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Hamdi Ali Elagab, Helmut G. Alt

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Structure-property-relationship studies with ethylene polymerization catalysts of Ti, Zr and V containing heterocyclic ligands

Hamdi Ali Elagab and Helmut G. Alt*^[a]

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^[a]Dr. H. Ali Elagab, Prof. Dr. H. G. Alt Laboratorium für Anorganische Chemie Universität Bayreuth Universitätsstraße 30, 95440 Bayreuth (Germany) E-mail: helmut.alt@uni-bayreuth.de

ABSTRACT

21 complexes of bis(benzimidazolyl, benzothiazolyl and benzoxazolyl)methane compounds with Zr(IV), Ti(IV), V(III) metal centers were synthesized, characterized, activated with methylalumoxane (MAO) and then tested for catalytic ethylene polymerization. The activities of the various catalysts were found to be functions of the hetero atoms in the ligand frameworks. The methylene moiety as bridging unit of the two heterocyclic ring systems gave higher catalyst activities than the corresponding 1,2-ethylidene derivatives indicating a strong influence of the bridging unit of the ligand on the catalyst activity. The activity of the catalyst system **10**/MAO was investigated with different cocatalyst concentrations. The highest activity was obtained with **23**/MAO (573 kg PE/mol cat. h). The produced polyethylenes showed high molecular weights (up to $1.77 \cdot 10^6$ g/mol) and broad molecular weight distributions (up to PD = 64.5). This could result from different interactions of the MAO counterion with the heteroatoms of the catalyst ligand generating different active sites. These catalysts open an easy access to single-reactor multimodal polyethylene technology.

1. Introduction

Recently [1-3] we have shown that benzimidazoles, benzothiazoles and benzoxazoles can be applied as suitable ligands in titanium, zirconium and vanadium complexes that can be activated with methyalumoxane (MAO) and then be applied successfully for catalytic ethylene polymerization [4-6]. In spite of their hetero atoms and the oxophilicity of the metals, the performances of such catalysts are remarkable. 1,2-Bis-benzimidazoles and 2,6bis(benzimidazolyl)pyridine are well known compounds together with their late transition metal complexes [7-17]. Benzothiazole and benzoxazole contain heterocyclic sulphur and oxygen atoms and a pseudo imidazole functional group and can act as N-donor ligands with transition metals [18-24]. Herein we report the first zirconium, titanium and vanadium complexes of bis(benzimidazolyl, benzothiazolyl, and benzoxazolyl)methane and the importance of the CH₂ bridging unit on the performance of such catalysts in ethylene polymerization after activation with MAO. Structure-property-relationship studies should help to design a catalyst with the best performance.

2.1. Synthesis of the heterocycles

The condensation reaction of a dicarboxylic acid or an acid anhydride with diamines, substituted diamines, 2-aminothiophenol, 2-aminophenol and substituted 2-aminophenols in preheated polyphosphoric acid is a well established procedure for the preparation of the benzimidazole, benzothiazole and benzoxazole based ligand precursors [25,26] in high yields (Scheme 1). The Philip's modified method was also used for the syntheses of benzimidazoles based ligand precursors [27, 28].



Compound No.	X	\mathbf{R}^{1}	\mathbf{R}^2
1	S	Н	Н
2	NH	Н	Н
3	NH	CH ₃	Н
4	NH	Cl	Н
5	0	Н	Н
6	0	CH ₃	Н
7	0	Н	CH ₃

Scheme 1. Synthesis of ligand precursors 1-7.

2.2. Synthesis of coordination compounds

2.2.1. Synthesis of titanium, zirconium and vanadium complexes

The complexes were synthesized according to Scheme 2 and characterized by ¹H NMR, ¹³C NMR and mass spectrometry. Table 1 summarizes their spectroscopic data. The titanium and zirconium complexes were prepared by ligand displacement reactions. After dissolving the tetrahydrofuran adducts of zirconium and titanium tetrachloride in an appropriate solvent, the corresponding heterocycle was added and an immediate colour change was observed. The complexes could be isolated in very high yields (80-95%). The complexes were characterized by NMR, mass spectrometry and representative examples by elemental analysis. Vanadium

complexes were synthesized by dissolving vanadium trichloride in diethyl ether followed by addition of the ligand precursor with constant stirring over night. The products were obtained in good yields (70-80%).



