Synthesis of Mononuclear Transition Metal Complexes and their Applications as Catalysts for Ethylene Polymerization

Dissertation

Zur Erlangung des akademischen Grades eines
Doktors der Naturwissenschaften (Dr. rer. nat.) an der Fakultät für
Biologie, Chemie und Geowissenschaften der
Universität Bayreuth

vorgelegt von

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The following work was achieved during the period from July 2006 to July 2008 at the Lehrstuhl für Anorganische Chemie II der Universität Bayreuth under the supervision of Prof. Dr. Helmut G. Alt.

Vollständiger Abdruck der von der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth genehmigten Dissertation zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.).

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My sincere acknowledgement to my supervisor

Herrn Professor Helmut G. Alt

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To
My Mother
Fatima

To

The Soul of my Father

Abbreviations

cat	catalyst
°C	Degree Celsius
δ	chemical shift [ppm]
dd	doublet of doublet (NMR)
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
Et	Ethyl
GPC	Gel Permeation Chromatography
d	doublet in NMR spectroscopy
h	hour
M	Metal
$M^{\circ+}$	Molecular ion in mass spectroscopy
MAO	Methylaluminoxane
Me	Methyl
M_n	Number average molecular weight (GPC)
M_w	Weight average molecular weight (GPC)
m	multiplet (NMR)
m/z	mass/elemental electric charge
mg	milligram
ml	milliliter
mmol	millimol
MS	mass spectroscopy
N	Normality
n.d.	not determined
PD	Polydispersity (= M_w / M_n)
PPA	Polyphosphoric Acid
Ph	Phenyl
ppm	part per million in NMR spectroscopy
r.t.	room temperature
s	singlet (NMR)
THF	Tetrahydrofuran
t	triplet (NMR)

Contents

1. Introduction and research goals

Catalysis is the key to many chemical transformations. For the successful industrial implementation of a catalyst, certain prerequisites have to be fulfilled. The ideal catalyst has to combine high selectivity, high efficiency, high total turnover number and low cost. The understanding how catalyst structures and properties can affect these parameters combined with chemical curiosity is the driving force for the future development and improvement of catalysis.

Transition metals are at the core of a wide range of catalyst systems [1]. In comparison with main group metals, they have more orbitals available for interactions. The possibility to distribute its valence electrons in nine valence shells [(n-1) d, ns and np] that can interact with other groups allows the formation of both σ- and π- bonds. The ability of transition metals to accommodate inert ligands in addition to reactive moieties creates a wide variety of environments which form the basis for an innovative transition metal catalyst design.

The US market for polyolefins and α-olefins is in the tens of billions of dollars, both indicating their importance and stimulating interest in academic and industrial research in this field. Polyethylene, and polypropylene with an annual market of over 110 million tons, are half of all synthesized plastics [2].

Linear α-olefins, on the other hand, with more than 5 million tons annual production, are important substances for the preparation of detergents, lubricants, plasticizers, oil field chemicals, and monomers for copolymerization. One challenge is to design catalysts with higher catalytic activities and performances for advanced polyolefin resins.

The industrial processes of ethylene polymerization have been developed with titanium[3], chromium[4,5], and recently zirconium[6-9] catalysts, while the processes of ethylene oligomerization have been achieved with the Ziegler (Alfen) process[10], chromium based complexes[11,12], and the Shell Higher Olefin Process (SHOP)[13]. Zirconocene dichloride and half sandwich complexes were used as single site catalysts in the 1980s[8,9,13], followed by late transition metal catalysts[14-17] in the middle 1990s. At present, various catalysts of complexes of early[18-20] and late transition metals dominate the scene.

The strong defect of deactivation caused by the oxophilicity of early transition metal complexes during storage paved the way for stable late transition metal complexes as catalysts for ethylene polymerization with the expectation of high activities.

The strategy of late transition metal catalysts in olefin activation started with the discovery of the “nickel effect” in the 1950s, and the optimization of the reaction conditions resulted in the development of the SHOP process. In contrast to the case for the development of early transition metal catalysts, the late transition metal catalysts have been less investigated due to higher rates of β-hydrogen elimination reactions occurring in competition with ethylene insertion and chain propagation in the polymerization process[21].

Late transition metal catalysts were initially induced by the development of bidentate ligands for nickel and palladium diimino halides (Scheme 1) by the Brookhart group[22-25] and tridentate ligands for iron and cobalt 2,6-bis(imino)pyridyl halides (Scheme 1) by both the Brookhart group[26] and the Gibson group[27].

Keim and Tkatchenko found that neutral [P,O] chelates, which afford cationic nickel complexes[28] allow ethylene oligomerization at much lower temperature and pressure[29]. Similar palladium compounds were found to dimerize ethylene to butenes[30]. This led to the development of group 10 complexes with neutral chelating ligands such as [N,N] and [P,N] ligands to provide highly active ethylene oligomerization catalysts.

[P,P] and [N,N] ligands are applied in catalytic olefin homo- and copolymerization reactions[31]. Alt and coworkers[32-34] reported the use of nickel – diimine complexes for olefin polymerization and oligomerization, the activities of the catalysts and the nature of the produced polymers were thought to depend on the structure of the catalyst. Catalysts with bulky ortho substituents at the aryl moieties produce polymers while those without bulky substituents produce almost only oligomers. Generally the presence of bulky imine substituents influences the polymerization properties (activity of the catalyst as well as molecular weight of the isolated polymer). It was also found that the bulky substituents retard the rate of chain transfer reactions.

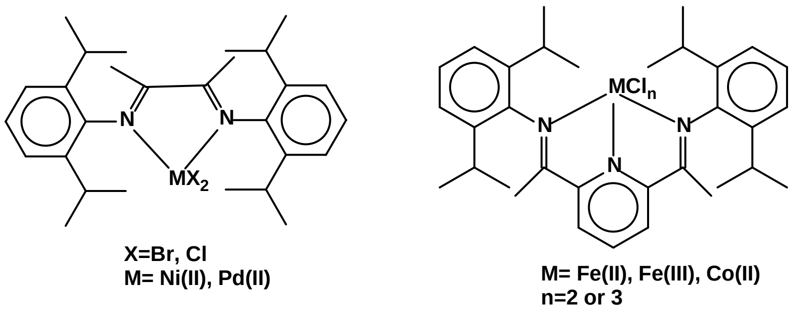
Few active group VIII and IX catalysts have been reported. The most active polymerization catalysts are iron(II) species stabilized with a 2,6-bis(imino)pyridine ligand with highly substituted aryl moities on the imino nitrogen atoms. It was reported that, by decreasing the size of the ortho substituents, the system could be converted into a very active olefin oligomerization catalyst[32-34]. The corresponding Co(II) complexes are less active compared to the Fe(II) complexes.

Generally speaking, cationic systems can be tuned to either ethylene polymerization or oligomerization activity by:

- Controlling the reaction conditions
- Subtle, easily accessible ligand variations.

Ligand variations offer a more elegant route to govern interconversion between polymerization and oligomerization active species. The key to successful switch is the control over the relative rates of chain propagation (K_P) and chain termination (K_t). Increasing K_t over K_P will lower the molecular weight of the polymer, and lead to the production of α-olefins.

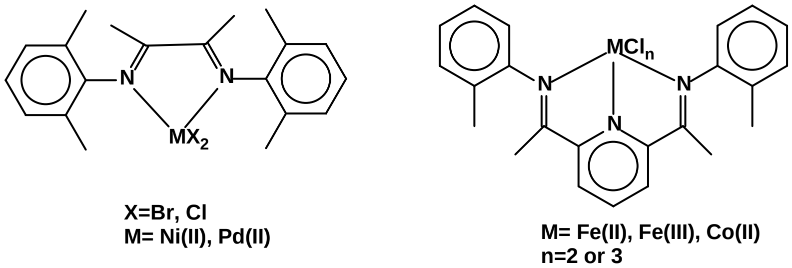
Recently transition metal catalysts have been developed that readily alternate between ethylene polymerization (Scheme 1) and oligomerization (Scheme 2) activity by changing the steric or electronic properties of the ancillary ligands. The progress in the use of late transition metal catalysts has been well documented with reviews[35-37]. Late transition metal complexes as catalysts for ethylene oligomerization and polymerization have currently drawn much attention to the design of new catalysts and optimization of the standard conditions. [38-40]



X=Br, Cl
M= Ni(II), Pd(II)

M= Fe(II), Fe(III), Co(II)
n=2 or 3

Scheme 1. Ethylene polymerization catalysts.

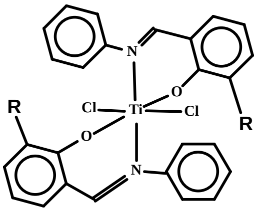


X=Br, Cl
M= Ni(II), Pd(II)

M= Fe(II), Fe(III), Co(II)
n=2 or 3

Scheme 2. Ethylene oligomerization catalysts.

The approach of transition metal complexes that contain nonsymmetric ligands with electronically flexible properties led to the discovery of a number of families of transition metal complexes featuring nonsymmetric $[O^{-},N]$, $[N^{-},N]$, [N, N], $[O^{-}, O]$,or $[O^{-},N,N]$ chelate ligands. Among these complexes, bis(phenoxyimine) zirconium and titanium complexes (Scheme 3) developed by the Fujita group[41-48] in the late 1990s are particularly useful for the preparation of a variety of polyolefinic materials that exhibit unique microstructures.



Scheme 3. Bis(phenoxyimine) titanium chloride (FI) complex.

