CH_3); ^{13}C -NMR: 166.6, 166.5, 153.6, 153.5, 141.1, 136.8, 136.8, 133.5, 131.8, 131.2, 131.1, 131.0, 129.8, 126.3, 126.2, 125.5, 125.4, 123.6, 123.5, 121.7, 121.6, 21.3(CH_3); MS (*m/z*, (relative abundance, %)): 358 (M^+ , 100).

Compound (3) 1,2-bis(benzothiazolyl)-4-methylbenzene: Yield: 85%; Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{S}_2\text{Cl}$: C, 63.3; H, 2.9; N, 7.4%. Found: C, 63.3, H, 2.9, N, 7.4%; ^1H -NMR: 8.11-8.01 (*m*, 4H, aromatic), 7.74-7.69 (*m*, 2H, aromatic), 7.64-7.60 (*m*, 2H, aromatic), 7.37 (*d*, 1H, $J = 7.6$ Hz, aromatic), 6.96 (*d*, 1H, $J = 7.6$ Hz, aromatic), 6.87 (*d*, 1H, $J = 7.6$ Hz, aromatic); ^{13}C -NMR: 166.6, 166.5, 153.9, 153.6, 141.3, 138.8, 138.6, 137.7, 137.5, 137.4, 130.0(2C), 129.1, 128.7(2C), 128.5(2C), 126.2(2C), 123.1; MS (*m/z*, (relative abundance, %)): 379 (M^+ , 100).

Compound (4) 1,2-bis(benzothiazolyl)-4-methylbenzene: Yield: 85%; Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{S}_2\text{Br}$: C, 56.7; H, 2.6; N, 6.6%. Found: C, 56.8, H, 2.6, N, 6.6%; ^1H -NMR: 8.05-8.01 (*m*, 4H), 7.66-7.57 (*m*, 2H), 7.55-7.45 (*m*, 2H), 7.43 (*d*, 1H, $J = 7.6$, aromatic), 6.95 (*d*, 1H, $J = 7.6$, aromatic), 6.77 (*d*, 1H, $J = 7.6$, aromatic); ^{13}C -NMR: 166.2, 166.1, 153.9(2C), 140.9, 138.8(2C),

137.5, 135.1, 134.6, 131.7, 130.0(2C), 129.6, 128.7(2C), 128.5(2C), 126.2(2C); MS (m/z , (relative abundance, %)): 423 (M⁺, 100).

Compound (5) 1,2-bis(benzoxazolyl)benzene: Yield: 77%; Anal. Calcd. for C₂₀H₁₂N₂O₂: C, 76.9; H, 3.9; N, 9.0%. Found: C, 77.1, H, 3.7, N, 8.8%; ¹H-NMR: 8.07 (*t*, 2H, *J* = 7.8 Hz, aromatic), 7.81 (*t*, 2H, *J* = 7.8 Hz, aromatic), 7.72 (*d*, 4H, *J* = 7.8 Hz, aromatic), 7.53 (*d*, 4H, *J* = 7.8 Hz, aromatic), 7.35 (*d*, 4H, *J* = 7.8 Hz, aromatic); ¹³C-NMR: 162.2, 151.20, 141.9, 132.5, 131.7, 127.4, 126.5, 125.5, 120.7; MS (m/z , (relative abundance, %)): 312 (M⁺, 100).

Compound (6) 1,2-bis(3-methylbenzoxazolyl)benzene: Yield: 73%; Anal. Calcd. for C₂₂H₁₆N₂O₂: C, 77.6; H, 4.7; N, 8.2%. Found: C, 77.7, H, 4.8, N, 8.4%; ¹H-NMR: 8.13 (*t*, 2H, *J* = 7.8 Hz, aromatic), 7.84 (*d*, 2H, *J* = 7.8 Hz, aromatic), 7.52 (*s*, 2H, aromatic), 7.44 (*d*, 2H, *J* = 7.8 Hz, aromatic), 7.19 (*d*, 2H, *J* = 7.8 Hz, aromatic), 2.40 (*s*, 6H, CH₃); ¹³C-NMR: 162.3, 149.4, 142.2, 134.9, 132.4, 131.6, 127.6, 127.4, 120.5, 110.9, 21.6(CH₃); MS (m/z , (relative abundance, %)): 340 (M⁺, 100).

Compound (7) 1,2-bis(4-methylbenzoxazolyl)benzene: Yield: 70%; Anal. Calcd. for C₂₂H₁₆N₂O₂: C, 77.6; H, 4.7; N, 8.2%. Found: C, 77.7, H, 4.7, N, 8.4%; ¹H-NMR: 8.12-8.09 (*m*, 2H, aromatic), 7.85-7.82 (*m*, 2H, aromatic), 7.60 (*d*, 2H, *J* = 7.8 Hz, aromatic), 7.37 (*s*, 2H, aromatic), 7.20 (*d*, 2H, *J* = 7.8 Hz, aromatic), 2.41 (*s*, 6H, -CH₃); ¹³C-NMR: 161.8, 151.4, 139.4, 136.5, 132.3, 131.7, 127.5, 126.7, 120.2, 111.4, 21.9(CH₃); MS (m/z , (relative abundance, %)): 340 (M⁺, 100).

Compound (8) 1,2-bis(benzoxazolyl)-4-methylbenzene: Yield: 77%; Anal. Calcd. for C₂₁H₁₄N₂O₂: C, 77.3; H, 4.3; N, 8.6%. Found: C, 76.9, H, 4.6, N, 8.9%; ¹H-NMR: 7.97 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.9 (*s*, 3 H, aromatic), 7.64 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.59 (*d*, 3H, *J* = 7.6 Hz, aromatic), 7.49 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.31 (*t*, 2H, *J* = 7.6 Hz, aromatic), 2.37 (*s*, 3H, CH₃); ¹³C-NMR: 162.7, 162.6, 151.2, 151.1, 142.2, 142.1, 132.1, 131.9, 131.2, 127.5, 125.5, 125.4, 124.9, 124.6, 124.5, 120.4, 120.2, 110.7, 110.6, 21.4(CH₃); MS (m/z , (relative abundance, %)): 326 (M⁺, 100).

Compound (9) 1,2-bis(3-methylbenzoxazolyl)-4-methylbenzene: Yield: 77%; Anal. Calcd. for C₂₃H₁₈N₂O₂: C, 78.0; H, 5.1; N, 7.9%. Found: C, 77.8, H, 5.3, N, 8.2%; ¹H-NMR: 8.33

(*d*, 1H, *J* = 7.6 Hz, aromatic), 7.75 (*s*, 2H, aromatic), 7.58 (*m*, 1H, *J* = 7.6 Hz, aromatic), 7.26 (*d*, 3H, *J* = 7.6 Hz, aromatic), 7.23 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.17 (*d*, 1H, *J* = 7.6 Hz, aromatic), 2.41 (*s*, 3H, CH₃), 2.37 (*s*, 6H, 2CH₃); ¹³C-NMR: 164.7, 163.6, 149.7, 149.6, 145.4, 141.6, 135.9, 131.6, 131.5, 131.1, 130.5, 128.3, 126.6, 122.0, 111.3, 20.9, 20.8; MS (m/z , (relative abundance, %)): 354 (M⁺, 100).

Compound (10) 1,2-bis(4-methylbenzoxazolyl)-4-methylbenzene: Yield: 77%; Anal. Calcd. for C₂₃H₁₈N₂O₂: C, 78.0; H, 5.1; N, 7.9%. Found: C, 78.3, H, 5.2, N, 8.4%; ¹H-NMR: 8.35 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.81-7.75 (*m*, 4H, aromatic), 7.58 (*s*, 1H, aromatic), 7.17 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.12 (*s*, 2H, aromatic), 2.43 (*s*, 3H, CH₃), 2.39 (*s*, 6H, 2CH₃); ¹³C-NMR: 162.7, 162.3, 149.8, 145.4, 141.6, 135.9, 133.4, 131.6, 131.1, 128.3, 126.6, 124.9, 123.4, 113.2, 21.1, 20.8, MS (m/z , (relative abundance, %)): 354 (M⁺, 100).

Compound (11) 1,2-bis(benzoxazolyl)-4-chlorobenzene: Yield: 77%; Anal. Calcd. for C₂₀H₁₁N₂O₂Cl: C, 69.2; H, 3.2; N, 8.1%. Found: C, 69.2, H, 3.2, N, 8.1%; ¹H-NMR: 8.16 (*d*, 1H *J* = 7.6 Hz, aromatic), 8.04 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.55-7.51 (*m*, 6H, aromatic), 7.33-7.29 (*m*, 2H, aromatic), 7.09 (*dd*, 1H *J* = 7.6 and 5.4 Hz, aromatic), ¹³C-NMR: 162.7, 162.6, 152.6(2C), 142.4(2C), 137.4(2C), 136.9, 136.2, 134.8, 131.5, 127.3(2C), 127.2(2C), 127.0(2C), 115.5(2C), MS (m/z , (relative abundance, %)): 347 (M⁺, 100).

Compound (12) 1,2-bis (3-methylbenzoxazolyl)-4-chlorobenzene: Yield: 77%; Anal. Calcd. for C₂₂H₁₅N₂O₂Cl: C, 70.4; H, 4.0; N, 7.5%. Found: C, 70.5, H, 4.2, N, 7.5%; ¹H-NMR: 8.01 (*s*, 1H, aromatic), 7.89 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.56 (*s*, 1H, aromatic), 7.26 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.21 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.09 (*d*, 1H, *J* = 7.6 Hz, aromatic), 2.43 (*s*, 6H, CH₃); ¹³C-NMR: 161.9, 161.8, 152.8(2C), 144.5, 144.3, 140.7, 137.4(2C), 136.3(2C), 134.6, 133.8, 131.1(2C), 129.5, 128.3(2C), 113.1(2C), 21.0 (2C), MS (m/z , (relative abundance, %)): 375 (M⁺, 100).

Compound (13) 1,2-bis(4-methylbenzoxazolyl)-4-chlorobenzene: Yield: 75%; Anal. Calcd. for C₂₂H₁₅N₂O₂Cl: C, 70.4; H, 4.0; N, 7.5%. Found: C, 70.3, H, 4.1, N, 7.5%; ¹H-NMR: 8.24 (*s*, 1H, aromatic), 7.92 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.63-7.57 (*m*, 4H, aromatic), 7.32 (*s*, 1H, aromatic), 7.11 (*d*, 1H, *J* = 7.6 Hz, aromatic),

2.52 (s, 6H, 2CH₃); ¹³C-NMR: 162.0, 161.9, 152.5, 152.4, 147.8, 147.7, 139.7, 139.52(C), 137.4(2C), 134.6, 133.7(2C), 130.5(2C), 129.5, 128.5(2C), 119.3(2C), 21.6(2C), MS (*m/z*, (relative abundance, %)): 375 (M⁺, 100).