Complex No.	X	\mathbf{R}^{1}	\mathbf{R}^2	Μ
8	S	Н	Н	Ti
9	S	Н	Н	Zr
10	S	Н	Н	V
11	NH	Н	Н	Ti
12	NH	Н	Н	Zr
13	NH	Н	Н	V
14	NH	CH ₃	Н	Ti
15	NH	CH ₃	Н	Zr
16	NH	CH ₃	Н	V
17	NH	Cl	Н	Ti
18	NH	Cl	Н	Zr
19	NH	Cl	Н	V
20	0	Н	Н	Ti
21	0	Н	Н	Zr
22	0	Н	Н	V
23	0	CH ₃	Н	Ti
24	0	CH ₃	Н	Zr
25	0	CH ₃	Н	V
26	0	Н	CH ₃	Ti
27	0	Н	CH ₃	Zr
28	0	H	CH ₃	V

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Scheme 2. The synthesized coordination compounds 8-28.

2.3. Characterization

Since the complexes did not crystallize properly, they were characterized spectroscopically.

2.3.1. ¹H NMR and ¹³C NMR spectroscopy:

The ligand precursors **1-7** and their titanium and zirconium complexes were characterized by ¹H NMR and ¹³C NMR spectroscopy. The vanadium complexes, due to their paramagnetism were characterized by mass spectrometry. The ¹H NMR spectrum of compound **1** (Figure 1) shows five sets of resonance signals: a doublet at $\delta = 8.04$ ppm [³*J*_{H,H} = 7.8 Hz] is assigned to the two aromatic protons H4, the doublet at $\delta = 7.95$ ppm [d, 2H, ³*J*_{H,H} = 7.8 Hz] is assigned to the aromatic protons H1. At $\delta = 7.47$ ppm a virtual triplet [³*J*_{H,H} = 7.8 Hz] can be assigned to two protons of the aromatic ring (H2), a virtual triplet at $\delta =$ 7.43 ppm [³*J*_{H,H} = 7.8 Hz] assigned to two aromatic protons (H3). At $\delta = 5.05$ ppm a singlet corresponds to the protons of the bridging methylene group H5.



Figure 1.¹H NMR spectrum of **1** in DMSO-d₆.

The ¹³C NMR spectrum of compound **1** (Figure 2) shows eight resonance signals: at δ = 167.0 ppm the two carbon atoms C7 appear. The signal at δ = 153.2 ppm is assigned to the carbon atoms C6. The signal at δ = 135.9 ppm represents the carbon atoms C1. At δ = 127.0 and 125.9 ppm the carbon atoms C4 and C3 appear. The signals at δ = 123.2 ppm and 122.9 ppm can be assigned to C2 and C5, while the signal at δ = 38.5 ppm corresponds to the carbon atom of the bridging CH₂ unit.



The ¹H NMR spectrum of complex **9** (Figure 3) shows three sets of signals. The two doublets at $\delta = 8.10$ and 8.00 ppm can be assigned to H4 and H1. The virtual triplets at $\delta = 7.53$ and 7,45 ppm can be assigned to the protons H2,3, while the protons of the bridging CH_2 group appear as a singlet at $\delta = 5.10$ ppm.



Figure 3. ¹H NMR spectrum of complex 9 in DMSO-d₆.

The ¹³C NMR spectrum of complex 9 (see Figure 4) shows eight signals: at $\delta = 167.2$, 153.3, 136.0, 127.0, 126.2, 123.4, 123.0 and 38.5 ppm that belong to C1, C7, C2, C5, C4, C3, C6 and C8.

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2.3.2. Mass spectrometry

The mass spectrum of compound **2** shows the molecular ion peak at m/z = 282. (Figure 5).



Figure 5. Mass spectrum of compound 2.

The mass spectrum of complex 9 (Figure 6) does not show the molecular ion peak at m/z = 514 but an incomplete fragmentation pattern and a peak for the free ligand. Complexes with donor ligands often do not survive the ionisation process without decomposition.