By the 1980s, it appeared that the development of heterogeneous catalysts was maturing rapidly. Shortly after the synthesis of the first group 4 metallocene complexes by Wilkinson[49] in 1953, the use of these compounds as catalysts was tested. Mixtures of Cp_2TiCl_2 and $AlClEt_2$ were found to polymerize ethylene with comparatively moderate activities; propene was not polymerized[50,51] by these systems. An important further development began with the unexpected observation that, although Ziegler catalysts are very sensitive to hydrolysis, traces of water actually increased the rate of polymerization, and the formation of aluminoxanes by partial hydrolysis of the aluminium alkyl compounds was suggested[52]. This phenomenon was investigated in details by Sinn, Kaminsky and co-workers who found that the normally inactive system Cp_2ZrMe_2 / $AlMe_3$ becomes highly active upon the addition of water[53]. The same effect is achieved when $AlMe_3$ is partially hydrolyzed to methylaluminoxane (MAO) before the addition of a transition metal complex.

Since then, specially designed metallocene complexes have proven to be excellent single-site catalysts for the polymerization of ethylene. The resulting polyolefin can be produced with a very high catalyst productivity[5,8,54,55]. The Cp_2ZrCl_2 / MAO system has a remarkable high activity in the polymerization of ethylene[56].

Research goals

It was the goal of this Ph.D. project to prepare new transition metal complexes with bidentate chelating ligands and to test their catalytic potentials toward ethylene polymerization and / or oligomerization.

The proposed ligands include

-1,2-bis(benzimidazole)s, 1,2-bis(benzothiazole)s, and 1,2-bis(benzoxazole)s.

-2-(benzimidazolyl)pyridine , 2-(benzoxazolyl)pyridine, and 2-(benzothiazolyl)pyridine.

-1,2-bis(N-allylbenzimidazolyl)methane, 1,2-bis(N-allylbenzimidazolyl)ethane, 1,2-bis(N-allylbenzimidazolyl)benzene, 2,6-bis(N-allylbenzimidazolyl)pyridine, and N-allyl-2(benzimidazolyl)pyridine.

-Titanium(IV), zirconium(IV) and vanadium(III) complexes should be prepared from the above mentioned ligand precursors and the catalytic activities should be tested towards ethylene polymerization after activation with methylaluminoxane (MAO).

-"Structure- property relation" studies should allow the design of tailored catalysts.

2. Synthesis of bis-benzimidazole titanium, zirconium, and vanadium complexes

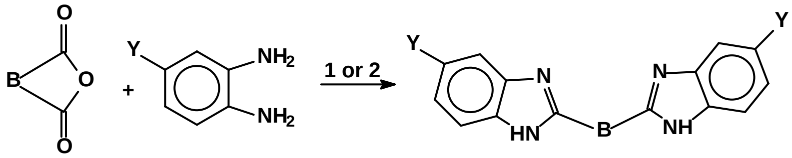
2.1. General remarks

Imidazole is a potential heterocyclic ligand with nitrogen as the donor atom. It is also a component of biologically important molecules[57]. Because of this, the coordination chemistry of related ligands has been the subject of numerous investigations[57]. Amongst them, the coordination behaviour of chelating benzimidazole type ligands has been studied by several research groups, some of them with an interest in mimicking biological activities[58-62]. 1,2-Bis-benzimidazoles and 2,6-bis(benzimidazolyl)pyridine are well known compounds together with their late transition metal complexes [63-73].

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[14,15,74]. For ethylene polymerization catalysis, only copper(II) complexes were reported[75]. 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[76]. 2,6-Bis(2-benzimidazolyl)pyridine zirconium dichloride / MAO polymerizes methylacrylate[77]. Herein we report the first zirconium, titanium and vanadium complexes of bis(benzimidazolyl), 1,2-bis(benzimidazolyl)benzene, 1,2-bis(benzimidazolyl)-ethane, 1,1-bis(benzimidazolyl)methane, and 1,2-bis(benzimidazolyl)-4-methylbenzene and their behaviour towards ethylene polymerization after activation with methylaluminoxane (MAO).

2.2. Synthesis of the bis(benzimidazoles) 1-14

The compounds **1-14** were synthesized via condensation reactions of di-carboxylic acids or acid anhydrides and substituted or unsubstituted o-phenylenediamine, in a preheated polyphosphoric acid[73] or by refluxing the reactants in 4 N hydrochloric acid [78-80] (see Scheme 4). The bis(benzimidazole)s were insoluble in all organic solvents except DMSO. Both methods are suitable for bis(benzimidazole)s, but the first method gives better yields.



1= polyphosphoric acid, 175°C
2= 4N HCl, reflux, 10h
B= 0, CH_2, CH_2CH_2, 1,2-phenylene , 4-methyl-1,2-phenylene
Y= H, CH_3, Cl

Scheme 4. Synthesis of ligand precursors **1-14.**

Table 1. The synthesized bis(benzimidazolyl) ligand precursors**1-14.**

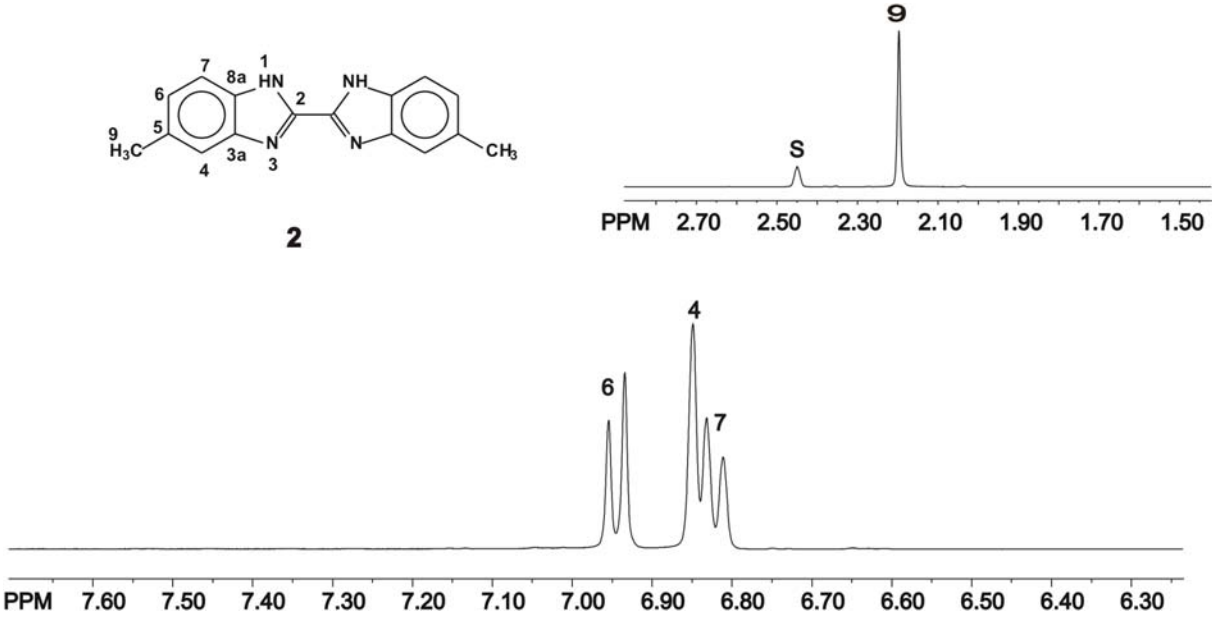
Compound No.	**Bridging unit (B)**	**Y**
1	-	H
2	-	CH_3
3	CH_2	H
4	CH_2	CH_3
5	CH_2	Cl
6	CH_2CH_2	H
7	CH_2CH_2	CH_3
8	CH_2CH_2	Cl
9	1,2-phenylene	H
10	1,2-phenylene	CH_3
11	1,2-phenylene	Cl
12	4-methyl-1,2-phenylene	H
13	4-methyl-1,2-phenylene	CH_3
14	4-methyl-1,2-phenylene	Cl

2.3. Characterization of the compounds 1-14

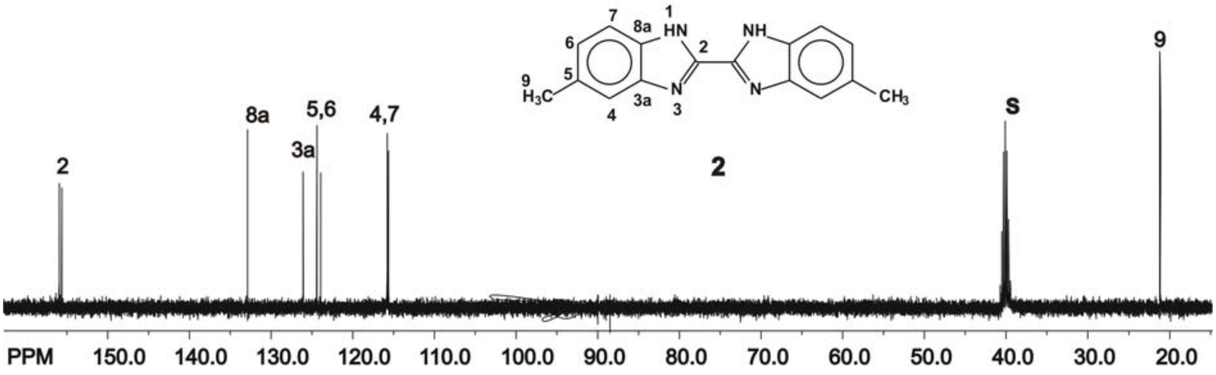
2.3.1. NMR spectroscopy

The ligand precursors were characterized by NMR spectroscopy using DMSO-D_6 as solvent. Table 2 includes the ^{1}H and ^{13}C NMR data for compounds **1-14.** For example, the ^{1}H NMR spectrum of compound **2** (see Scheme 5) shows four signals at δ = 6.93 ppm [d,2H, $J_{H,H}$ = 8.1 Hz] assigned to aromatic protons H6, the singlet at δ = 6.85 ppm corresponds to two protons H4. At δ = 6.82 ppm [d,2H, $J_{H,H}$ = 8.1 Hz] assigned to H7, and the signal upfield at δ = 2.20 ppm assigned to the six protons of the methyl groups (H9).