Compound (14) 1,2-bis(benzoxazolyl)-4-bromobenzene: Yield: 77%; Anal. Calcd. for C₂₀H₁₁N₂O₂Br: C, 61.4; H, 2.8; N, 7.2%. Found: C, 61.4, H, 2.8, N, 7.2%; ¹H-NMR: 8.13 (*d*, 1H, *J*=7.6 Hz, aromatic), 8.02 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.40-7.32 (*m*, 6H, aromatic), 7.26-7.22 (*m*, 2H, aromatic), 7.15 (*dd*, 1H *J*= 7.6 and 5.4 Hz, aromatic); ¹³C-NMR: 162.5, 162.4, 152.6, 152.4, 142.6(2C), 137.2(2C), 136.6, 136.3, 134.6, 131.7, 127.4(2C), 127.1(2C), 127.0(2C), 115.6(2C), MS (*m/z*, (relative abundance, %)): 391 (M⁺, 100).

Compound (15) 1,2-bis(3-methylbenzoxazolyl)-4-bromobenzene: Yield: 77%; Anal. Calcd. for C₂₂H₁₅N₂O₂Br: C, 63.0; H, 3.6; N, 6.7%. Found: C, 62.7, H, 3.9, N, 7.0%; ¹H-NMR: 8.11 (*s*, 1H, aromatic), 7.75 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.63 (*s*, 2H, aromatic), 7.35 (*d*, 2H, *J*=7.6 Hz, aromatic), 7.23 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.15 (*d*, 2H, *J*=7.6 Hz, aromatic), 2.45 (*s*, 6H, 2CH₃); ¹³C-NMR: 162.4(2C), 149.7(2C), 144.1, 143.9, 137.4(2C), 136.9, 136.3(2C), 136.2, 134.8, 133.1(2C), 131.5, 128.3(2C), 113.1(2C), 21.1 (2C), MS (*m/z*, (relative abundance, %)): 419 (M⁺, 100).

Compound (16) 1,2-bis(4-methylbenzoxazolyl)-4-bromobenzene: Yield: 74%; Anal. Calcd. for C₂₂H₁₅N₂O₂Br: C, 63.0; H, 3.6; N, 6.7%. Found: C, 63.3, H, 3.4, N, 6.8%; ¹H-NMR: 8.15 (*s*, 1H), 7.82 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.59-7.55 (*m*, 4H, aromatic), 7.34 (*s*, 1H, aromatic), 7.15 (*d*, 1H, *J*=7.6 Hz, aromatic), 2.49 (*s*, 6H, 2CH₃); ¹³C-NMR: 162.6, 162.5, 152.5(2C), 147.1, 147.0, 139.5(2C), 137.4(2C), 136.9, 136.2, 134.8, 131.5, 130.5(2C), 128.8(2C), 119.3(2C), 21.8(2C), MS (*m/z*, (relative abundance, %)): 419 (M⁺, 100).

Compound (17) 1,2-bis(benzimidazolyl)benzene: Yield: 82%; Anal. Calcd. for C₂₀H₁₄N₄: C, 77.4; H, 4.5; N, 18.1%. Found: C, 77.6, H, 4.2, N, 18.4%; ¹H-NMR: 12.98 (*br*, 2H, -NH), 7.88 (*d*, 2H, *J*=7.5 Hz), 7.73-7.65 (*m*, 8H), 7.241 (*d*, 2H, *J*=7.8 Hz) ; ¹³C-NMR: 152.3, 145.5, 139.7, 134.1, 131.6, 130.9, 130.8, 130.3, 122.7, 115.8, MS (*m/z*, (relative abundance, %)): 310 (M⁺, 100).

Compound (18) 1,2-bis(3-methylbenzimidazolyl)benzene: Yield:

76%; Anal. Calcd. for C₂₂H₁₈N₄: C, 78.1; H, 5.3; N, 16.6%. Found: C, 78.6, H, 5.2, N, 17.1%; ¹H-NMR: 12.82 (*br*, 2H, -NH), 8.05 (*d*, 2H, *J*=7.8 Hz, aromatic), 7.63 (*s*, 2H, aromatic), 7.56 (*d*, 2H, *J*=7.8 Hz, aromatic), 7.35 (*d*, 2H, *J*=7.8 Hz, aromatic), 7.00 (*t*, 2H, *J*=7.8 Hz, aromatic), 2.37 (*s*, 6H, CH₃); ¹³C-NMR: 151.6, 139.0, 137.8, 132.2, 132.0, 130.4, 129.9, 115.9, 115.1, 22.0 (CH₃); MS (*m/z*, (relative abundance, %)): 338 (M⁺, 100).

Compound (19) 1,2-bis(3-chlorobenzimidazolyl)benzene: Yield: 71%; Anal. Calcd. for C₂₀H₁₂N₄Cl₂: C, 63.3; H, 3.2; N, 14.8%. Found: C, 64.1, H, 3.5, N, 15.2%; ¹H-NMR: 12.77 (*br*, 2H, -NH), 8.14 (*s*, 2H, aromatic), 7.61 (*br*, 4H, aromatic), 7.55 (*d*, 2H, *J*=7.8 Hz, aromatic), 7.12 (*d*, 2H, *J*=7.8 Hz, aromatic); ¹³C-NMR: 154.3, 141.4, 138.9, 132.1, 130.4, 130.3, 126.6, 122.4, 117.1, 115.8; MS (*m/z*, (relative abundance, %)): 378 (M⁺, 100).

Compound (20) 1,2-bis(benzimidazolyl)-4-methylbenzene: Yield: 72%; Anal. Calcd. for C₂₁H₁₆N₄: C, 77.8; H, 4.9; N, 17.3%. Found: C, 78.1, H, 5.2, N, 17.6%; ¹H-NMR: 12.67 (*br*, 2H, N-H), 7.97 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.92 (*s*, 1H, aromatic), 7.56-7.51 (*m*, 4H, aromatic), 7.47 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.18-7.15 (*m*, 4H, aromatic), 2.40 (*s*, 3H, CH₃); ¹³C-NMR: 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(CH₃); MS (*m/z*, (relative abundance, %)): 324 (M⁺, 100).

Compound (21) 1,2-bis(3-methylbenzimidazolyl)-4-methylbenzene: Yield: 72%; Anal. Calcd. for C₂₃H₂₀N₄: C, 78.4; H, 5.7; N, 15.9%. Found: C, 78.1, H, 5.2, N, 15.6%; ¹H-NMR: 12.60 (*br*, 2H, N-H), 7.96 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.91 (*s*, 1H, aromatic), 7.44-7.43 (*m*, 3H, aromatic), 7.35 (*s*, 2H, aromatic), 6.98 (*d*, 2H, *J*=7.6 Hz, aromatic), 2.42 (*s*, 3H, CH₃), 2.36 (*s*, 6H, CH₃); ¹³C-NMR: 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, 22.5(CH₃), 21.4(2CH₃); MS (*m/z*, (relative abundance, %)): 352 (M⁺, 100).

Compound (22) 1,2-bis(3-chlorobenzimidazolyl)-4-methylbenzene: Yield: 75%; Anal. Calcd. for C₂₁H₁₄N₄Cl₂: C, 64.1; H, 3.6; N, 14.2%. Found: C, 64.5, H, 3.9, N, 13.9%; ¹H-NMR: 8.09 (*d*, 1H, *J*=7.6 Hz, aromatic), 8.04 (*s*, 3H, aromatic), 7.62 (*d*, 2H, *J*=7.6 Hz, aromatic), 7.56-7.53 (*m*, 2H, aromatic), 7.36 (*d*, 1H, *J*=7.6 Hz, aromatic), 7.10 (*d*, 2H, *J*=7.6 Hz, aromatic), 2.38 (*s*, 3H, CH₃); ¹³C-NMR: 155.1, 155.0, 141.7, 141.6, 139.2,

139.1, 132.5, 132.1(C₈), 130.8, 130.3, 127.6, 126.3, 126.2, 122.2, 122.1, 117.0(C₁₆), 116.9, 115.7, 115.6, 21.4(CH₃); MS (*m/z*, (relative abundance, %)): 393 (M⁺, 100).

Compound (23) 1,2-bis(benzimidazolyl)-4-chlorobenzene: Yield: 70%; Anal. Calcd. for C₂₀H₁₃N₄Cl: C, 69.6; H, 3.8; N, 16.2%. Found: C, 69.2, H, 3.9, N, 16.6%; ¹H-NMR: 11.53 (*br*, 2H, N-H), 8.53 (*d*, 1H, *J* = 7.6 Hz, aromatic), 8.33 (*s*, 1H, aromatic), 7.82-7.73 (*m*, 8H, aromatic), 7.14 (*d*, 1H, *J* = 7.6 Hz, aromatic); ¹³C-NMR: 153.0, 150.4, 145.8(C₃), 145.7(2C), 141.9, 140.5, 137.4(2C), 134.7, 132.8, 129.7, 124.0(2C), 123.8(2C), 121.3(2C), 119.7(2C); MS (*m/z*, (relative abundance, %)): 345 (M⁺, 100).

Compound (24) 1,2-bis(3-methylbenzimidazolyl)-4-chlorobenzene: Yield: 75%; Anal. Calcd. for C₂₂H₁₇N₄Cl: C, 70.8; H, 4.6; N, 15.0%. Found: C, 71.3, H, 4.4, N, 15.6%; ¹H-NMR: 11.53 (*br*, 2H, N-H), 8.67 (*dd*, 1H, *J* = 7.6 and 5.4 Hz, aromatic), 7.34 (*d*, 2H, *J* = 7.6 Hz, aromatic), 8.41 (*s*, 1H, aromatic), 7.32-7.22 (*m*, 4H, aromatic), 7.14 (*d*, 1H, *J* = 7.6 Hz, aromatic), 2.51 (*s*, 6H, 2CH₃); ¹³C-NMR (: 153.0, 150.6, 140.8, 140.7, 140.5, 139.1, 137.4(2C), 135.1(2C), 134.7, 132.8, 129.7, 127.4(2C), 125.0(2C), 122.9(2C), 21.0(2C); MS (*m/z*, (relative abundance, %)): 373 (M⁺, 100).

Compound (25) 1,2-bis(3-chlorobenzimidazolyl)-4-chlorobenzene: Yield: 75%; Anal. Calcd. for C₂₀H₁₁N₄Cl₃: C, 57.8; H, 2.7; N, 13.5%. Found: C, 58.2, H, 2.9, N, 13.9%; ¹H-NMR: 11.46 (*br*, 2H, N-H), 9.42 (*s*, 1H, aromatic), 8.11 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.34-7.22 (*m*, 6H, aromatic), 7.13 (*d*, 1H, *J* = 7.6 Hz, aromatic); ¹³C-NMR: 153.1, 150.2, 141.3, 141.2, 141.0, 140.7, 140.5, 134.7, 134.5, 134.4, 132.8(2C), 130.9(2C), 130.7, 129.9(2C), 125.4(2C); MS (*m/z*, (relative abundance, %)): 415 (M⁺, 100).