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2.4. Polymerization results

All coordination compounds 8-28 were activated with MAO in toluene solution. The mechanism should be the same as proposed for the activation of metallocene [29, 30] and 2, 6-bis(imino)pyridine iron [31] complexes. The homogeneous catalyst solution was used for ethylene polymerization. The solutions showed variable activities for ethylene polymerization depending on the coordination sphere of the active centres. The activities are greatly influenced by the hetero atoms in addition to the ligand environment and the nature of the coordinated central metal atom. The catalysts generally showed moderate to good activities compared to the benchmark catalyst Cp_2ZrCl_2 [32].

Table 1. Ethylene	polymerization	activities of c	complexes 8-28	a)
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Complex	Activity		Polymerization	Mw [g/	PDI
No.	[kg PE/ mol cat·h]	Al: M	temperature	mol]	
			[°C]		
8	279	2500:1	50	527920	6.6
9	41	2500:1	50	362920	4.3
9 ^{b)}	22	2500:1	40	n.d	n.d.
10	380	2500:1	50	288590	11.5
10 ^{c)}	493	1000:1	50	420140	3.0
11	316	2500:1	50	1149590	8.4
12	172	2500:1	50	1906470	5.4
13	173	2500:1	50	424280	3.2
14	245	2500:1	50	466380	5.6

15	43	2500:1	50	268280	4.9
16	179	2500:1	50	247000	3.1
17	148	2500:1	50	1770460	5.3
18	22	2500:1	50	n.d.	n.d.
19	338	2500:1	50	920240	1.8
20	472	2500:1	50	356540	3.3
21	424	2500:1	50	964100	23.1
22	403	2500:1	50	417410	2.0
23	573	2500:1	50	514040	5.6
24	145	2500:1	50	468550	5.4
25	208	2500:1	50	642360	-6.3
26	374	2500:1	50	425870	64.5
27	138	2500:1	50	n.d.	n.d.
28	158	2500:1	50	1273130	19.2

a) All polymerization reactions were carried out in 250 ml pentane with MAO as cocatalyst (Al: M = 2500:1) at 50°C, 10 bar ethylene pressure, 1 h reaction time).

- b) Reaction temperature 40° C. Other parameters the same.
- c) Al: M = 1000: 1. Other parameters the same. n.d.= not determined



Figure 7. Polymerization activities of the unsubstituted bis(benzothiazolyl) methane (8-10), bis(benzimidazolyl) methane (11-13) and bis(benzoxazolyl) methane complexes (20-22) after activation with MAO.

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The activities of the titanium complexes follow the order 20 > 11 > 8, and the activities of the zirconium complexes show the same trend: 21 > 12 > 9. The vanadium complexes behave differently with complex 22 having the highest activity: 22 > 10 > 13. The differences in catalytic activities can be accounted for by the hetero atom effect (S, N, and O) (see Figures 7 and 8).



Figure 8: Effect of hetero atoms on the activities of vanadium complexes 10, 13 and 22.

Among the catalyst systems derived from bis(benzimidazolyl) methane, a substituent in *meta* position to the imino nitrogen atom influences the catalytic activities of the systems compared to the unsubstituted ones. The methyl substituted titanium and zirconium complexes 14 and 15 were more active than the chloro substituted complexes 17 and 18 (see Figure 9). However, both show lower activities compared to the unsubstituted complexes 11 and 12. The lower activities of the chloro substituted complexes may result from the interaction of the chloro Lewis base of the substituted with the active centre of a neighbouring catalyst molecule blocking this active site. On the other hand, for the vanadium complexes 13, 16 and 19 (Figure 10), the chloro substituted complex 19 shows higher activity than the unsubstituted complex 13 and the methyl substituted complex 16. This order of activities may arise from an advantageous electronic effect of the chloro substituent imposed on the active centre (increase its Lewis acidity) and a weaker oxophilicity of vanadium.



Figure 9. Effect of substituents on polymerization activities of bis(benzimidazolyl)methane complexes **11-19**.



Figure 10: Effect of the nature of the substituent on the activity of vanadium complexes 13, 16 and 19.