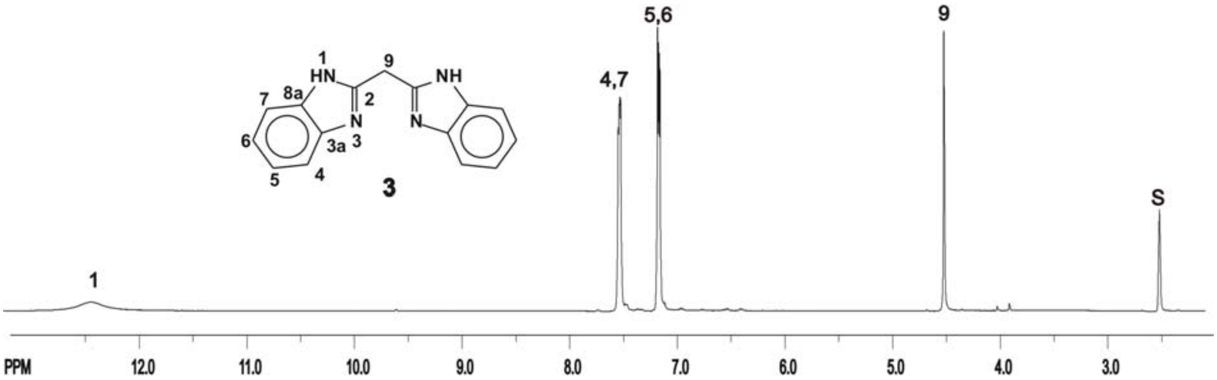
The ^{13}C NMR spectrum of compound **2** (see Scheme 6) shows nine signals. The two signals downfield at δ = 155.9 ppm and at δ = 155.6 ppm correspond to the carbon atoms 2 respectively, due to hindered rotation resulting from the N-H-N bond formation. Each of the six signals at δ = 132.9, 126.1, 124.4, 123.2, 115.8 and 115.6 ppm corresponds to two carbon atoms (8a, 3a, 5, 6, 4 and 7 respectively) of the aromatic rings. The methyl group carbon atoms (C9) appear upfield at δ = 21.2 ppm.



Scheme 5. ^{1}H NMR spectrum of compound **2.**



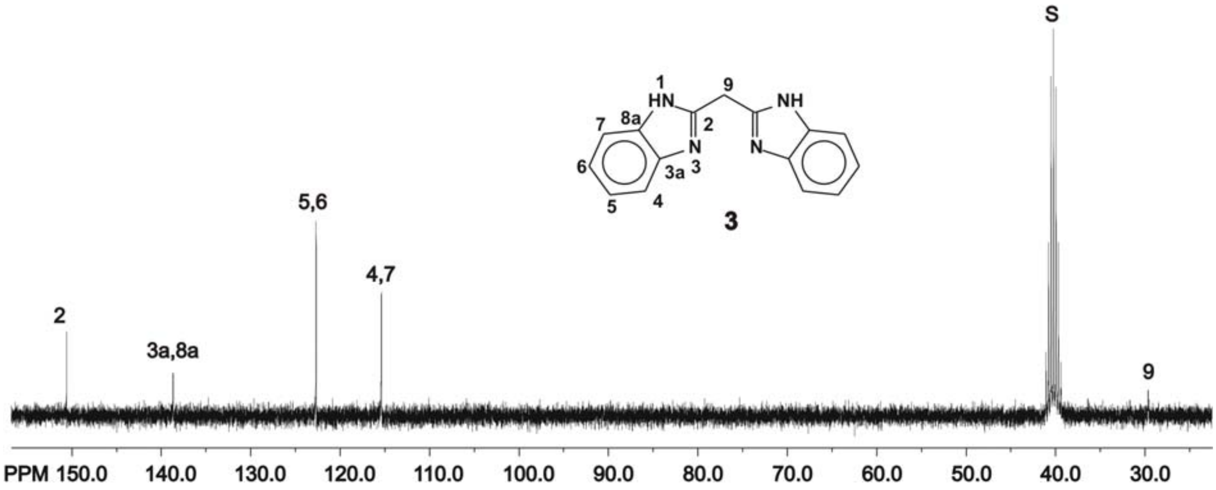
Scheme 6. ^{13}C NMR spectrum of compound **2.**



Scheme 7. ^{1}H NMR spectrum of compound **3.**

The ^{1}H NMR spectrum of compound **3** (Scheme 7) shows four sets of resonance signals. The one downfield at δ =12.41 ppm is assigned to the NH protons, while the multiplet signal at δ = 7.49-7.46 ppm corresponds to four aromatic protons of the phenyl rings (H4,7). The signal at δ = 7.12- 7.10 ppm is assigned to four protons H5 and H6. The methylene protons appear as a singlet at δ = 4.46 ppm.

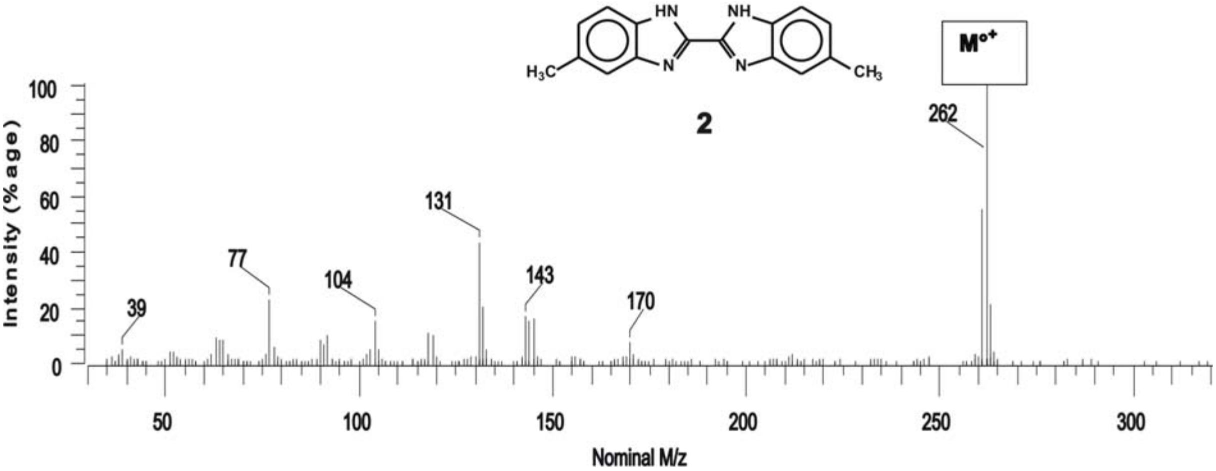
The ^{13}C NMR spectrum of compound **3** (see Scheme 8) reveals five signals which can be assigned as follows: at δ = 150.8 ppm the imino carbon atoms appear (C2). The signal at δ = 138.4 ppm represents four carbon atoms of the aromatic rings (C3a and C8a), the signal at δ =122.9 ppm corresponds to four carbon atoms of the phenyl ring (C5 and C6). The signal at δ =115.2 ppm can be assigned to the four carbon atoms C4 and C7, while at δ = 29.8 ppm the methylene carbon atoms appear. The NMR data for the other compounds are given in Table 2.



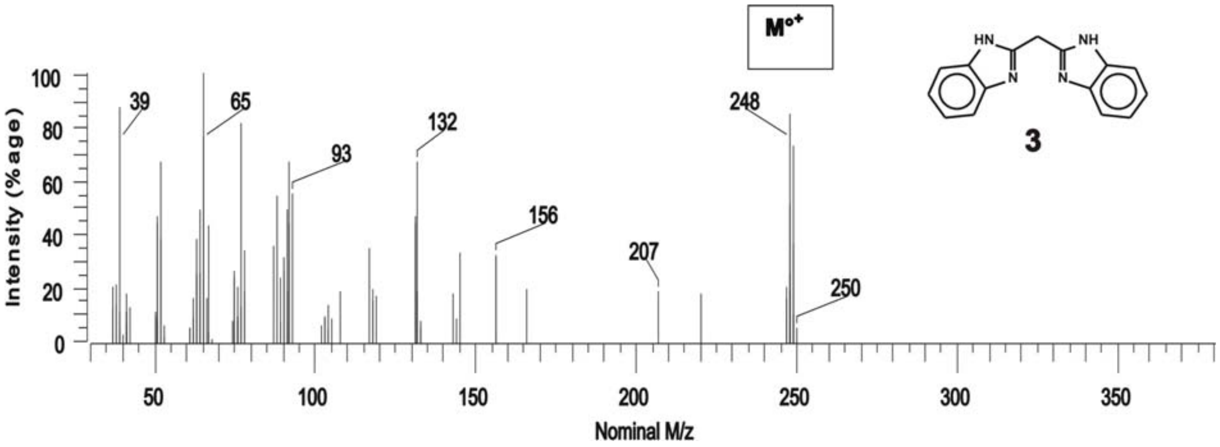
Scheme 8. ^{13}C NMR spectrum of compound **3.**

2.3.2. Mass spectroscopy

The ligand precursors were also characterized by their mass spectra. The mass spectrum of compound **2** (see Scheme 9), shows the molecular ion peak m/z = 262 and m/z = 170 ($M^{\circ+}$-$CH_3C_6H_3$). The ion with the mass m/z = 131 can be explained by the loss of one benzimidazole unit. Scheme 10 shows the mass spectrum of compound **3**. The peak with m/z = 248 represents the molecular ion peak, m/z = 156 is obtained by loss of one phenylene group. The data for the other compounds are given in Table.2.