Compound (26) 1,2-bis(benzimidazolyl)-4-bromobenzene: Yield: 75%; Anal. Calcd. for C₂₀H₁₃N₄Br: C, 61.7; H, 3.3; N, 14.4%. Found: C, 61.5, H, 3.7, N, 13.9%; ¹H-NMR: 11.64 (*br*, 2H, N-H), 9.39 (*s*, 1H, aromatic), 8.05 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.88-7.83 (*m*, 8H, aromatic), 7.15 (*d*, 1H, *J* = 7.6 Hz, aromatic); ¹³C-NMR: 152.8(2C), 145.8(2C), 141.9(2C), 137.4(2C), 136.6, 135.8, 134.8, 130.4, 124.0(2C), 123.8(2C), 121.2(2C), 119.7(2C); MS (*m/z*, (relative abundance, %)): 389 (M⁺, 100).

Compound (27) 1,2-bis(3-methylbenzimidazolyl)-4-

bromobenzene: Yield: 75%; Anal. Calcd. for C₂₂H₁₇N₄Br: C, 63.3; H, 4.1; N, 13.4%. Found: C, 63.7, H, 3.9, N, 13.1%; ¹H-NMR: 11.64 (*br*, 2H, N-H), 9.36 (*s*, 1H, aromatic), 8.03 (*d*, 1H, *J* = 7.6 Hz, aromatic), 7.86-7.78 (*m*, 6H, aromatic), 7.18 (*d*, 1H, *J* = 7.6 Hz, aromatic), 2.49 (*s*, 6H, 2CH₃); ¹³C-NMR: 153.0(2C), 139.0, 138.6, 135.8, 137.4(2C), 135.1(2C), 134.8, 136.6, 130.4, 127.4(2C), 125.0, 122.9(2C), 21.2(2C); MS (*m/z*, (relative abundance, %)): 417 (M⁺, 100).

Compound (28) 1,2-bis(3-chlorobenzimidazolyl)-4-bromobenzene: Yield: 75%; Anal. Calcd. for C₂₀H₁₁N₄BrCl₂: C, 52.4; H, 2.4; N, 12.2%. Found: C, 52.7, H, 2.9, N, 11.9%; ¹H-NMR: 11.55 (*br*, 2H, N-H), 9.44 (*s*, 1H, aromatic), 8.15 (*d*, 1H, *J* = 7.6 Hz, aromatic), 8.00 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.89 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.23 (*d*, 1H, *J* = 7.6 Hz, aromatic); ¹³C-NMR: 153.1(2C), 141.1, 141.0, 139.1, 139.0, 137.4(2C), 136.6, 135.8, 134.8, 131.8(2C), 130.4, 128.3, 125.3(2C); MS (*m/z*, (relative abundance, %)): 458 (M⁺, 100).

Compound (29) 2,6-bis(benzothiazolyl)pyridine: Yield: 70%; Anal. Calcd. for C₁₉H₁₁N₃S₂: C, 66.1; H, 3.2; N, 12.2%. Found: C, 66.5, H, 3.1, N, 12.5%; ¹H-NMR: 8.41 (*d*, 2H, *J* = 7.6 Hz, aromatic), 8.09 (*d*, 2H, *J* = 7.6 Hz, aromatic), 8.00-7.95 (*m*, 2H, aromatic), 7.51 (*t*, 2H, *J* = 7.6 Hz, aromatic), 7.42 (*t*, 2H, *J* = 7.6 Hz, aromatic); ¹³C-NMR: 168.18, 154.5, 151.5, 138.4, 136.6, 126.6, 126.2, 124.0, 122.2, 122.1; MS (*m/z*, (relative abundance, %)): 345 (M⁺, 100).

Compound (30) 2,6-bis(benzoxazolyl)pyridine: Yield: 73 %; Anal. Calcd. for C₁₉H₁₁N₃O₂: C, 72.8; H, 3.5; N, 13.4%. Found: C, 73.2, H, 3.3, N, 13.0%; ¹H-NMR: 8.49 (*d*, 2H, *J* = 7.6 Hz, aromatic), 8.08 (*t*, 1H, *J* = 7.6 Hz, aromatic), 7.84 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.70 (*d*, 2H, *J* = 7.6 Hz, aromatic), 7.44-7.37 (*m*, 4H, aromatic); ¹³C-NMR: 160.9, 151.5, 146.9, 141.9, 138.5, 126.6, 125.6, 125.3, 121.0, 111.8; MS (*m/z*, (relative abundance, %)): 313 (M⁺, 100).

Compound (31) 2,6-bis(4-methylbenzoxazolyl)pyridine: Yield: 71%; Anal. Calcd. for C₂₁H₁₅N₃O₂: C, 73.9; H, 4.4; N, 12.3%. Found: C, 73.3, H, 4.7, N, 12.1%; ¹H-NMR: 8.40 (*d*, 2H, *J* = 7.8 Hz, aromatic), 7.98 (*t*, 1H, *J* = 7.6 Hz, aromatic), 7.56-7.51 (*m*, 4H, aromatic), 7.17 (*d*, 2H, *J* = 7.8 Hz, aromatic), 2.43 (*s*, 6H, CH₃); ¹³C-NMR: 161.1, 153.7, 149.3, 143.2, 139.6, 131.5, 128.3, 122.0, 121.2, 109.2, 20.9(CH₃); MS (*m/z*, (relative abundance, %)): 341 (M⁺, 100).

Compound (32) 2,6-bis(3-

methylbenzoxazolyl)pyridine: Yield: 68%; Anal. Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.9; H, 4.4; N, 12.3%. Found: C, 73.6, H, 4.2, N, 12.5%; 1H -NMR: 8.74 (*t*, 1H, $J = 7.8$ Hz, aromatic), 8.21 (*d*, 2H, $J = 7.6$ Hz, aromatic), 7.63-7.59 (*m*, 4H, aromatic), 7.34(*s*, 2H, aromatic), 2.41 (*s*, 6H, CH_3); ^{13}C -NMR: 161.1, 153.7, 151.0, 143.2, 139.6, 133.4, 124.9, 121.3, 121.2, 111.0, 21.1(CH_3); MS (*m/z*, (relative abundance, %)): 341 (M^+ , 100).

Compound (33) 2,6-bis(benzimidazolyl)pyridine: Yield: 78%; Anal. Calcd. for $C_{19}H_{13}N_5$: C, 73.2; H, 4.2; N, 22.5%. Found: C, 73.3, H, 4.7, N, 22.1%; 1H -NMR: 11.67 (*br*, 2H, N-H), 9.15 (*t*, 1H, $J = 7.8$ Hz, aromatic), 8.20 (*d*, 1H, $J = 7.6$ Hz, aromatic), 7.51 (*d*, 4H, aromatic), 7.39 (*t*, 4H, $J = 7.8$ Hz, aromatic); ^{13}C -NMR (400MHz, DMSO-*d*₆, δ / ppm): 153.6, 151.0, 142.1, 142.0, 138.8, 123.5, 123.4, 121.4, 116.4, 116.2; MS (*m/z*, (relative abundance, %)): 311 (M^+ , 100).

Compound (34) 2,6-bis(3-methylbenzimidazolyl)pyridine: Yield: 76 %; Anal. Calcd. for $C_{21}H_{17}N_5$: C, 74.3; H, 5.0; N, 20.7%. Found: C, 74.7, H, 4.7, N, 20.3%; 1H -NMR: 11.45 (*br*, 2H, N-H) 9.13 (*t*, 1H, $J = 7.8$ Hz, aromatic), 8.19 (*d*, 2H, $J = 7.6$ Hz, aromatic), 7.26-7.11 (*m*, 6H, aromatic), 2.43 (*s*, 6H, CH_3); ^{13}C -NMR: 154.1, 151.3, 139.7, 138.8, 138.6, 135.6, 127.0, 122.6, 121.4, 118.4, 20.8(CH_3); MS (*m/z*, (relative abundance, %)): 339 (M^+ , 100).

Compound (35) 2,6-bis(3-chlorobenzimidazolyl)pyridine: Yield: 73%; Anal. Calcd. for $C_{19}H_{11}N_5Cl_2$: C, 60.0; H, 2.9; N, 18.4%. Found: C, 59.7, H, 3.1, N, 18.2%; 1H -NMR: 11.57 (*br*, 2H, N-H) 9.40 (*t*, 1H, $J = 7.8$ Hz, aromatic), 8.21 (*d*, 2H, $J = 7.6$ Hz, aromatic), 7.51 (*d*, 2H, $J = 7.6$ Hz, aromatic), 7.44 (*d*, 2H, $J = 7.8$ Hz, aromatic), 7.26 (*d*, 2H, $J = 7.8$ Hz, aromatic); ^{13}C -NMR: 153.7, 150.8, 139.4, 138.6, 138.0, 127.5, 126.1, 121.6, 121.4(C_9), 119.4; MS (*m/z*, (relative abundance, %)): 380 (M^+ , 100).

2.1.2. Vanadium (III) complexes 36-70.

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 over night 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 and elemental analysis. Due to their paramagnetic nature, their NMR spectra are not

so informative.

Complex (36) 1,2-bis(benzothiazolyl)benzenevanadium(III) chloride: Yield: 75%; Anal. Calcd. for $C_{20}H_{12}N_2S_2VCl_3$: C, 47.9; H, 2.4; N, 5.6%. Found: C, 48.3, H, 2.0, N, 5.9%; MS (*m/z*, (relative abundance, %)): 501(M^+ , 10), 465, 429, 394, 344.

Complex (37) 1,2-bis(benzothiazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 75%; Anal. Calcd. for $C_{21}H_{14}N_2S_2VCl_3$: C, 48.3; H, 2.7; N, 5.4%. Found: C, 48.0, H, 2.9, N, 5.8%; MS (*m/z*, (relative abundance, %)): 515 (M^+ , 20), 478, 464, 443, 407, 392, 358.

Complex (38) 1,2-bis(benzothiazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 71%; Anal. Calcd. for $C_{20}H_{12}N_2S_2VCl_3$: C, 44.8; H, 2.2; N, 5.2%. Found: C, 44.3, H, 2.6, N, 5.8%; MS (*m/z*, (relative abundance, %)): 536 (M^+ , 20), 500, 465, 429, 379.

Complex (39) 1,2-bis(benzothiazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 67%; Anal. Calcd. for $C_{20}H_{12}N_2S_2BrVCl_3$: C, 41.4; H, 2.1; N, 4.8%. Found: C, 41.0, H, 1.9, N, 4.6%; MS (*m/z*, (relative abundance, %)): 580 (M^+ , 10), 544, 509, 500, 473, 423.

Complex (40) 1,2-bis(benzoxazolyl)benzenevanadium(III) chloride: Yield: 77%; Anal. Calcd. for $C_{20}H_{12}N_2O_2VCl_3$: C, 51.2; H, 2.6; N, 6.0%. Found: C, 50.8, H, 2.9, N, 5.8%; MS (*m/z*, (relative abundance, %)): 469 (M^+ , 10), 433, 398, 361, 312.