The catalytic activities of complexes derived from 1,1-bis(benzoxazolyl) methane were affected by the nature and the position of the corresponding substituent [33,34]. The introduction of a methyl substituent in *meta* position to the imino nitrogen atoms decreased the activities of the titanium complex **26**, the zirconium complex **27** and the vanadium complex **28** compared to the unsubstituted complexes **20-22**. On the other hand, a methyl

group *para* to the imino nitrogen atoms increased the activity of titanium complex 23, while the activities of the zirconium complex 24 and vanadium complex 25 decreased compared to the unsubstituted complexes 21 and 22 (see Figure 11).



Figure 11. Effect of substituent position on the polymerization activities of the bis (benzoxazolyl) methane complexes **20-28**.

The activity of the catalyst **10**/MAO was tested with different MAO concentrations (Figure 12). At 50°C with an aluminum to vanadium ratio of 1000 : 1, the catalyst shows an activity of 493 [kg PE/mol cat·h]. Increasing the cocatalyst concentration to 2500 equivalents results in an activity decrease to 379 [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.



Figure 12: Effect of cocatalyst concentration on the activity of complex 10.

Applying complex **9**, the temperature dependence of the polymerization activities was investigated (Figure 13). Under the same cocatalyst concentration and at a reaction temperature of 40°C the catalyst system **9**/MAO shows an activity of 22.4 [kg PE/mol cat·h]. Increasing the temperature to 50°C lead to an activity of 40.5 [kg PE/mol cat·h]. This behaviour is in agreement with the fact that kinetics are accelerated with rising temperatures.



Figure 13: Effect of temperature on the activity of complex 9.

GPC analyses of the polyethylenes produced with benzimidazolyl, benzothiazolyl and benzoxazolyl methane based complexes revealed that the symmetric catalyst systems were capable to produce resins with moderate to high molecular weights associated with broad molecular weight distributions. The broad molecular weight distribution may arise from the

fact that the MAO counterion induces various active sites in the activation process [35] due to different interactions with the hetero atoms of the catalyst ligand. For example, the catalyst system 17/MAO produced a resin with M_w = 1.77·10⁶g/mol (PDI = 5.3) (Figure 14).



Figure 14. GPC profile for polyethylene produced with catalyst 17/MAO.

The GPC profiles of polyethylenes produced with the catalyst **28/MAO** (Figure 15) show a molecular weight of $M_w = 1.27 \cdot 10^6$ g/mol, (PDI = 19.2).



Figure 15. GPC profile for polyethylene produced with catalyst 17/MAO.

Differential scanning calorimetric (DSC) measurements for representative samples of polyethylenes produced with 1,1-bis-(benzimidazolyl, benzothiazolyl, and benzoxazolyl) methane titanium, zirconium and vanadium complexes revealed that the catalyst systems were capable to produce high density polyethylenes with melting temperatures > 135°C. The crystallization temperatures of the polymers range from 118-120°C and the polymers have high degrees of crystallinities (see Table 2). For example, DSC curves for polyethylene produced with the catalysts **9**/MAO and **17**/MAO show melting temperatures of 135.6 and 138.1°C and crystallization temperatures of 118.3 and 118.1°C. The degrees of crystallinity are 30.1 and 25.5%.

Table 2. Thermal analysis data representative polymer samples produced with complexes 9,10, 12, 15, 17, 20, 22, 23, 25, 28.

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Complex No.	$T_m[^{\circ}C]$	T _{cryst} [°C]	α[%]
9	135.6	118.3	30.1
10	139.2	119.7	26.7
12	137.2	118.8	28.3
15	136.5	118.6	27.3
17	138.1	118.1	25.5
20	135.9	119.1	33.0
22	136.1	119.5	31.6
23	138.3	119.2	34.4
25	135.8	118.7	33.5
28	139.4	118.4	32.6





Figure 16. DSC curve for polyethylene produced with catalyst 9/MAO.

R



Figure 17. DSC curve for polyethylene produced with catalyst 17/MAO.

3. Experimental

3.1. General considerations

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 then additionally with calciumhydride. Methanol and ethanol were dried over molecular sieves. Deuterated solvents (CDCl₃, DMSO-d₆) 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 titanium and zirconium adducts were synthesized via published procedures [36].