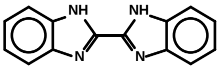
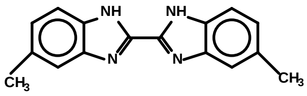
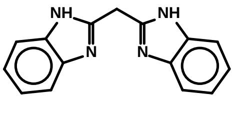
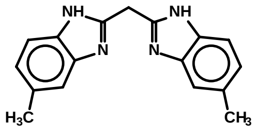
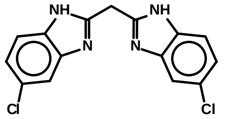
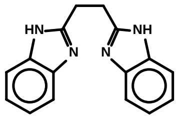
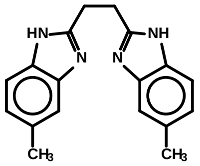


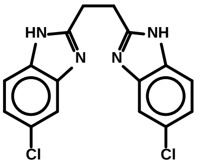
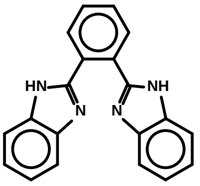
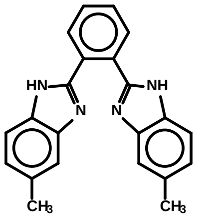
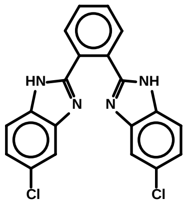
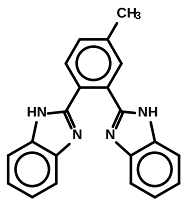
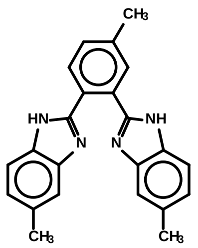
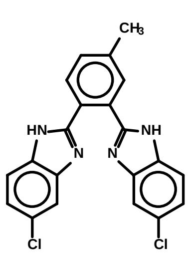
Scheme 9. Mass spectrum of compound **2.**



Scheme 10. Mass spectrum of compound **3.**

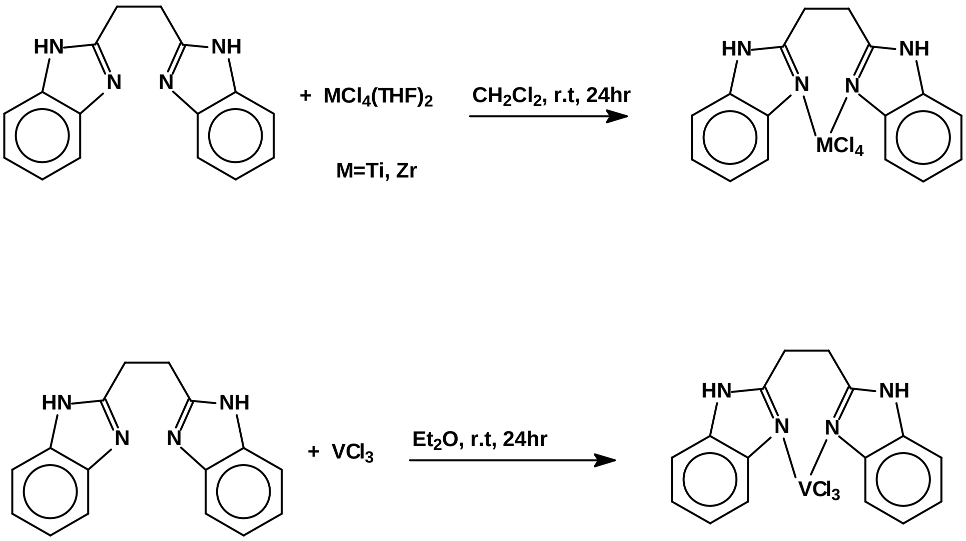
Table 2. NMR and mass spectroscopic data of compounds **1-14.**

No	**Compound**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**Mass m/z (%)**
1		7.11- 6.99(m,8H)	156.0, 126.4, 123.8, 116.0	234 M$^{\circ+}$ (100)
2		6.99-6.96(m,2H), 6.87-6.84(m,4H), 2.23(s,6H,CH_3)	156.0, 155.6, 132.9, 126.1, 124.4, 123.2, 115.8, 115.6, 21.2	262 M$^{\circ+}$ (100)
3		12.41(s,2H, NH), 7.46(m,4H), 7.11(m,4H), 4.43(s,2H,CH_2)	150.8, 138.4 122.9, 115.4, 29.8	248 M$^{\circ+}$ (100)
4		7.32(d,2H), 7.23(s,2H), 6.91(d,2H), 4.35(s,2H,CH_2), 2.33(s,6H,CH_3)	150.6, 139.2 137.9, 131.2, 123.5, 115.3, 114.7, 30.0, 21.9	276 M$^{\circ+}$ (100)
5		7.54(s,2H), 7.48(d,2H), 7.14(d,2H), 4.46(s,2H,CH_2)	n.d.	316 M$^{\circ+}$ (100)
6		7.57 (d,4H), 7.26 (t,4H), 3.56(s,4H,2CH_2)	153.8, 135.4, 124.3, 114.6, 25.4	262 M$^{\circ+}$ (100)
7		7.31 (d,2H), 7.22(s,2H),) 6.90 (d,2H), 3.51 (s,4H,CH_2), 2.33(s,6H,CH_3)	154.2, 138.7, 137.4, 131.2, 123.5, 115.0, 114.5, 27.0, 21.9	290 M$^{\circ+}$ (100)

No	Compound	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
8		7.50 (s,2H), 7.44(d,2H), 7.09(d,2H), 3.36 (s,4H,2CH_2)	156.2, 140.6, 138.0, 126.3, 122.1, 116.2, 115.1 27.0	330 $M^{\circ+}$ (100)
9		7.88 (d,1H), 7.80(d,1H), 7.69(t,2H), 7.64(s,2H, N-H), 7.61(m,4H), 7.26(m,4H),	151.6, 137.9, 133.5, 131.9, 129.4, 123.5, 115.5	310 $M^{\circ+}$ (100)
10		8.05(s,2H), 7.78(s,2H,N-H), 7.63(s,2H), 7.56(d,2H), 7.35(s,2H), 7.00(d,2H), 2.37(s,6H,CH_3)	151.6, 139.0, 137.8, 132.2, 132.0, 130.4, 129.9, 115.9, 115.1, 22.0	338 $M^{\circ+}$ (100)
11		8.14 (s,2H), 7.61 (br,4H), 7.55 (d,2H), 7.12(d,2H)	154.3, 141.4, 138.9, 132.1, 130.4, 130.3, 126.6, 122.4, 117.1, 115.8	378 $M^{\circ+}$ (100)
12		9.67(s,2H,N-H), 7.97(d,1H), 7.92(s,1H), 7.56-7.51(m,4H), 7.48-7.46(d,1H), 7,18-7.15(m,4H), 2.40(s;3H,CH_2)	152.1,152.0,140.3, 132.6, 132.5, 131.1, 131.0 129.9, 127.3, 122.8, 122.7, 115.2, 21.5	324 $M^{\circ+}$ (100)
13		7.96(d,1H), 7.91(s,1H), 7.44-7.43(m,3H), 7.35(s,2H), 6.98(d,2H), 2.42(s,3H,CH_3), 2.36(s,6H,2CH_3)	151.7,151.6,140.1, 132.5, 132.2, 132.1, 132.0, 131.0, 129.7, 127.2, 124.3, 124.2, 116.3, 115.5, 22.0, 21.4	352 $M^{\circ+}$ (100)
14		8.09(d,1H), 8.04(s,1H), 7.62(d,2H), 7.56-7.53(m,2H), 7.36(d,1H), 7.10(d,2H), 2.38(s,3H,CH_3)	155.0,155.1, 141.7,141.6, 139.2,139.1, 132.5,132.1, 130.8,130.3, 127.6,126.3,126.2 122.2,122.1 117.0,116.9, 115.7,115.6, 21.4	392 $M^{\circ+}$ (100)

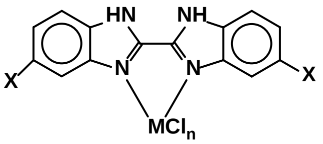
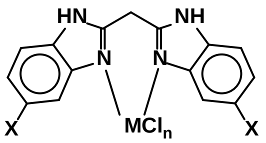
2.4. Synthesis of the complexes 15-56

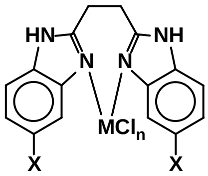
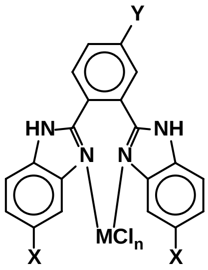
The transition metal complexes **15-56** were synthesized according to Scheme 11, by dissolving the metal chloride (in case of V(III) complexes) or the tetrahydrofuran adducts of zirconium tetrachloride or titanium tetrachloride and the ligand in an appropriate solvent and stirring the mixture over night. The complexes formed in a 1:1 metal: ligand ratio and were obtained in quantitative yields. All other complexes were synthesized in a similar way.