Complex (41) 1,2-bis(3-methylbenzoxazolyl)benzenevanadium(III) chloride: Yield: 73%; Anal. Calcd. for $C_{22}H_{16}N_2O_2VCl_3$: C, 53.1; H, 3.2; N, 5.6%. Found: C, 53.7, H, 3.0, N, 5.3%; MS (*m/z*, (relative abundance, %)): 497(M^+ , 10), 431, 426, 390, 340.

Complex (42) 1,2-bis(4-methylbenzoxazolyl)benzenevanadium(III) chloride: Yield: 73%; Anal. Calcd. for $C_{22}H_{16}N_2O_2VCl_3$: C, 53.1; H, 3.2; N, 5.6%. Found: C, 53.4, H, 2.9, N, 5.5%; MS (*m/z*, (relative abundance, %)): 497(M^+ , 10), 432, 426, 390, 340.

Complex (43) 1,2-bis(benzoxazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 72%; Anal. Calcd. for $C_{21}H_{14}N_2O_2VCl_3$: C, 52.2; H, 2.9; N, 5.8%. Found: C, 52.6, H, 3.2, N, 6.2%; MS (*m/z*, (relative abundance, %)): 483 (M^+ , 10), 447, 411, 326.

Complex (44) 1,2-bis(3-methyl-benzoxazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 78%; Anal. Calcd. for $C_{23}H_{18}N_2O_2VCl_3$: C, 52.2; H, 2.9; N, 5.8%. Found: C, 52.6, H, 3.2, N, 6.2%; MS (m/z, (relative abundance, %)): 483 (M⁺, 25), 475, 440, 354.

Complex (45) 1,2-bis(4-methyl-benzoxazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 72%; Anal. Calcd. for $C_{23}H_{18}N_2O_2VCl_3$: C, 54.0; H, 3.5; N, 5.5%. Found: C, 54.6, H, 3.2, N, 5.4%; MS (m/z, (relative abundance, %)): 511 (M⁺, 20), 475, 440, 354.

Complex (46) 1,2-bis(benzoxazolyl)-4-chlorobenzenevanadium(III) chloride: Yield: 67%; Anal. Calcd. for $C_{20}H_{11}N_2O_2ClVCl_3$: C, 47.6; H, 2.2; N, 5.6%. Found: C, 47.4, H, 2.4, N, 5.2%; MS (m/z, (relative abundance, %)): 504 (M⁺, 10), 468, 432, 397, 347.

Complex (47) 1,2-bis (3-methyl-benzoxazolyl)-4-chlorobenzenevanadium(III) chloride: Yield: 76%; Anal. Calcd. for $C_{22}H_{15}N_2O_2ClVCl_3$: C, 49.6; H, 2.8; N, 5.3%. Found: C, 49.3, H, 2.9, N, 5.1%; MS (m/z, (relative abundance, %)): 532 (M⁺, 25), 496, 460, 425, 375.

Complex (48) 1,2-bis(4-methyl-benzoxazolyl)-4-chlorobenzenevanadium(III) chloride: Yield: 75%; Anal. Calcd. for $C_{23}H_{18}N_2O_2VCl_3$: C, 49.6; H, 2.8; N, 5.3%. Found: C, 49.5, H, 3.1, N, 5.6%; MS (m/z, (relative abundance, %)): 532 (M⁺, 20), 517, 481, 461, 425, 375.

Complex (49) 1,2-bis(benzoxazolyl)-4-bromobenzenevanadium(III) chloride: Yield: 73%; Anal. Calcd. for $C_{20}H_{11}N_2O_2BrVCl_3$: C, 43.8; H, 2.0; N, 5.1%. Found: C, 43.6, H, 2.2, N, 5.4%; MS (m/z, (relative abundance, %)): 548 (M⁺, 10), 512, 477, 432, 397, 391

Complex (50) 1,2-bis(3-methylbenzoxazolyl)-4-bromobenzenevanadium(III) chloride: Yield: 78%; Anal. Calcd. for $C_{22}H_{15}N_2O_2BrVCl_3$: C, 45.8; H, 2.6; N, 4.9%. Found: C, 45.6, H, 2.5, N, 4.6%; MS (m/z, (relative abundance, %)): 576 (M⁺, 25), 540, 505, 496, 460, 425, 419.

Complex (51) 1,2-bis(4-methylbenzoxazolyl)-4-bromobenzenevanadium(III) chloride: Yield: 73%; Anal. Calcd. for $C_{22}H_{15}N_2O_2BrVCl_3$: C, 45.8; H, 2.6; N, 4.9%. Found: C, 45.9, H, 2.7, N, 4.8%; MS (m/z, (relative abundance, %)): 576 (M⁺, 20), 540, 505, 496, 469, 419.

Complex (52) 1,2-

bis(benzimidazolyl)benzenevanadium(III) chloride: Yield: 73%; Anal. Calcd. for $C_{20}H_{14}N_4VCl_3$: C, 51.4; H, 3.0; N, 12.20%. Found: C, 51.8, H, 3.5, N, 12.3%; MS (m/z, (relative abundance, %)): 467 (M⁺, 10), 431, 395, 359, 310.

Complex (53) 1,2-bis(3-methylbenzimidazolyl)benzenevanadium(III) chloride: Yield: 70%; Anal. Calcd. for $C_{22}H_{18}N_4VCl_3$: C, 53.3; H, 3.6; N, 11.3%. Found: C, 52.8, H, 3.4, N, 11.2%; MS (m/z, (relative abundance, %)): 495 (M⁺, 20), 459, 424, 388, 338.

Complex (54) 1,2-bis(3-chlorobenzimidazolyl)benzenevanadium(III) chloride: Yield: 74%; Anal. Calcd. for $C_{20}H_{12}N_4Cl_2VCl_3$: C, 44.38; H, 2.2; N, 10.4%. Found: C, 45.3, H, 1.9, N, 10.8%; MS (m/z, (relative abundance, %)): 535 (M⁺, 10), 499, 463, 428, 378.

Complex (55) 1,2-bis(benzimidazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 75%; Anal. Calcd. for $C_{21}H_{16}N_4VCl_3$: C, 52.4; H, 3.3; N, 11.6%. Found: C, 52.7, H, 3.2, N, 11.4%; MS (m/z, (relative abundance, %)): 481 (M⁺, 20), 466, 445, 408, 374, 324.

Complex (56) 1,2-bis(3-methylbenzimidazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 72%; Anal. Calcd. for $C_{23}H_{16}N_4VCl_3$: C, 49.5; H, 3.9; N, 11.0%. Found: C, 48.8, H, 3.9, N, 10.9%; MS (m/z, (relative abundance, %)): 511 (M⁺, 20), 468, 439, 403, 352.

Complex (57) 1,2-bis (3-chlorobenzimidazolyl)-4-methylbenzenevanadium(III) chloride: Yield: 78%; Anal. Calcd. for $C_{21}H_{14}N_4Cl_2VCl_3$: C, 45.8; H, 2.5; N, 10.2%. Found: C, 45.7, H, 2.8, N, 9.9%; MS (m/z, (relative abundance, %)): 550 (M⁺, 20), 535, 514, 508, 478, 428, 393.

Complex (58) 1,2-bis(benzimidazolyl)-4-chlorobenzenevanadium(III) chloride: Yield: 75%; Anal. Calcd. for $C_{20}H_{13}N_4ClVCl_3$: C, 47.8; H, 2.6; N, 11.2%. Found: C, 47.7, H, 2.8, N, 11.4%; MS (m/z, (relative abundance, %)): 502 (M⁺, 20), 466, 445, 408, 374, 324.

Complex (59) 1,2-bis(3-methylbenzimidazolyl)-4-chlorobenzenevanadium(III) chloride: Yield: 72%; Anal. Calcd. for $C_{22}H_{17}N_4ClVCl_3$: C, 49.8; H, 3.2; N, 10.6%. Found: C, 49.5, H, 3.1, N, 10.9%; MS (m/z, (relative abundance, %)): 530 (M⁺, 20), 468, 439, 403, 352.

Complex (60) 1,2-bis(3-chlorobenzimidazolyl)-4-chlorobenzenevanadium(III) chloride: Yield:

78%; Anal. Calcd. for $C_{20}H_{11}N_4Cl_3VCl_3$: C, 42.0; H, 1.9; N, 9.8%. Found: C, 42.4, H, 2.2, N, 9.4%; MS (m/z , (relative abundance, %)): 572 (M^+ , 20), 535, 514, 508, 478, 428, 393.

Complex (61) 1,2-bis(benzimidazolyl)-4-bromobenzenevanadium(III) chloride: Yield: 75%; Anal. Calcd. for $C_{20}H_{13}N_4BrVCl_3$: C, 44.0; H, 2.4; N, 10.3%. Found: C, 44.3, H, 2.7, N, 10.6%; MS (m/z , (relative abundance, %)): 546 (M^+ , 20), 466, 445, 408, 374, 324.

Complex (62) 1,2-bis(3-methylbenzimidazolyl)-4-bromobenzenevanadium(III) chloride: Yield: 72%; Anal. Calcd. for $C_{22}H_{17}N_4BrVCl_3$: C, 46.0; H, 3.0; N, 9.8%. Found: C, 46.3, H, 2.8, N, 9.6%; MS (m/z , (relative abundance, %)): 574 (M^+ , 20), 468, 439, 403, 352.

Complex (63) 1,2-bis(3-chlorobenzimidazolyl)-4-bromobenzenevanadium(III) chloride: Yield: 71%; Anal. Calcd. for $C_{20}H_{11}N_4BrCl_2VCl_3$: C, 39.0; H, 1.8; N, 9.2%. Found: C, 39.3, H, 1.8, N, 9.5%; MS (m/z , (relative abundance, %)): 615 (M^+ , 20), 535, 514, 508, 478, 428, 393.

Complex (64) 2,6-bis(benzothiazolyl)pyridinevanadium(III) chloride: Yield: 77%; Anal. Calcd. for $C_{19}H_{11}N_3S_2VCl_3$: C, 45.4; H, 2.2; N, 8.4%. Found: C, 45.9, H, 2.6, N, 8.1%; MS (m/z , (relative abundance, %)): 501 (M^+ , 20), 465, 429, 393, 345.

Complex (65) 2,6-bis(benzoxazolyl)pyridinevanadium(III) chloride: Yield: 73%; Anal. Calcd. for $C_{19}H_{11}N_3O_2VCl_3$: C, 48.5; H, 2.3; N, 8.9%. Found: C, 48.3, H, 2.1, N, 9.3%; MS (m/z , (relative abundance, %)): 470 (M^+ , 20), 398, 362, 325, 313.