NMR spectroscopy

The spectrometers Varian Inova 300/400 M Hz 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 CDCl₃, $\delta =$

2.5 ppm for DMSO-d₆) and in ¹³C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for CDCl₃, $\delta = 39.5$ ppm for DMSO-d₆).

Mass spectrometry

Mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 eV) and a VARIAN MAT 8500 spectrometer.

Gel permeation chromatography (GPC)

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

Elemental analysis

Elemental analyses were performed with a VarioEl III CHN instrument. Calibration compound: acetamide.

3.2. General procedures for the synthesis of the transition metal complexes

Synthesis of organic compounds 1-7

A diamine compound (0.05mol) was mixed with a dicarboxylic acid or an acid anhydride (0.025mol) and the mixture was poured in 50 ml of preheated (100°C) polyphosphoric acid. The mixture was stirred and heated at 175°C for 3-5 hours. The reaction mixture was then poured into ice cold water and allowed to stand overnight. The precipitate was removed by filtration and washed several times with diluted sodium hydrogen carbonate solution and finally with water. The reaction product was then air dried and weighed. The products were characterized by NMR and mass spectroscopy (Table 4). Representative samples were characterized by elemental analysis (Table 3).

3.3. Titanium complexes

To an amount of 0.87g (2.6 mmol) $TiCl_4(THF)_2$ in dichloromethane was added an amount of 2.6 mmol of the corresponding heterocycle. The reaction mixture was stirred overnight at room temperature and filtered. The residue was washed several times with dichloromethane and pentane, dried in vacuo and weighed (80-95%). The products were characterized by

NMR and mass spectroscopy (Table 4). Representative samples were characterized with elemental analysis (Table 3).

3.4. Zirconium complexes

To an amount of 0.45g (1.2mmol) ZrCl₄(THF)₂ in dichloromethane was added an amount of 1.2 mmol of the corresponding heterocycle. The reaction mixture was stirred overnight at room temperature and filtered, washed several times with dichloromethane, then with npentane, dried in vacuo and weighed (80-95%). The products were characterized by NMR and mass spectroscopy (Table 4). Representative samples were characterized with elemental analysis (Table 3).

3.5. Vanadium complexes

To an amount of 0.41g (2.6 mmol) VCl₃ in ether was added an amount of 2.6 mmol of the ligand. The reaction mixture was stirred overnight at room temperature and filtered. The residue was washed several times with ether and n-pentane, dried in vacuo and weighed (70-80%). The products were characterized by mass spectroscopy and representative samples were characterized with elemental analysis (Table 3).

Table 3. Elemental analysis data for representative free ligands 1-7 and complexes 8, 10, 13,16, 18, 20, 22, 23, 25, 28.

Compoun	d	Calculated			Found	
No.	С	Н	Ν	С	Н	Ν
1	63.8	3.5	9.9	63.6	3.4	10.2
2	72.6	4.8	22.6	71.8	4.6	22.4
3	73.9	5.8	20.3	73.7	6.0	20.1
5	72.0	4.0	11.2	71.8	4.2	11.4
6	73.4	5.0	10.1	73.6	5.1	9.8
8	38.1	2.1	5.9	37.7	2.3	6.2
10	41.0	2.3	6.4	40.8	2.5	6.2
13	44.3	3.00	13.8	44.6	3.2	13.5
16	47.1	3.7	12.9	46.7	3.9	13.1
18	32.8	1.8	10.2	33.2	2.2	10.0

20	41.1	2.3	6.4	40.7	2.5	6.7
22	44.2	2.5	6.9	43.8	2.3	7.2
23	43.6	3.0	6.0	43.8	3.2	5.8
25	46.9	3.2	6.4	47.1	2.9	6.6
28	46.9	3.2	6.4	46.7	3.0	6.2

3.6. Polymerization of ethylene in a 1 litre 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 colour change. The mixture was added to a 1 litre Schlenk flask filled with 250 ml npentane. This mixture was transferred to a 1 litre 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.