Scheme 11. General synthesis of complexes **15-56;** the figure exemplarily shows the synthesis of complexes **30-38**

Table 3. Bis – benzimidazole titanium, zirconium, and vanadium complexes **15-56.**

Structure	No.	X	Y	M
	**15**	H	-	Ti
	16	H	-	Zr
	17	H	-	V
	18	CH_3	-	Ti
	19	CH_3	-	Zr
	20	CH_3	-	V
	**21**	H	-	Ti
	22	H	-	Zr
	23	H	-	V
	24	CH_3	-	Ti
	25	CH_3	-	Zr

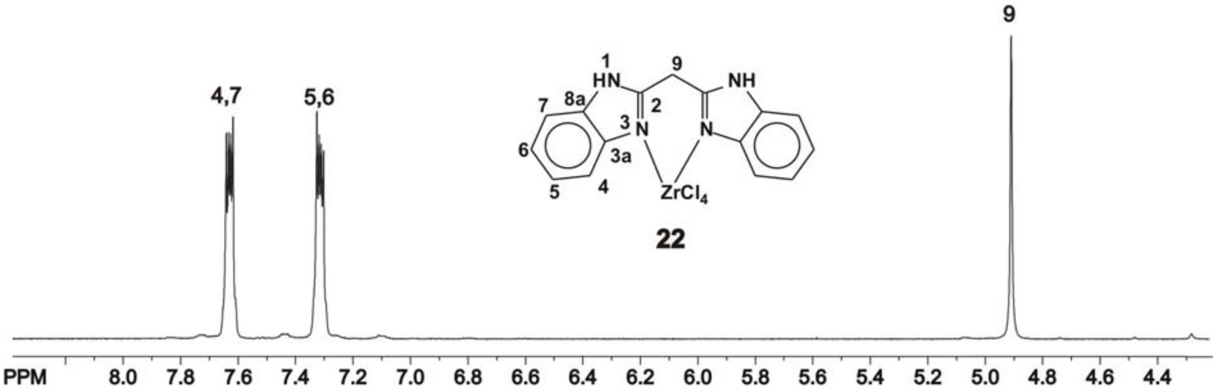
Structure	No.	X	Y	M
	26	CH_3	-	V
	27	Cl	-	Ti
	28	Cl	-	Zr
	29	Cl	-	V
	**30**	H	-	Ti
	31	H	-	Zr
	32	H	-	V
	33	CH_3	-	Ti
	34	CH_3	-	Zr
	35	CH_3	-	V
	36	Cl	-	Ti
	37	Cl	-	Zr
	38	Cl	-	V
	**39**	H	H	Ti
	40	H	H	Zr
	41	H	H	V
	42	CH_3	H	Ti
	43	CH_3	H	Zr
	44	CH_3	H	V
	45	Cl	H	Ti
	46	Cl	H	Zr
	47	Cl	H	V
	48	H	CH_3	Ti
	49	H	CH_3	Zr
	50	H	CH_3	V
	51	CH_3	CH_3	Ti
	52	CH_3	CH_3	Zr
	53	CH_3	CH_3	V
	54	Cl	CH_3	Ti
	55	Cl	CH_3	Zr
	56	Cl	CH_3	V

2.5. Spectroscopic characterization of the transition metal complexes 15-56

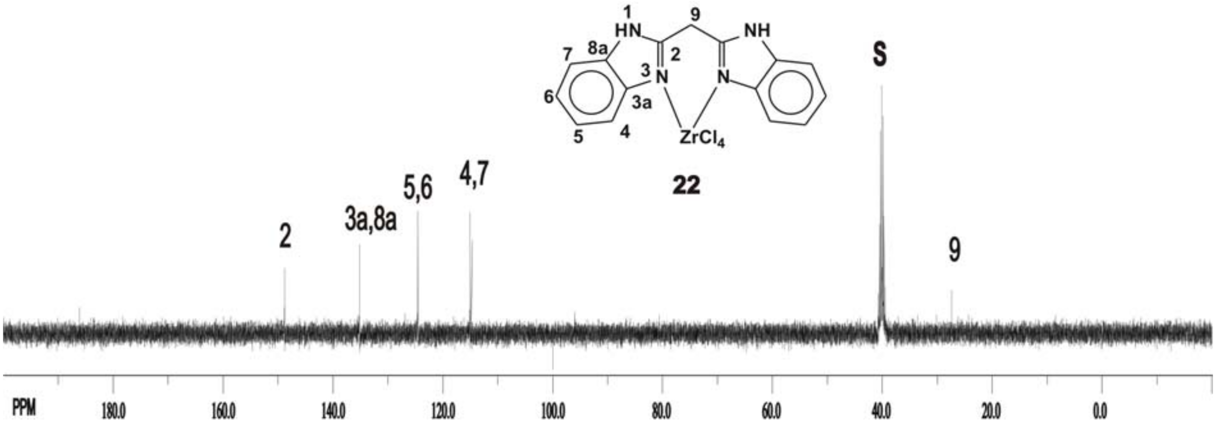
2.5.1. ^{1}H NMR and ^{13}C NMR spectroscopy

The titanium(IV), and zirconium(IV) complexes of the ligands **1-14** were characterized by their ^{1}H NMR and ^{13}C NMR spectra. For the V(III) complexes, NMR spectra are not informative due to their paramagnetism. The ^{1}H NMR spectrum of complex **22** shows three signals, the multiplet at δ = 7.64 ppm, and 7.33 ppm (each corresponding to four aromatic protons, see Scheme 12), while the protons of the bridging CH_2 group appear as singlet at δ = 4.91 ppm. The N-H protons for all of the above mentioned compounds appear as very small signals downfield at δ value ranges between 8.50 ppm and 12.00 ppm.

The ^{13}C NMR spectrum of complex **22** (see Scheme 13) shows five signals: at δ = 148.9 ppm (C2) for the imidazole carbon atoms, at δ = 135.4 ppm for (C3a,C8a) and the signal at δ = 124.4 ppm can be assigned to C5 and C6. The carbon atoms C4, and C7 appear at δ = 115.1 ppm, and at δ = 27.5 ppm the bridging CH_2 group (C9) can be detected.



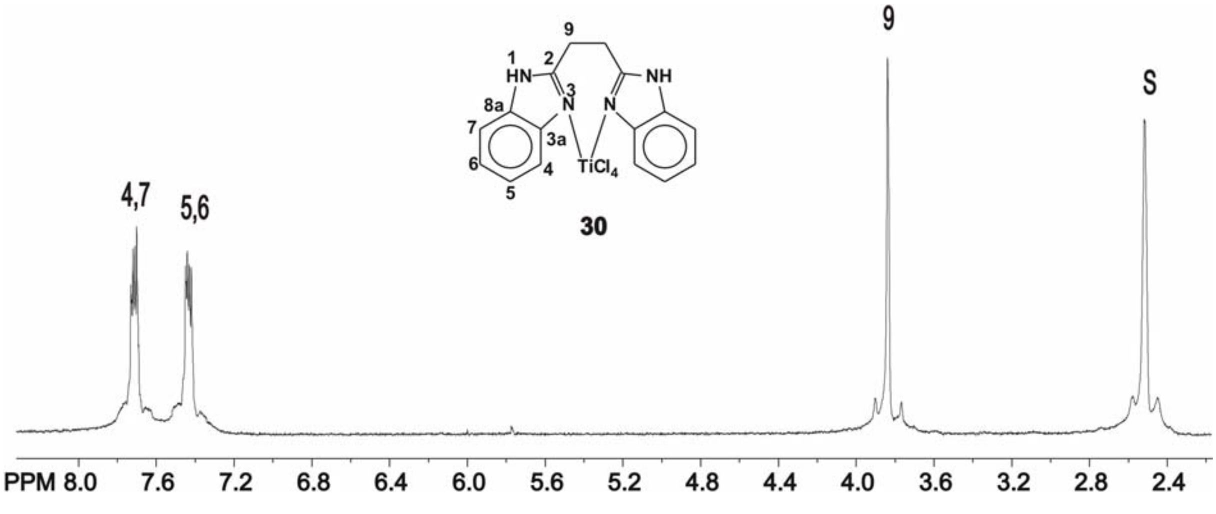
Scheme 12. ^{1}H NMR spectrum of complex **22.**



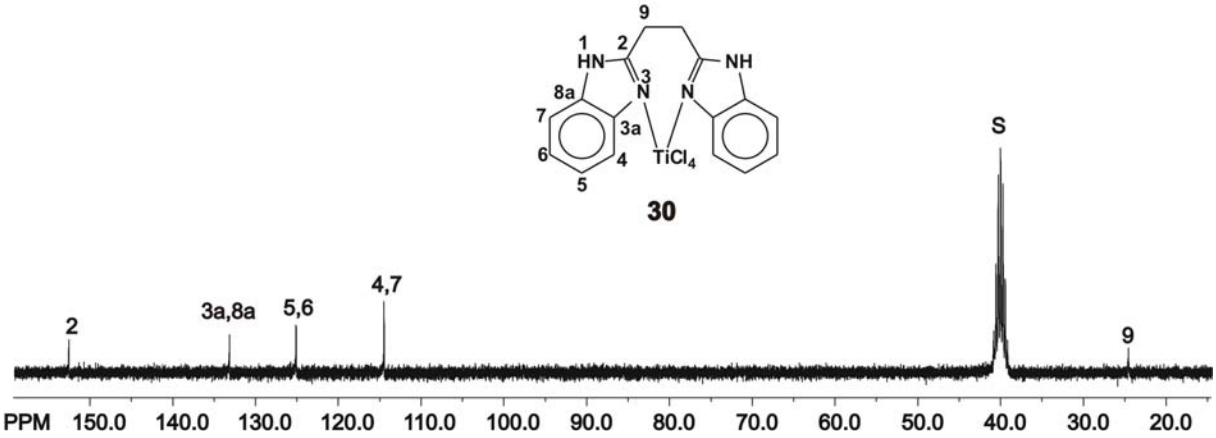
Scheme 13. ^{13}C NMR spectrum of complex **22.**

The ^{1}H NMR spectrum of complex **30** (see Scheme 14) shows three sets of resonance signals. The multiplet signal at δ = 7.76-7.70 ppm can be assigned to the aromatic protons (H 4, 7). The two aromatic protons H 5, 6 appear multiplet at δ = 7.50-7.43 ppm. The four protons of the ethylene bridging unit can be assigned at δ = 3.95 ppm.