Complex (66) 2,6-bis(4-methylbenzoxazolyl)pyridinevanadium(III) chloride: Yield: 82%; Anal. Calcd. for $C_{21}H_{15}N_3O_2VCl_3$: C, 50.6; H, 3.0; N, 8.4%. Found: C, 50.1, H, 3.3, N, 8.7%; MS (m/z , (relative abundance, %)): 498 (M^+ , 25), 462, 432, 390, 341.

Complex (67) 2,6-bis(3-methylbenzoxazolyl)pyridinevanadium(III) chloride: Yield: 69%; Anal. Calcd. for $C_{21}H_{15}N_3O_2VCl_3$: C, 50.6; H, 3.0; N, 8.4%. Found: C, 50.1, H, 3.3, N, 8.7%; MS (m/z , (relative abundance, %)): 498 (M^+ , 20), 462, 390, 341.

Complex (68) 2,6-bis(benzimidazolyl)pyridinevanadium(III) chloride: Yield: 70%; Anal. Calcd. for $C_{19}H_{13}N_5VCl_3$: C, 48.7;

H, 2.8; N, 15.0%. Found: C, 49.1, H, 3.3, N, 14.7%; MS (m/z , (relative abundance, %)): 468 (M^+ , 20), 432, 397, 361, 311.

Complex (69) 2,6-bis(3-methylbenzimidazolyl)pyridinevanadium(III) chloride: Yield: 66%; Anal. Calcd. for $C_{21}H_{17}N_5VCl_3$: C, 50.8; H, 3.4; N, 14.1%. Found: C, 50.5, H, 3.3, N, 14.4%; MS (m/z , (relative abundance, %)): 496 (M^+ , 20), 460, 424, 389, 339.

Complex (70) 2,6-bis(3-chlorobenzimidazolyl)pyridinevanadium(III) chloride: Yield: 73%; Anal. Calcd. for $C_{19}H_{11}N_5Cl_2VCl_3$: C, 42.5; H, 2.1; N, 13.0%. Found: C, 42.8.1, H, 2.4, N, 13.5%; MS (m/z , (relative abundance, %)): 537 (M^+ , 25), 501, 466, 430, 393, 380.

2.2. Polymerization of ethylene

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

3. RESULTS AND DISCUSSION

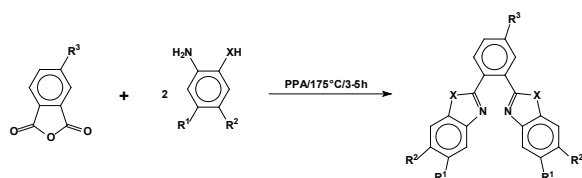
3.1. General synthesis of ligand precursors

The condensation reaction of a dicarboxylic acid or an acid anhydride with diamine compound in preheated polyphosphoric acid is a well-established procedure for the preparation of the imidazole based ligand precursors [47, 48], in high yields (Scheme 1 and 2). The ligand precursors were characterized by NMR, mass spectroscopy and elemental analysis.

3.2. Synthesis of vanadium complexes 36-70.

The complexes were synthesized according to Scheme 2. The vanadium complexes were prepared by dissolving the ligand and V (III) chloride in an appropriate solvent. The reaction resulted in an immediate color change and the complexes could be isolated in high yields (65- 82 %). The complexes were characterized by elemental analysis and mass

spectrometry. All attempts to obtain single crystals were failed.



Compound	X	R ¹	R ²	R ³
1	S	H	H	H
2	S	H	H	CH ₃
3	S	H	H	Cl
4	S	H	H	Br
5	O	H	H	H
6	O	CH ₃	H	H
7	O	H	CH ₃	H
8	O	H	H	CH ₃
9	O	CH ₃	H	CH ₃
10	O	H	CH ₃	CH ₃
11	O	H	H	Cl
12	O	CH ₃	H	Cl
13	O	H	CH ₃	Cl
14	O	H	H	Br
15	O	CH ₃	H	Br
16	O	H	CH ₃	Br
17	NH	H	H	H
18	NH	CH ₃	H	H
19	NH	Cl	H	H
20	NH	H	H	CH ₃
21	NH	CH ₃	H	CH ₃
22	NH	Cl	H	CH ₃
23	NH	H	H	Cl
24	NH	CH ₃	H	Cl
25	NH	Cl	H	Cl
26	NH	H	H	Br
27	NH	CH ₃	H	Br
28	NH	Cl	H	Br

Scheme 1. Synthesis of ligand precursors 1-28.



Compound	X	R ¹	R ²
29	S	H	H
30	O	H	H
31	O	CH ₃	H
32	O	H	CH ₃
33	NH	H	H
34	NH	CH ₃	H
35	NH	Cl	H

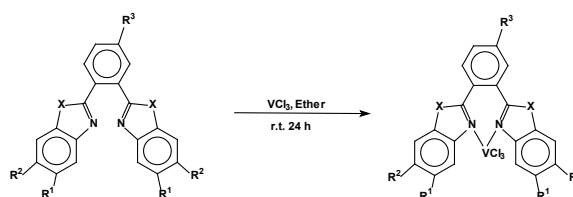
Scheme 2. Synthesis of ligand precursors 29-35.

3.3. Characterization

3.3.1. NMR spectroscopy

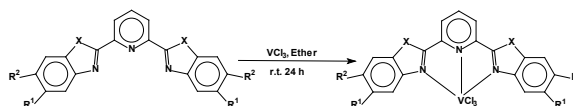
The ligand precursors were characterized by NMR spectroscopy using DMSO as solvent. For example, the ¹H NMR spectrum of compound 17 (see Figure 1) shows four signals, the broad signal at $\delta = 12.98$ ppm assigned to NH proton, the signal at $\delta =$

7.88 ppm [t, 2H, $J_{H,H} = 7.5$ Hz] assigned to aromatic protons H1, the signal at $\delta = 7.73$ -7.65 ppm [m, 8H] corresponds to the protons H3, H4, H5 and H6. The signal at $\delta = 7.24$ ppm [d, 2H, $J_{H,H} = 7.8$ Hz] assigned to the aromatic protons H2



Complex	X	R ¹	R ²	R ³
36	S	H	H	H
37	S	H	H	CH ₃
38	S	H	H	Cl
39	S	H	H	Br
40	O	H	H	H
41	O	CH ₃	H	H
42	O	H	CH ₃	H
43	O	H	H	CH ₃
44	O	CH ₃	H	CH ₃
45	O	H	CH ₃	CH ₃
46	O	H	H	Cl
47	O	CH ₃	H	Cl
48	O	H	CH ₃	Cl
49	O	H	H	Br
50	O	CH ₃	H	Br
51	O	H	CH ₃	Br
52	NH	H	H	H
53	NH	CH ₃	H	H
54	NH	Cl	H	H
55	NH	H	H	CH ₃
56	NH	CH ₃	H	CH ₃
57	NH	Cl	H	CH ₃
58	NH	H	H	Cl
59	NH	CH ₃	H	Cl
60	NH	Cl	H	Cl
61	NH	H	H	Br
62	NH	CH ₃	H	Br
63	NH	Cl	H	Br

Scheme 3. Synthesis of the coordination compounds 36-63.



Complex	X	R ¹	R ²
64	S	H	H
65	O	H	H
66	O	CH ₃	H
67	O	H	CH ₃
68	NH	H	H
69	NH	CH ₃	H
70	NH	Cl	H

Scheme 4. Synthesis of the coordination compounds 64-70.

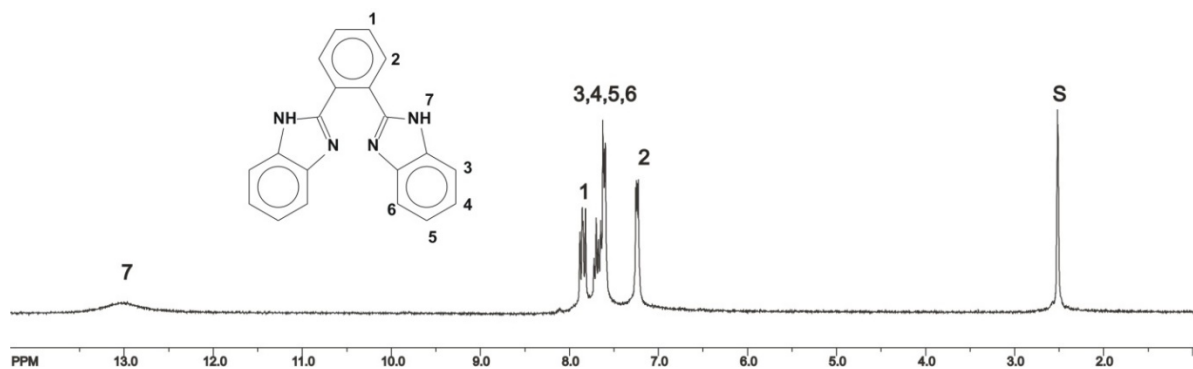


Figure 1. ^1H NMR spectrum of compound 17.

The ^{13}C NMR spectrum of compound 5 (Figure 2) shows ten signals. The two signals downfield at $\delta = 169.3$ ppm and at $\delta = 152.4$ ppm correspond to the carbon atoms 4 and 10 respectively, each of the eight

signals at $\delta = 139.7, 134.1, 131.6, 130.9, 130.8, 130.3, 122.7$ and 115.8 ppm corresponds to two carbon atoms (5, 3, 7, 8, 9, 6, 1 and 2, respectively) of the aromatic rings.

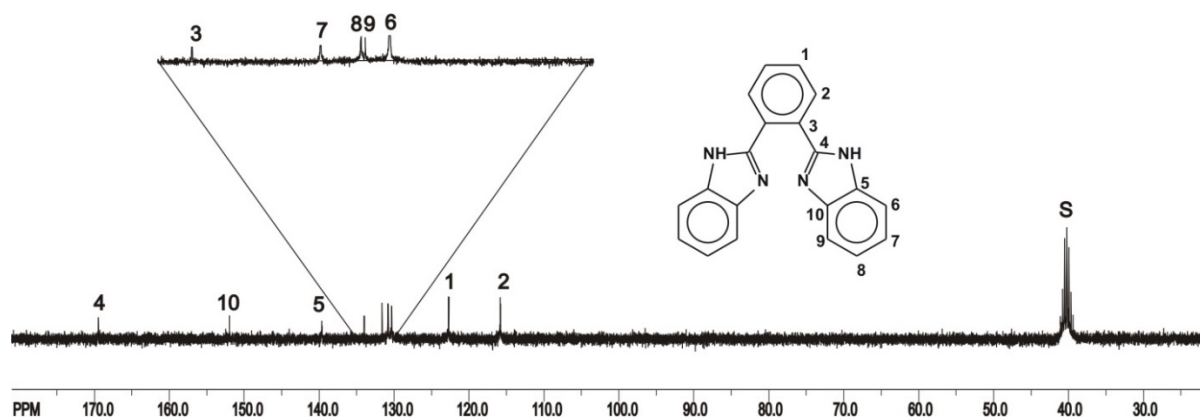


Figure 2. ^{13}C NMR spectrum of compound 17.