Compound No.	¹ H NMR	¹³ C NMR	Mass
Compound No.	δ [ppm]	δ [ppm]	m/z [%]
	8.04(d,2H, J = 7.8 Hz)	167.0, 153.2, 135.9,	282 M ^{°+} (100)
	, 7.95(d,2H, J = 7.8	127.0, 125.9, 123.2,	
1	Hz), $7.47(t, 2H, J = 7.8$	122.9, 38.5	
	Hz), 7.43(t,2H, J = 7.8		
	Hz), 5.05(s,2H,CH ₂)		
	12.41(s,2H, NH),	150.8, 138.4 122.9,	248 M ^{°+} (100)
	7.46(m,4H),	115.4, 29.8	
2	7.11(m,4H),		
	4.43(s,2H,CH ₂)		
	7.32(d,2H, J = 7.8 Hz),	150.6, 139.2 137.9,	276 M ^{°+} (100)
	7.23(s,2H), 6.91(d,2H,	131.2, 123.5, 115.3,	
3	J = 7.8 Hz),	114.7, 30.0, 21.9	
	4.35(s,2H,CH ₂),		
	2.33(s,6H,CH ₃)		
	1		

Table 4. NMR and mass s	pectroscopic data	of the free ligands 1	-7 and complexes 8-28.
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0
M°+-
2C1
Cl (5),
00)
M ^{°+} -
-2Cl
Cl (5),
100)
M°+-
2C1
(10),

Compound No.	¹ H NMR	¹³ C NMR	Mass
	δ [ppm]	δ [ppm]	m/z [%]
			282 M°+-VCl ₃ (100)
11	7.52-7.49(m,4H), 7.52-	149.0, 135.4, 124.4,	438 M°+(1), 402 M°+-
	7.14(m,4H),	115.1, 27.5	Cl (2), 367 M°+-2Cl
	4.55(s,2H,CH ₂)		(2), 248 M ^{°+} -TiCl ₄
			(100)
	7.63-7.62(m,4H), 7.33-	150.6, 138.7, 122.6,	481 M°+(1), 444 M°+-
	7.30 (m,4H),	115.3, 29.6	Cl (2), 407 M°+-2Cl
12	4.91(s,2H,CH ₂)		(1), 370 M ^{°+} -3Cl (2),
			336 M ^{°+} -4Cl (1), 248
			M ^{°+} -ZrCl ₄ (100)
13			406 M°+(3), 368 M°+-
			Cl (7), 334 M°+-2Cl
	n.d.	n.d.	(10), 299 M ^{°+} -3Cl
			(20), 248 M°+-VCl ₃
			(100)
	7.63(d,2H, J = 8.1 Hz)	146.3, 136.3, 132.3,	466 M°+(1), 428 M°+-
	, 7.54(s,2H),	130.1, 127.8, 114.3,	Cl(5), 393 M°+-2Cl (5),
14	7.31(d,2H, J = 8.1 Hz),	114.1, 25.8, 21.8	357 M ^{°+} -3Cl (3), 319
	5.25(s,2H,CH ₂),		M ^{°+} -4Cl (2), 276 M ^{°+} -
	2.42(s,6H,2CH ₃)		TiCl ₄ (100)
	7.55(d,2H, J = 8.1 Hz),	147.5, 135.0, 134.0,	510 M ^{°+} (2), 477 M ^{°+} -
	7.47(s,2H), 7.21(d,2H,	132.2, 126.7, 114.6,	Cl (5), 440 M°+-2Cl
15	J = 8.1 Hz), 5.05	114.3, 26.6, 21.8	(5), 405 M ^{°+} -3Cl (2),
	(s,2H,CH ₂),		276 M ^{°+} -ZrCl ₄ (100)
	2.40(s,6H,2CH ₃)		
16			433 M°+(2), 397 M°+-
			Cl (5), 360 M°+-2Cl
	n.d.	n.d.	(10), 324 M ^{°+} -3Cl (5),
			276 M ^{°+} -VCl ₃ (100)
	7.88(s,2H), 7.80(d,2H,	149.3, 134.7, 132.6,	506 M°+(3), 470 M°+-
17	J = 8.1 Hz), 7.51(d,2H,	129.8, 125.9, 116.5,	Cl (2), 434 M°+-2Cl