Scheme 15 shows the ^{13}C NMR spectrum of complex **30**. Five set of signals were displayed. At δ = 152.5 ppm the two imino carbon atoms C2 appear, the signal at δ = 132.6 ppm corresponds to the carbon atoms C3a,C8a. At δ = 125.6 ppm C5 and C6 appear. The carbon atoms C4 and C7 appear at δ = 114.6 ppm. Finally the ethylene carbon atoms are found at δ = 25.4 ppm. The data for the other complexes are given in Table 4.



Scheme 14. ^{1}H NMR spectrum of complex **30.**

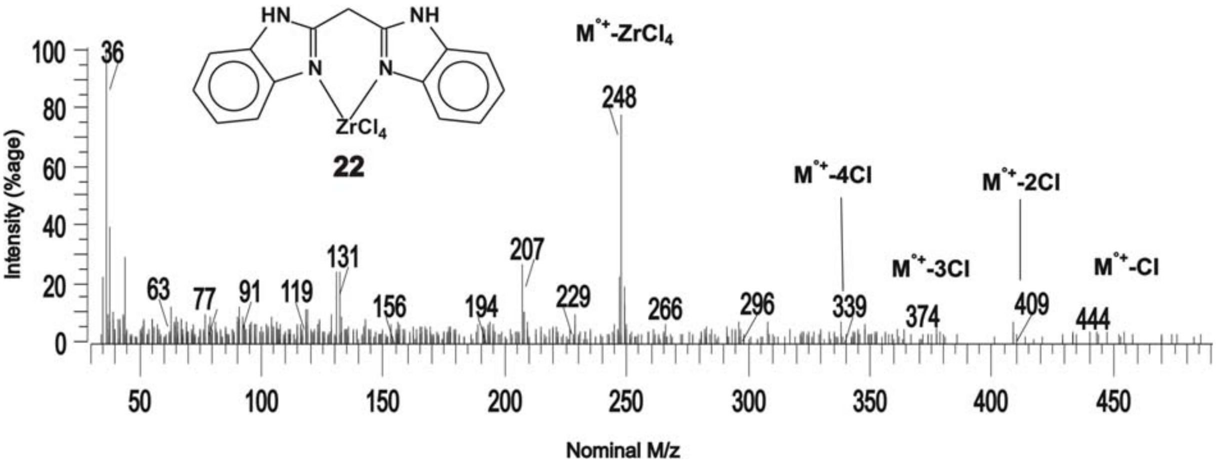


Scheme 15. ^{13}C NMR spectrum of complex **30.**

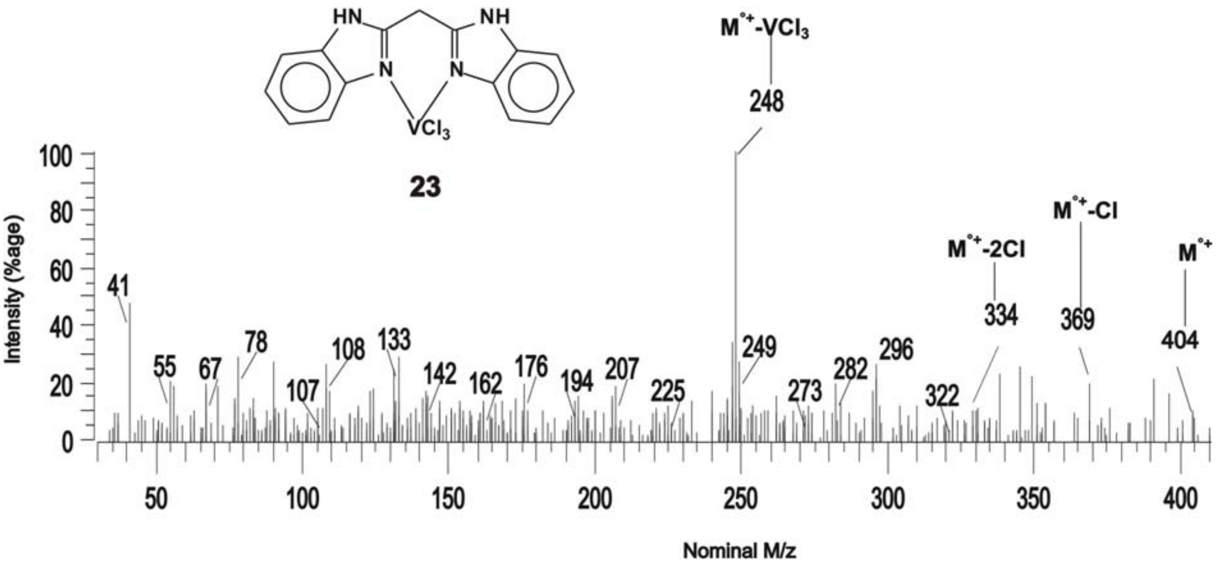
2.5.2. Mass spectroscopy

The complexes **15-56**, in addition to their NMR spectra, were also characterized by mass spectroscopy. The mass spectrum of complex **22** (Scheme 16) shows the molecular ion peak at m/z = 481. The ion resulting from the loss of one chloride has a mass of m/z = (447-451). The ion with the mass m/z = 340 can be explained with the loss of four chloride ions ($M^{\circ+}$-4Cl. The mass spectrum of complex **23** (see Scheme 17), for example, shows, the molecular ion peak, at m/z = 406 with a relatively low intensity. The peak at m/z = 368 corresponds to $M^{\circ+}$-Cl, and the peak at m/z = 338 can be assigned to $M^{\circ+}$-2Cl. The peak at m/z = 247 corresponds to the mass of the ligand. The mass spectrum of complex **29** (see Scheme 18) shows the molecular ion at m/z = 473, and the ion with the mass m/z = 401 corresponds to ($M^{\circ+}$-2Cl). The mass spectrum of complex **30** (Scheme 19) shows the molecular ion peak at m/z = 451, the loss of one chloride results in an ion with m/z = 419. The loss of three chlorides leads to the ion with m/z = 343 and the ion with m/z = 262 is representing the free ligand.

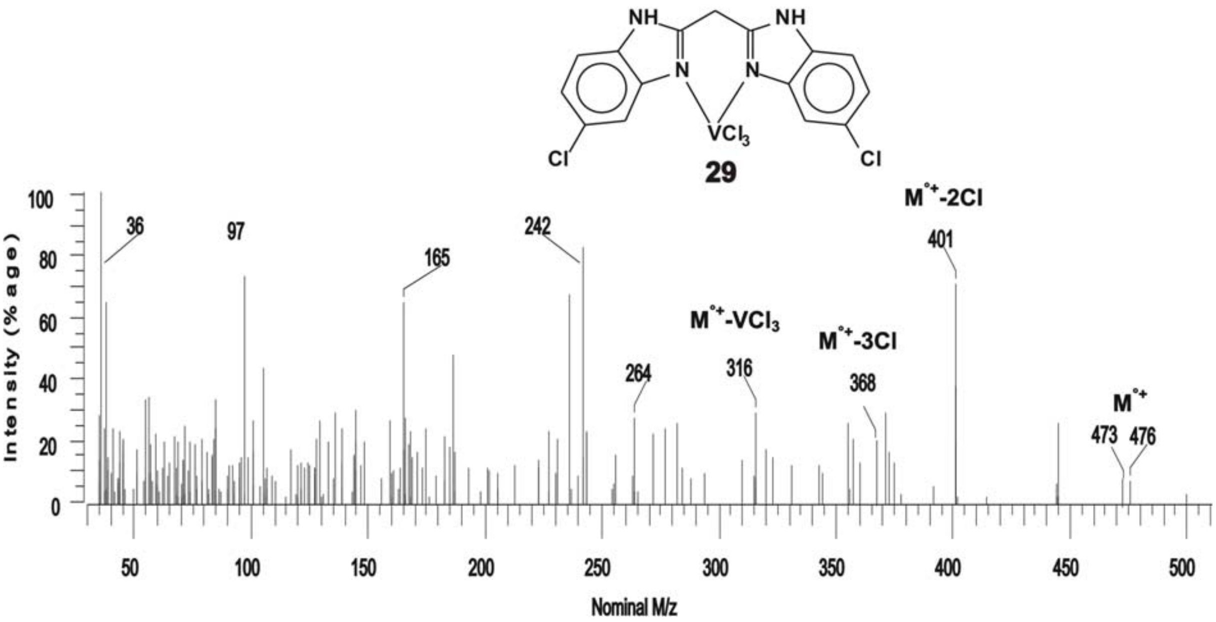
The most important feature revealed by the mass spectra of these complexes is that always the base peak is corresponding to the ligand mass. This can be attributed to the relatively weak dative bonds involved in the formation of such type of adduct. The data for all other complexes are given in Table 4.