3.3.2. Mass spectrometry

The ligand precursors were also characterized by their mass spectra. The mass spectrum of compound 17 (Figure 3), shows the molecular ion peak $m/z = 310$

and $m/z = 194$ ($\text{M}^+ - \text{C}_7\text{H}_5\text{N}_2$). The ion with the mass $m/z = 102$ correspond to the ion ($\text{C}_7\text{H}_4\text{N}$). The data for the other compounds are given in the experimental section.

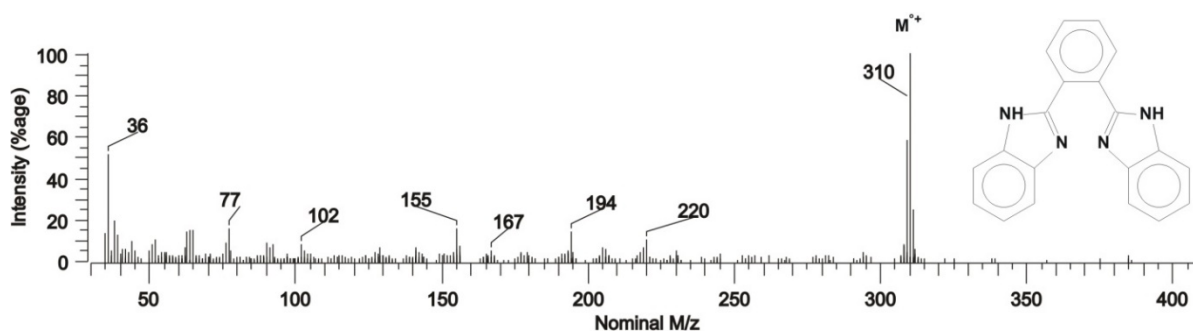


Figure 3. Mass spectrum of compound 17.

The vanadium complexes were also characterized by their mass spectra. The mass spectrum

of complex **52** (Figure 4), shows the molecular ion peak $m/z = 467$ and $m/z = 431$ ($M^{+} - Cl$). The ion with

the mass $m/z = 395$ correspond ($M^{+} - 2Cl$), at $m/z = 310$ the free ligand appeared.

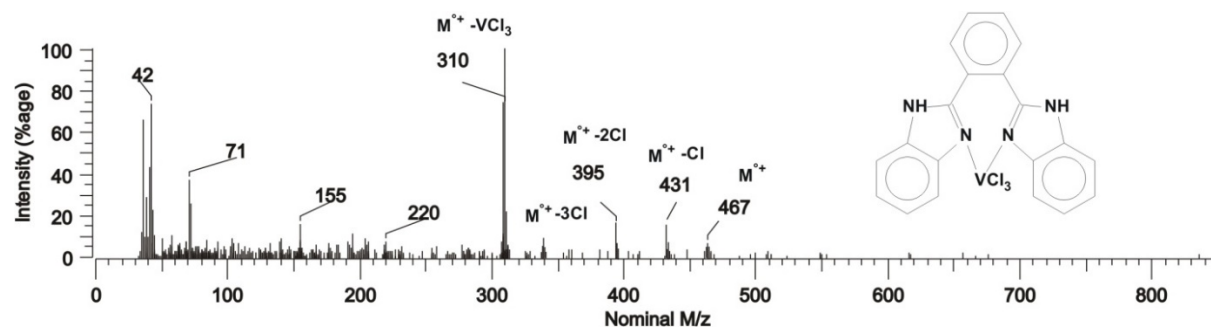


Figure 4. Mass spectrum of complex **52**.

3.4 Polymerization experiments and polymer analysis

All coordination compounds were activated with MAO according to the mechanism proposed for the activation of metallocene [49, 50], and 2, 6-bis(imino) pyridine iron (II) [51], catalyst precursors.

The complexes of Vanadium with ligands derived from bis (benzimidazolyl), bis (benzoxazolyl) and bis (benzothiazolyl) compounds showed variable activities for ethylene polymerization. The activities are greatly influenced by the heteroatoms in addition to the ligand environment (see Table 1). The activities of the vanadium complexes at higher temperatures (50°C) are in contrast to the typical behavior of vanadium catalysts which invariably require temperatures below room temperatures to maintain their productivity [52]. Figure 5 shows the catalytic activity of the vanadium complexes derived from 1, 2-bis(benzothiazolyl, benzoxazolyl and benzoimidazolyl)benzene. Their catalytic activities were greatly influenced by the heteroatom and substituent position and type [37-39].

The activities of vanadium complexes derived from the ligands 1,2-bis(benzothiazolyl **36**, benzoxazolyl **40**, and benzimidazolyl **52**) follow the order **36** > **52** > **40**. The differences in the catalytic activities can be accounted for by the heteroatom effect (S, N, and O). The catalytic activities of complexes **40-42** derived from 1,2-bis-(benzoxazolyl)benzene were affected by both substitution pattern and type. The introduction of methyl substituents in *meta* position to the imino nitrogen atoms increased the activities of the complex **41** compared to the unsubstituted complex **40**. On the other hand a methyl group *para* to the imino nitrogen atom decreased the activities of complex **42** (see Figure 5). This could be due to a more favorable

steric interaction of the cationic catalyst with the bulky anionic MAO counterion. The *meta* methyl substituted benzimidazole complex **53** shows lower activity than the *meta* methyl substituted benzoxazolyl complex **41**[37-39]. This is indicative for the fact that the amount of electronegativity of the hetero atoms has more influence on the catalyst activity than the position of the substituent at the six membered rings. The heteroatom reduces the electron density at the active center and thus it favors the coordination of the olefin. The activities of 1,2-bis(benzothiazolyl, benzoxazolyl, benzimidazolyl)-4-methylbenzene vanadium complexes showed the following order 1,2-bis benzothiazolyl **37** > 1,2-bisbenzimidazolyl **55** > 1,2-bisbenzoxazolyl **43** (Figure 6). 1,2-bis (benzimidazolyl)-4-methylbenzene vanadium complexes generally showed the following activity order **55** > **56** > **57** (Figure 8) where the unsubstituted complexes **55** showed the highest activity, and the chloro substituted complex **57** showed the least activity. Vanadium complexes derived from the ligand systems 1,2-bis(benzothiazolyl, benzoxazolyl, benzimidazolyl)-4-chlorobenzene (Figure 7) and 1,2-bis(benzothiazolyl, benzoxazolyl, benzimidazolyl)-4-bromobenzene (figure 8) behave in a manner similar to complexes derived from the ligand 1,2-bis(benzimidazolyl)-4-methylbenzene.

The activities of vanadium complexes derived from the ligands 2,6-bis(benzothiazolyl, benzoxazolyl and benzimidazolyl)pyridine **64-70** (Figure 9), showed the following activity order 2,6-bis(benzothiazolyl)pyridine complex **64** > 2,6-bis(benzimidazolyl)pyridine complex **68** > 2, 6-bis(benzoxazolyl)pyridine complex **65**. On the other hand the methyl substituted 2,6-bis (benzoxazolyl)pyridine complex **66** was found to be

the more active catalyst in this series and the chloro substituted 2, 6-bis(benzimidazolyl)pyridine complex **70** showed the least activity.

Table 1. Polymerization activities of complexes **36 - 70**.

Complex no.	Activity [kg PE/ mol cat·h]	T (°C)	Mw [g/mol]	PD
36	54	20	1.3×10 ⁶	3.0
36	213	30	1.4×10 ⁶	3.0
36	324	40	5.6×10 ⁵	6.3
36	442	50	2.1×10 ⁶	4.5
36	178	65	7.2×10 ⁵	6.5
37	241	50	1.6×10 ⁶	16.6
38	311	50	1.2×10 ⁶	5.3
39	255	50	9.4×10 ⁵	4.1
40	261	50	n.d.	n.d.
41	391	50	1.6×10 ⁶	5.6
42	167	50	1.8×10 ⁶	4.4
43	27	50	n.d.	n.d.
44	82	50	4.5×10 ⁵	3.3
45	17	50	n.d.	n.d.
46	97	50	n.d.	n.d.
47	176	50	7.5×10 ⁵	3.9
48	77	50	n.d.	n.d.
49	80	50	n.d.	n.d.
50	143	50	4.8×10 ⁵	7.2
51	57	50	n.d.	n.d.
52	405	50	4.1×10 ⁵	6.7
53	308	50	6.7×10 ⁵	3.6
54	165	50	1.3×10 ⁶	9.3
55	106	50	6.8×10 ⁵	7.9
56	104	50	1.1×10 ⁶	2.1
57	70	50	n.d.	n.d.
58	211	50	9.5×10 ⁵	3.1
59	162	50	1.5×10 ⁶	4.7
60	88	50	n.d.	n.d.
61	193	50	1.4×10 ⁶	6.2
62	144	50	1.1×10 ⁶	4.6
63	71	50	n.d.	n.d.
64	284	50	1.7×10 ⁶	6.0
65	138	50	1.5×10 ⁶	10.2
66	193	20	1.8×10 ⁶	2.6
66	244	30	9.7×10 ⁵	1.8
66	283	40	1.7×10 ⁶	2.3
66	315	50	2.7×10 ⁶	1.6
66	237	60	1.2×10 ⁶	2.1
67	102	50	1.2×10 ⁶	1.4
68	243	50	1.4×10 ⁶	2.4
69	271	50	8.3×10 ⁵	4.1
70	81	50	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 effect of bridging unit was also studied applying the catalyst system derived from 1,2-bis(benzothiazolyl, benzoxazolyl and benzimidazolyl)-

4-methylbenzene (**37**, **43**, **55**), 1,2-bis(benzothiazolyl, benzoxazolyl and benzimidazolyl)-4-chlorobenzene (**38**, **46**, **58**), 1,2-bis(benzothiazolyl, benzoxazolyl and

benzimidazolyl)-4-bromobenzene (**39**, **49**, **61**) (see Figure 10). They follow the general activity order
benzothiazolyl catalyst (**37**, **38** and **39**) >

benzimidazolyl catalysts (**55**, **58**, and **61**) >
benzoxazolyl catalyst (**43**, **46** and **49**).

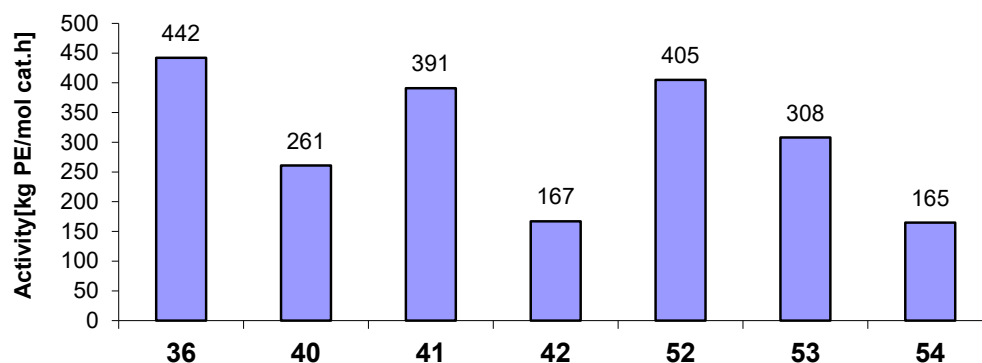


Figure 5. Activities of 1, 2-bis(benzothiazolyl, benzoxazolyl and benzimidazolyl)benzene vanadium(III) complexes.