Compound No.	¹ H NMR	¹³ C NMR	Mass
	δ [ppm]	δ [ppm]	m/z [%]
	J = 8.1 Hz),	114.9, 26.9	(5), 397 M ^{°+} -3Cl (10),
	5.18(s,2H,CH ₂)		316 M ^{°+} -TiCl ₄ (100)
18	7.89(s,2H, 7.80(d,2H,	149.1, 134.3, 132.2,	549 M°+(2), 513 M°+-
	J = 8.1 Hz), 7.52(d,2H,	130.1, 126.1, 116.5,	Cl (5), 476 M°+-2Cl
	J = 8.1 Hz), 5.23(s,2H,	114.8, 26.7	(10), 440 M°+-3Cl (5),
	CH ₂)		316 M ^{°+} -ZrCl ₄ (100)
			473 M°+(5), 437 M°+-
			Cl (2), 401 M°+-2Cl
19	n.d.	n.d.	(70), 368 M ^{°+} -3Cl
			(10), 316 M°+-VCl ₃
			(20)
	7.69(d,4H, J = 7.8 Hz),	161.4, 151.2, 141.3,	438 M°+(5), 368 M°+-
	7.36(t, 4H, J = 7.8 Hz),	126.1, 125.4, 120.4,	2Cl (10), 331 M°+-
20	4.85(s,2H,CH ₂)	111.5, 29.3	3Cl(10), 295 M ^{°+} -4Cl
			(5), 250 M ^{°+} -TiCl ₄
			(100)
	7.76(d, 4H, J = 7.8 Hz),	161.78, 151.4, 151.2,	483 M°+(2), 447 M°+-
	7.47(t, 4H, J = 7.8 Hz),	141.5, 141.1, 126.6,	Cl (5), 411 M°+-2Cl
21	4.99(s,2H,CH ₂)	126.4, 125.7, 125.6,	(5), 375 M ^{°+} -3Cl (10),
0		120.7, 120.6, 111.8,	250 M ^{°+} -ZrCl ₄ (100)
		29.6	
22			407 M°+(3), 371 M°+-
	n.d.	n.d.	Cl (5), 335 M°+-2Cl
			(10), 300 M ^{°+} -3Cl (5),
			250 M°+-VCl ₃ (100)
▶	7.61(d,2H, J = 7.6 Hz),	161.5, 149.4, 141.5,	$A(0, M^{0+}(5), A(0, 0, M^{0+})$
	7.53(s,2H), 7.23(d,2H,	134.8, 127.0, 120.2,	$(3), 432 \text{ M}^{-1}$
23	J = 7.6Hz),	111.0, 29.4, 21.7	$CI(2), SOI M^{-3}CI(3),$
	4.84(s,2H,CH ₂),		290 MI -4CI-2CH ₃ (5),
	2.41(s,6H,2CH ₃)		278 Mi $-11Cl_4$ (100)
24	7.57(d,2H, J = 7.6 Hz),	161.4, 149.4, 141.5,	511 M°+(3), 474 M°+-
	1	i i i i i i i i i i i i i i i i i i i	1