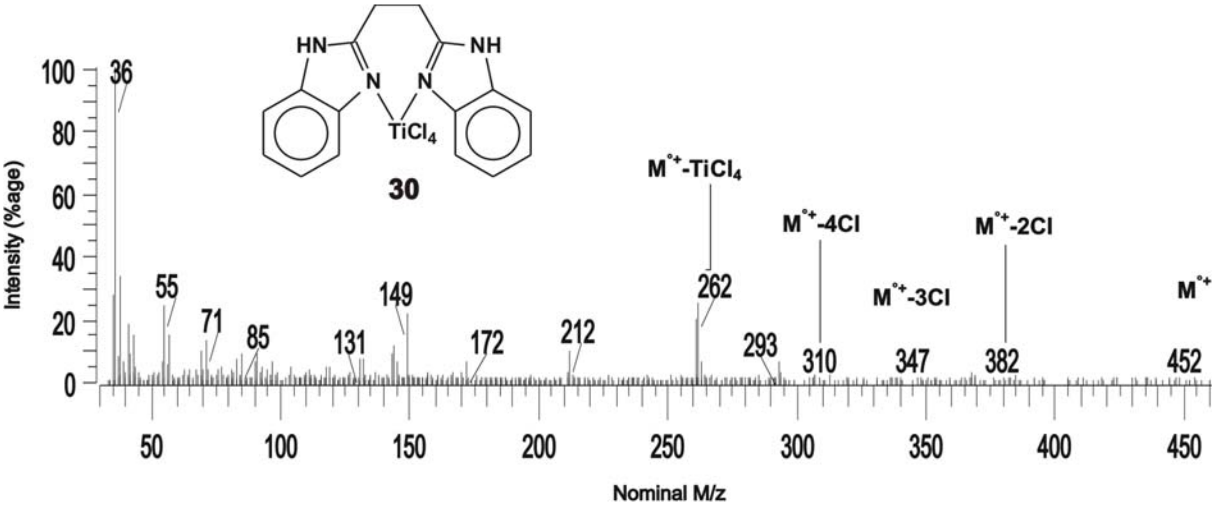
Scheme 16. Mass spectrum of complex **22.**



Scheme 17. Mass spectrum of complex **23.**

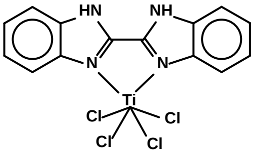
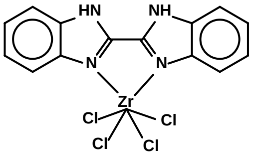
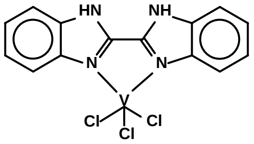
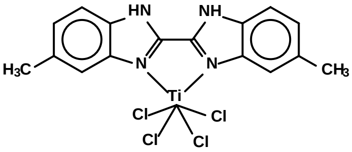
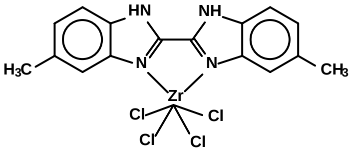
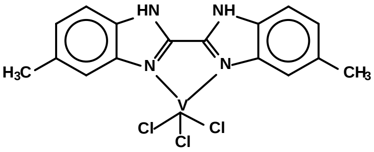


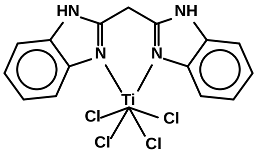
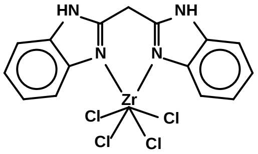
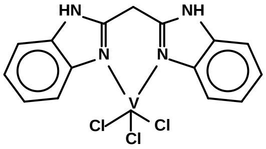
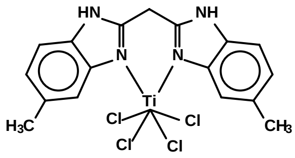
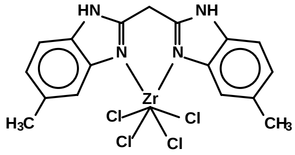
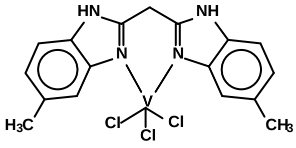
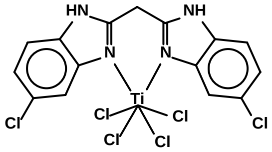
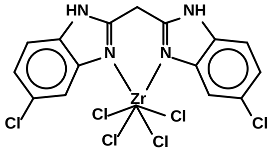
Scheme 18. Mass spectrum of complex **29.**

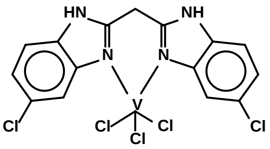
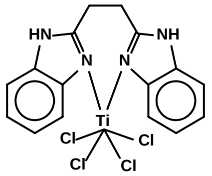
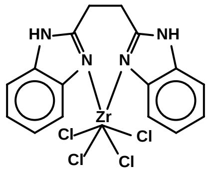
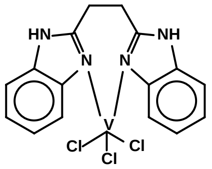
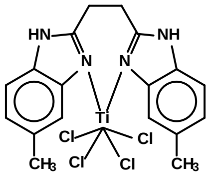
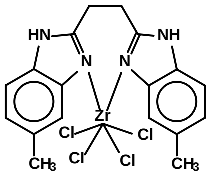
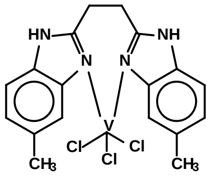


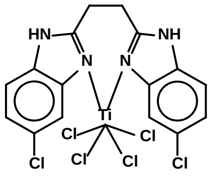
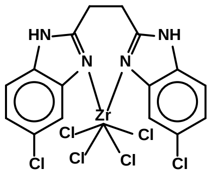
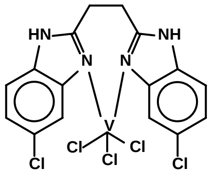
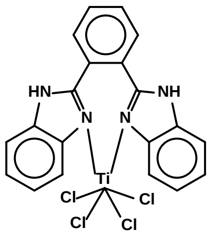
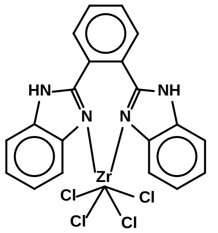
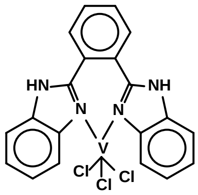
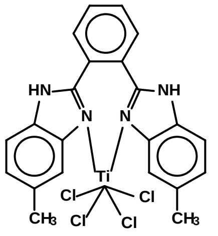
Scheme 19. Mass spectrum of complex **30.**

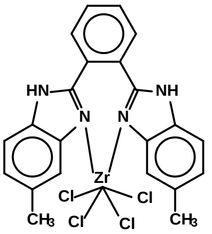
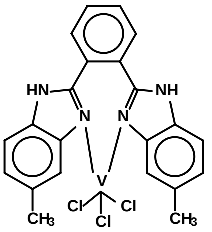
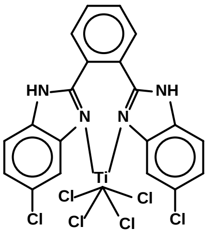
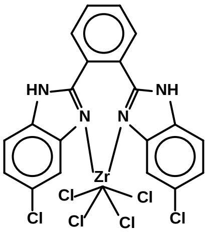
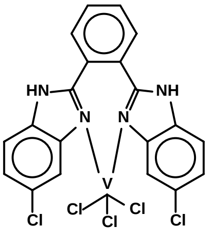
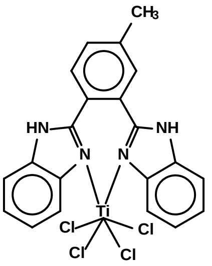
Table 4. NMR and Mass spectroscopic data of complexes **15-56**

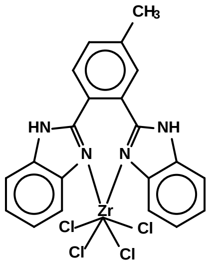
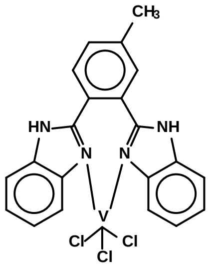
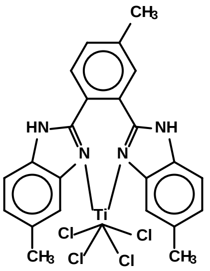
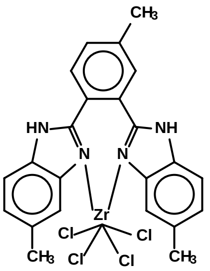
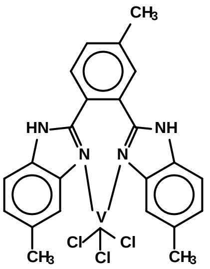
No.	**Complex**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**Mass m/z (%)**
15		7.40(d,4H), 7.15(t,4H)	156.1, 126.6, 123.8, 116.2	$425^{\circ+}$(2), 352 $M^{\circ+}$-2Cl (2), 317 $M^{\circ+}$-3Cl (10),234 $M^{\circ+}$-$TiCl_4$ (100)
16		7.18(d,4H), 7.04(t,4H)	156.2, 126.6, 124.0, 116.2	$467^{\circ+}$(5), 397 $M^{\circ+}$-2Cl (2), 361 $M^{\circ+}$-3Cl (10), 234 $M^{\circ+}$-$ZrCl_4$ (100)
17		n.d.	n.d.	$392^{\circ+}$(5), 323 $M^{\circ+}$-2Cl (2), 288 $M^{\circ+}$-3Cl (10), 234 $M^{\circ+}$-VCl_3 (50)
18		7.01(d,2H), 6.90(s,2H), 6.75(d,2H), 2.15(s,6H,2CH_3)	155.9, 155.6, 132.8, 126.1, 124.3, 123.9, 115.8, 21.2	452 $M^{\circ+}$(2), 437 $M^{\circ+}$-CH_3 (10), 381 $M^{\circ+}$-2Cl (2), 345 $M^{\circ+}$-3Cl (5), 309 $M^{\circ+}$-4Cl (5) 262 $M^{\circ+}$-$ZrCl_4$ (100)
19		7.06(d,2H), 6.97(s,2H), 6.82(d,2H), 2.17(s,6H, 2CH_3)	156.1, 155.8, 133.0, 126.2, 124.6, 124.1, 115.9, 21.3	495 $M^{\circ+}$, 478 $M^{\circ+}$-CH_3 (15), 423 $M^{\circ+}$-2Cl (2), 389 $M^{\circ+}$-3Cl (5), 352 $M^{\circ+}$-4Cl(5) 262 $M^{\circ+}$-$ZrCl_4$ (50)
20		n.d.	n.d.	420 $M^{\circ+}$(2), 405 $M^{\circ+}$-CH_3 (10), 349 $M^{\circ+}$-2Cl (2), 312 $M^{\circ+}$-3C l(5), 262 $M^{\circ+}$-VCl_3 (100)