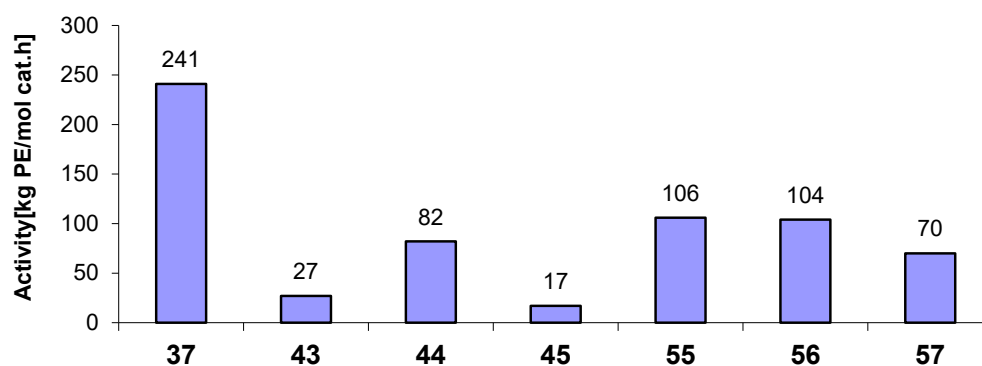


Figure 6. Activities of 1,2-bis (benzothiazolyl, benzoxazolyl, benzimidazolyl)-4-methylbenzenevanadium(III) complexes.

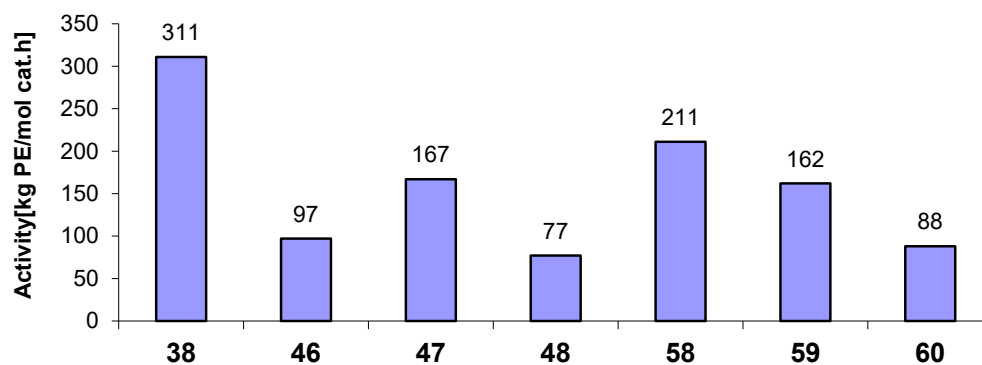


Figure 7. Activities of 1,2-bis(benzothiazolyl, benzoxazolyl, benzimidazolyl)-4-chlorobenzenevanadium(III) complexes.

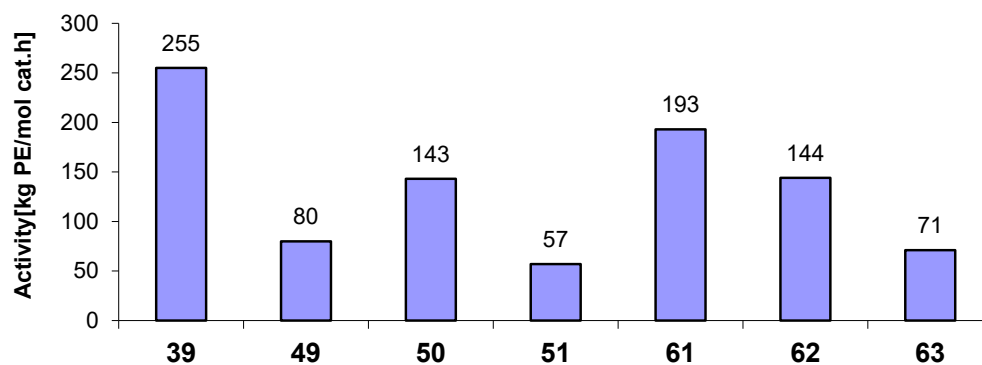


Figure 8. Activities of 1,2-bis(benzothiazolyl, benzoxazolyl, benzimidazolyl)-4-bromobenzenevanadium(III) complexes.

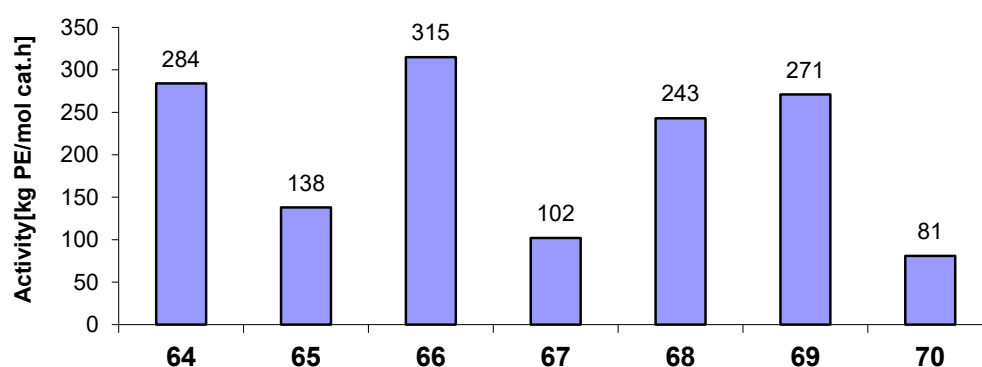


Figure 9. Activities of 2,6-bis(benzothiazolyl, benzoxazolyl and benzimidazolyl)pyridine vanadium(III) complexes.

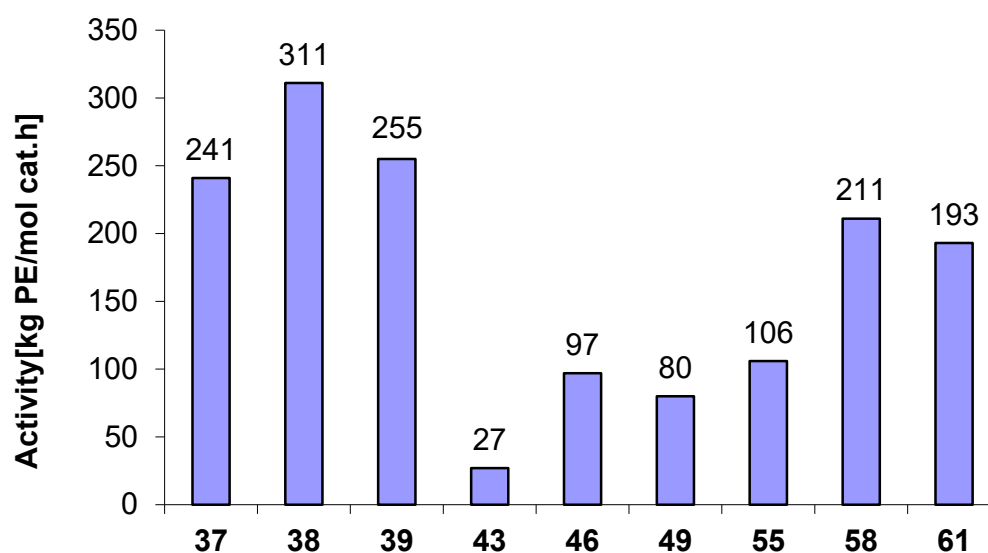


Figure 10. Effect of bridging unit on the activities of the catalysts system (37-39), (43, 46, 49) and (55, 58, 61).

The position of the methyl group relative to the imino nitrogen influences the catalytic activity of the 1,2-bis-benzoxazolyl benzene (**41**, **42**), 1,2-bis-benzoxazolyl-4-methylbenzene (**44**, **45**), 1,2-bis-benzoxazolyl-4-chlorobenzene (**47**, **48**), 1,2-bis-benzoxazolyl-4-bromobenzene (**50**, **51**) and 2,6-bis-benzoxazolyl pyridine (**66**, **67**) vanadium complexes, the methyl group in *para* position to the imino nitrogen (**42**, **45**, **48**, **51** and **67**) increases the electron density on the metal atom and hence this is leading to a weaker

interaction between the metal centre and the π -electrons of ethylene resulting in a lower activity [53], (Figure 11). On the other hand, a methyl group *meta* to the imino nitrogen (**41**, **44**, **47**, **50** and **66**) increases the activities of the complexes which can be explained with electronic effects [36]. For example, the catalyst system **41**/MAO (391 kg PE / mol cat. h) compared to 167 (kg PE / mol cat. h) for **42** / MAO, similarly the catalyst pair derived from bisbenzoxazolyl-4-methylbenzene **44** / MAO and **45** / MAO shows activities of 82 and 17 (kg PE / mol cat. h) respectively.

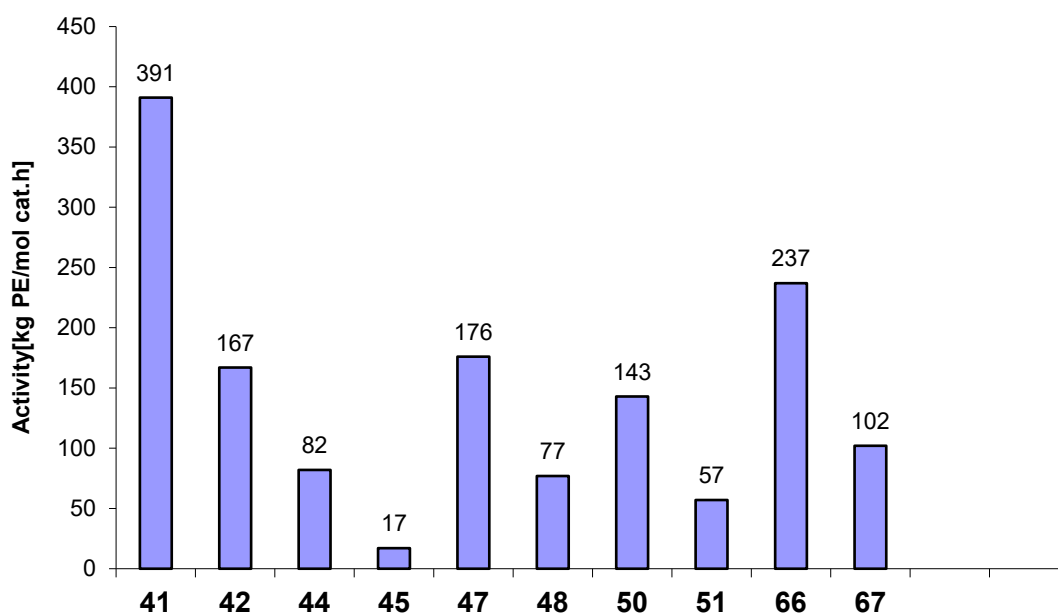


Figure 11. Effect of substituent position on the activities of 1, 2-bis-benzoxazolylbenzene (**41**, **42**), 1, 2-bis-benzoxazolyl-4 methylbenzene (**44**, **45**), 1,2-bis-benzoxazolyl-4-chlorobenzene (**47**, **48**), 1,2-bis-benzoxazolyl-4-bromobenzene (**50**, **51**) and 2,6-bis-benzoxazolylpyridine (**66**, **67**) vanadium complexes.