¹ H NMR	¹³ C NMR	Mass
δ [ppm]	δ [ppm]	m/z [%]
7.51(s,2H),	134.7, 127.0, 120.2,	Cl (2), 404 M°+-3Cl
7.20(d,2H,J = 7.6 Hz),	110.9, 29.4, 21.6	(1), 340 $M^{\circ +}$ -4Cl-2CH ₃
4.82(s,2H,CH ₂),		(3), 278 M ^{°+} -ZrCl ₄
2.40(s,6H,2CH ₃)		(100)
		$435 \text{ M}^{\circ+}(1), 399 \text{ M}^{\circ+}-$
		Cl (3), 363 M°+-2Cl
n.d.	n.d.	(3), 300 $M^{\circ +}$ -3Cl-2CH ₃
		(5), 278 M ^{°+} -VCl ₃
	G	(100)
7.60(d,2H, J = 7.6 Hz),	160.8, 151.5, 139.1,	468 M°+(2), 432 M°+-
7.54(s,2H), 7.21(d,2H,	136.1, 126.5, 119.8,	Cl (3), 361 M°+-3Cl
J = 7.6Hz),	111.5, 29.3, 21.9	(2), 296 M ^{°+} -4Cl-2CH ₃
4.82(s,2H,CH ₂),		(2), 278 M ^{°+} -TiCl ₄
2.44(s,6H,2CH ₃)		(100)
7.58(d,2H, J = 7.6 Hz),	160.8, 151.5, 139.1,	511 $M^{\circ+}(1)$, 474 $M^{\circ+}$ -
J = 7.6 Hz.	136.0, 126.4, 119.7, 111.5, 29.3, 21.9	$(3), 404 \text{ M}^{\circ}-3Cl$ (3), 340 M ^{°+} -4Cl-2CH ₃
4.81(s,2H,CH ₂),	,,,	(2), 278 $M^{\circ+}$ -ZrCl ₄
2.42(s,6H,2CH ₃)		(100) 425 $M^{\circ+}(2)$ 200 $M^{\circ+}$
X		$(2), 399 M - Cl (5), 363 M^{+}-2Cl$
n.d.	n.d.	(3), 300 M^{+} -3Cl-2CH ₃
		$(3), 278 \text{ M}^{-+}\text{-VCl}_3$
	¹ H NMR δ [ppm] 7.51(s,2H), 7.20(d,2H,J = 7.6 Hz), 4.82(s,2H,CH ₂), 2.40(s,6H,2CH ₃) n.d. 7.60(d,2H, J = 7.6 Hz), 7.54(s,2H), 7.21(d,2H, J = 7.6Hz), 4.82(s,2H,CH ₂), 2.44(s,6H,2CH ₃) 7.58(d,2H, J = 7.6 Hz), 7.52(s,2H), 7.19(d,2H, J = 7.6 Hz), 4.81(s,2H,CH ₂), 2.42(s,6H,2CH ₃) n.d.	¹³ C NMR δ [ppm] δ [ppm] 7.51(s,2H), 134.7, 127.0, 120.2, 7.20(d,2H,J = 7.6 Hz), 110.9, 29.4, 21.6 4.82(s,2H,CH ₂), 2.40(s,6H,2CH ₃) n.d. n.d. 7.60(d,2H, J = 7.6 Hz), 160.8, 151.5, 139.1, 7.54(s,2H), 7.21(d,2H, 136.1, 126.5, 119.8, J = 7.6Hz), 111.5, 29.3, 21.9 4.82(s,2H,CH ₂), 160.8, 151.5, 139.1, 7.58(d,2H, J = 7.6 Hz), 160.8, 151.5, 139.1, 7.58(d,2H, J = 7.6 Hz), 160.8, 151.5, 139.1, 7.52(s,2H), 7.19(d,2H, 136.0, 126.4, 119.7, J = 7.6 Hz), 111.5, 29.3, 21.9 4.81(s,2H,CH ₂), 111.5, 29.3, 21.9 n.d. n.d.

Solvent = DMSO- d_6 n.d. = not determined

4. Conclusions

Titanium, zirconium and vanadium chloride complexes containing benzimidazolyl, benzothiazolyl and benzoxazolyl building blocks are suitable catalyst precursors for ethylene polymerization inspite of their hetero atoms and the oxophilicity of the metals. When two of these heterocycles are connected via a CH_2 bridge, the two nitrogen atoms of the five membered heterocycle form a chelating complex with the corresponding metal. It is

surprising that the CH₂ bridge has a very strong influence on the corresponding catalyst performances compared to other bridging units. Obviously the rigidity of the ligand system is favourable for catalyst cation and cocatalyst anion interactions. 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. These catalyst features open the access to single-reactor multimodal polyethylene technology with mononuclear complexes.

Acknowledgements

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Graphical Abstract Hamdi5

Complexes of Ti, Zr, and V with heterocyclic ligands can be activated with methylalumoxane (MAO) and applied for catalytic ethylene polymerization. The produced polyolefins have high molecular weights and broad molecular weight distributions.



Scalt

Highlights Hamdi 5

- Ti, Zr and V complexes with heterocyclic chelating ligands -
- Catalytic ethylene polymerization _

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