For the vanadium complexes of 1,2-bis(benzimidazolyl)benzene, 1,2-bis(benzimidazolyl)-4-methylbenzene, 1,2-bis(benzimidazolyl)-4-chlorobenzene, 1,2-bis(benzimidazolyl)-4-bromobenzene and 2,6-bis(benzimidazolyl)pyridine. The methyl substituted catalysts **53**, **56**, **59**, **62** and **69** (Figure 12) are more active than the chloro-substituted compounds **54**, **57**, **60**, **63** and **70**. The lower activities of the chloro substituted complexes may result from the interaction of the Lewis base (chloro substituent) with the active center of a neighbouring catalyst molecule blocking them from ethylene coordination. From (Figure 12) it is obvious that the activities of the complexes are controlled by the ligand structures.

Applying complex **36**/MAO and **66** / MAO, the temperature dependence of the polymerization

activities was investigated. Under the same cocatalyst concentration and at a reaction temperature of 20 °C the catalyst system **36**/MAO shows an activity of 54 [kg PE/mol cat·h]. Increasing the temperature to 50 °C lead to an activity of 442 [kg PE/mol cat·h] further increase in temperature the activity drops to 178 [kg PE/mol cat·h] (see Figure 13). This behavior is in agreement with the fact that kinetics is accelerated with rising temperatures.

Similarly, under the same cocatalyst concentration and at a reaction temperature of 20 °C the catalyst system **66**/MAO shows an activity of 193 [kg PE/mol cat·h]. Increasing the temperature to 50 °C lead to an activity of 315 [kg PE/mol cat·h] further increase in temperature the activity drops to 237 [kg PE/mol cat·h] (see Figure 14).

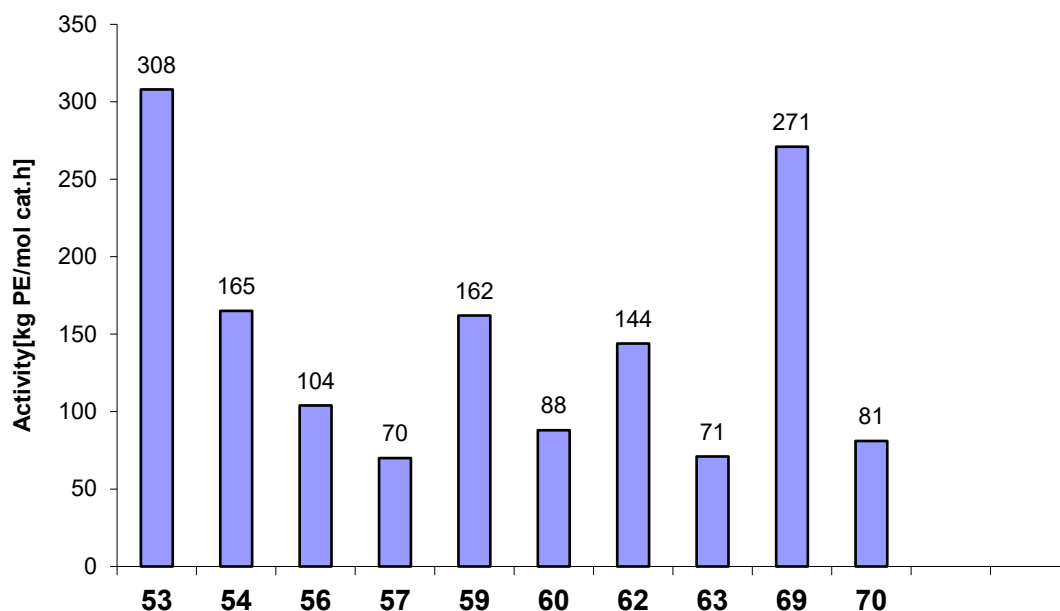


Figure 12. Effect of substituent type on the activities of 1, 2-bis benzimidazolyl benzene (53, 54), 1, 2-bis benzimidazolyl-4-methylbenzene (56, 57), 1,2-bis (benzimidazolyl)-4-chlorobenzene (59, 60), 1,2-bis(benzimidazolyl)-4-bromobenzene (62, 63) and 2,6-bis(benzimidazolyl) pyridine (69, 70) vanadium complexes.

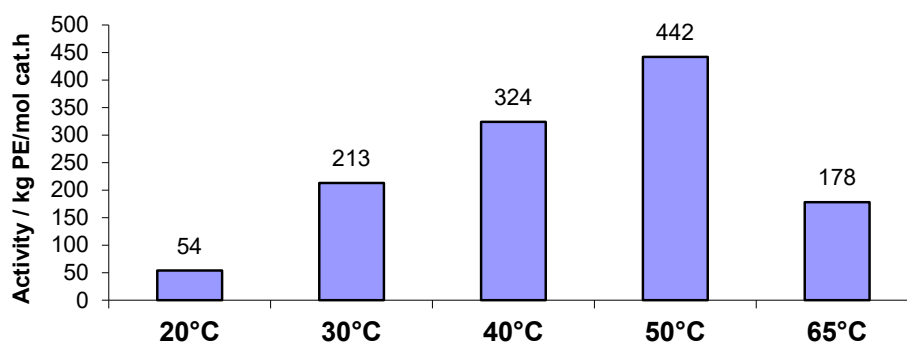


Figure 13. Effect of temperature on polymerization activity of catalyst 36/MAO.

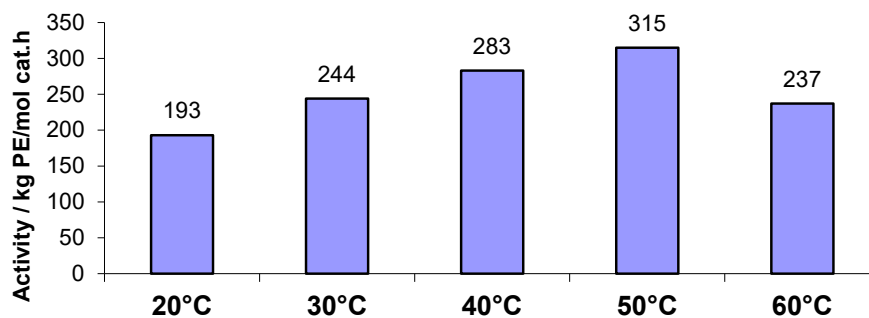


Figure 14. Effect of temperature on polymerization activity of catalyst 66/MAO.

GPC analysis of the polyethylenes produced with benzothiazole, benzoxazole, and benzimidazole based vanadium complexes revealed that the symmetric catalysts system 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. [54]. The molecular weight M_w and polydispersity of the polymer produced with catalyst systems **66** / MAO (see Figure 15) was determined to be 1.8×10^6 g / mol, (PD = 2.6).

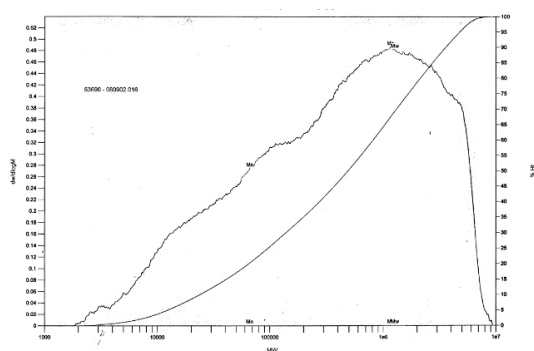


Figure 15. GPC profile for polyethylene produced with catalyst **66**/ MAO.

Differential scanning calorimetric (DSC) measurements for representative samples of polyethylenes produced with bis-(benzimidazolyl, benzothiazolyl, and benzoxazolyl)vanadium complexes revealed that the catalyst systems were capable to produce high density polyethylenes with melting temperatures > 135 °C (see Table 2). The crystallization temperatures of the polymers range from 117-120 °C and the polymers have high degrees of crystallinity. For example, the catalysts **66** / MAO show melting temperatures of 137.4 °C and crystallization temperatures of 119.7 °C. The degrees of crystallinity are 30.4 % (Figure 16).

Table 2. Melting, crystallization temperatures and degrees of crystallinity of representative polyethylene samples obtained with some catalyst systems.

Catalyst system	T_m [°C]	T_{cryst} [°C]	α [%]
36/MAO	135.4	118.1	28.4
55/MAO	136.9	117.9	33.6
66/MAO	137.4	119.6	30.4
67/MAO	135.5	118.3	30.6
69/MAO	137.2	118.7	29.1

T_m =melting temperature, T_{cryst} = crystallization temperature, α =degree of crystallinity.

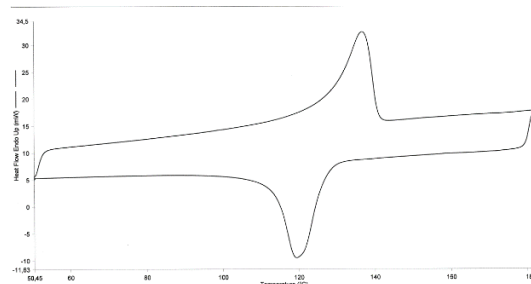


Figure 16. DSC curve of polyethylene produced with the catalyst system **66**/MAO.

4. CONCLUSION

Bis-(benzimidazole, benzothiazole and benzoxazole) form symmetric chelate complexes with V (III) chlorides. After activation with MAO the generated catalysts polymerize ethylene in solution with various activities. Structure-property-relationships indicate that the catalyst structure, the nature and position of substituents and the heteroatoms determine the performance of such catalysts. The highest activity (442 kg PE / mol cat. h) was obtained with the vanadium catalyst **36** / MAO. The catalyst system **66** / MAO produce resin with very high molecular weight (1.8×10^6 g / mol), which indicates low energy barriers for the olefin insertion and high barriers for the termination steps. Relative broad molecular weight distributions of the produced polyethylenes (PD = 1.5 – 16) could result from the existence of several active sites in the polymerization process

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6. REFERENCES AND NOTES

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