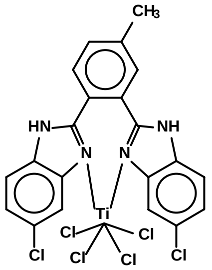
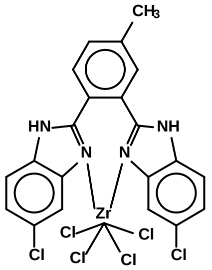
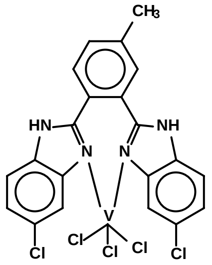
No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
21		7.52-7.49(m,4H), 7.52-7.14(m,4H), 4.55(s,2H,CH_2)	149.0, 135.4, 124.4, 115.1, 27.5	438 $M^{\circ+}$(1), 402 $M^{\circ+}$-Cl (2), 367 $M^{\circ+}$-2Cl (2), 248 $M^{\circ+}$-$TiCl_4$ (100)
22		7.63-7.62(m,4H), 7.33-7.30 (m,4H), 4.91(s,2H,CH_2)	150.6, 138.7, 122.6, 115.3, 29.6	481 $M^{\circ+}$(1), 444 $M^{\circ+}$-Cl (2), 407 $M^{\circ+}$-2Cl (1), 370 $M^{\circ+}$-3Cl (2), 336 $M^{\circ+}$-4Cl (1), 248 $M^{\circ+}$-$ZrCl_4$ (100)
23		n.d.	n.d.	406 $M^{\circ+}$(3), 368 $M^{\circ+}$-Cl (7), 334 $M^{\circ+}$-2Cl (10), 299 $M^{\circ+}$-3Cl (20), 248 $M^{\circ+}$-VCl_3 (100)
24		7.63(d,2H), 7.54(s,2H), 7.31(d,2H), 5.25(s,2H,CH_2), 2.42(s,6H,2CH_3)	146.3, 136.3, 132.3, 130.1, 127.8, 114.3, 114.1, 25.8, 21.8	466 $M^{\circ+}$(1), 428 $M^{\circ+}$-Cl(5), 393 $M^{\circ+}$-2Cl (5), 357 $M^{\circ+}$-3Cl (3), 319 $M^{\circ+}$-4Cl (2), 276 $M^{\circ+}$-$TiCl_4$ (100)
25		7.55(d,2H), 7.47(s,2H), 7.21(d,2H), 5.05 (s,2H,CH_2), 2.40(s,6H,2CH_3)	147.5, 135.0, 134.0, 132.2, 126.7, 114.6, 114.3, 26.6, 21.8	510 $M^{\circ+}$(2), 477 $M^{\circ+}$-Cl (5), 440 $M^{\circ+}$-2Cl (5), 405 $M^{\circ+}$-3Cl (2), 276 $M^{\circ+}$-$ZrCl_4$ (100)
26		n.d.	n.d.	433 $M^{\circ+}$(2), 397 $M^{\circ+}$-Cl (5), 360 $M^{\circ+}$-2Cl (10), 324 $M^{\circ+}$-3Cl (5), 276 $M^{\circ+}$-VCl_3 (100)
27		7.88(s,2H), 7.80(d,2H), 7.51(d,2H), 5.18(s,2H,CH_2)	149.3, 134.7, 132.6, 129.8, 125.9, 116.5, 114.9, 26.9	506 $M^{\circ+}$(3), 470 $M^{\circ+}$-Cl (2), 434 $M^{\circ+}$-2Cl (5), 397 $M^{\circ+}$-3Cl (10), 316 $M^{\circ+}$-$TiCl_4$ (100)
28		7.89(s,2H), 7.80(d,2H), 7.52(d,2H), 5.23(s,2H, CH_2)	149.1, 134.3, 132.2, 130.1, 126.1, 116.5, 114.8, 26.7	549 $M^{\circ+}$(2), 513 $M^{\circ+}$-Cl (5), 476 $M^{\circ+}$-2Cl (10), 440 $M^{\circ+}$-3Cl (5), 316 $M^{\circ+}$-$ZrCl_4$ (100)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
29		n.d.	n.d.	473 $M^{\circ+}$(5), 437 $M^{\circ+}$-Cl (2), 401 $M^{\circ+}$-2Cl (70), 368 $M^{\circ+}$-3Cl (10), 316 $M^{\circ+}$-VCl_3 (20)
30		7.76-7.70(m,4H), 7.50-7.43(m,4H), 3.95(s,4H,$2CH_2$)	152.5, 132.6, 125.6, 114.6, 24.5	452 $M^{\circ+}$(5), 416$M^{\circ+}$-Cl (2), 380 $M^{\circ+}$-2Cl (5), 343 $M^{\circ+}$-3Cl (10), 310 $M^{\circ+}$-4Cl (2), 262 $M^{\circ+}$-$TiCl_4$ (10)
31		7.73-7.71(m,4H), 7.45-7.42(m,4H), 3.84(s,4H,$2CH_2$)	152.7, 133.3, 125.3, 114.7, 24.7	495$M^{\circ+}$(2), 458$M^{\circ+}$-Cl (2), 422 $M^{\circ+}$-2Cl (5), 387 $M^{\circ+}$-3Cl (3), 351 $M^{\circ+}$-4Cl (2), 262 $M^{\circ+}$-$ZrCl_4$ (50)
32		n.d.	n.d.	420 $M^{\circ+}$(15), 385 $M^{\circ+}$-Cl (15), 343 $M^{\circ+}$-2Cl (10), 310 $M^{\circ+}$-4Cl (2), 262 $M^{\circ+}$-VCl_3 (80)
33		7.62(d,2H), 7.53(s,2H), 7.30(d,2H), 3.87(s,4H,$2CH_2$), 2.46(s,6H,$2CH_3$)	151.1, 136.3, 133.0, 130.0, 126.7, 114.7, 114.4, 24.7, 21.9	480 $M^{\circ+}$(2), 443 $M^{\circ+}$-Cl (2), 408 $M^{\circ+}$-2Cl (5), 372 $M^{\circ+}$-3Cl (5), 336 $M^{\circ+}$-4Cl (2), 290 $M^{\circ+}$-$TiCl_4$ (100)
34		7.66(d,2H), 7.57(s,2H), 7.35(d,2H), 3.85(s,4H,$2CH_2$), 2.48 (s,6H,$2CH_3$)	151.6, 136.0, 132.3, 130.0, 127.5, 114.1, 114.0, 24.4, 21.8	523 $M^{\circ+}$(2), 487 $M^{\circ+}$-Cl (2), 451 $M^{\circ+}$-2Cl (5), 414 $M^{\circ+}$-3Cl (3), 377 $M^{\circ+}$-4Cl (2), 290 $M^{\circ+}$-$ZrCl_4$ (100)
35		n.d.	n.d.	447 $M^{\circ+}$(5), 411 $M^{\circ+}$-Cl (5), 376 $M^{\circ+}$-2Cl (2), 340 $M^{\circ+}$-3Cl (2), 290 $M^{\circ+}$-VCl_3 (100)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
36		7.84(s,2H), 7.78(d,2H), 7.50(d,2H), 3.78(s,4H,2CH_2)	154.3, 135.5, 133.6, 130.3, 125.0, 116.2, 115.0, 25.7	518 $M^{\circ+}$(1), 485 $M^{\circ+}$-Cl (5), 450 $M^{\circ+}$-2Cl (1), 413 $M^{\circ+}$-3Cl (1),377 $M^{\circ+}$-4Cl (3) 330 $M^{\circ+}$-$TiCl_4$ (100)
37		7.83(s,2H), 7.75(d,2H), 7.48(d,2H), 3.76(s,4H,2CH_2)	154.4, 134.6, 132.5, 129.7, 125.5, 116.2, 114.7, 24.9	564 $M^{\circ+}$(1), 528 $M^{\circ+}$-Cl (5), 493 $M^{\circ+}$-2Cl (2), 456 $M^{\circ+}$-3Cl (3),419 $M^{\circ+}$-4Cl (2) 330 $M^{\circ+}$-$ZrCl_4$ (100)
38		n.d.	n.d.	488 $M^{\circ+}$(2), 452 $M^{\circ+}$-Cl (5), 415 $M^{\circ+}$-2Cl (2), 379 $M^{\circ+}$-3Cl (2), 330 $M^{\circ+}$-VCl_3 (100)
39		8.37(d,2H), 8.08(t,2H), 7.924-7.835(m,4H), 7.637-7.625(m,4H)	148.2, 134.0, 133.8, 133.6, 126.5, 125.1, 115.4	500 $M^{\circ+}$(1), 463 $M^{\circ+}$-Cl (2), 428 $M^{\circ+}$-2Cl (3), 394 $M^{\circ+}$-3Cl (5), 357 $M^{\circ+}$-4Cl (2), 310 $M^{\circ+}$-$TiCl_4$ (100)
40		8.28-8.25(dd,2H), 7.94(t,2H), 7.71-7.67(m,4H), 7.45-7.42(m,4H)	149.1, 135.0, 132.5, 126.2, 125.4, 115.3, 114.8	543 $M^{\circ+}$(1), 506 $M^{\circ+}$-Cl (1), 437 $M^{\circ+}$-3Cl (3), 400 $M^{\circ+}$-4Cl (5), 310 $M^{\circ+}$-$ZrCl_4$ (100)
41		n.d.	n.d.	467 $M^{\circ+}$(1), 430 $M^{\circ+}$-Cl (5), 393 $M^{\circ+}$-3Cl (2), 310 $M^{\circ+}$-VCl_3 (100)
42		8.18-8.16(dd,2H), 7.92-7.90(dd,2H), 7.54(d,2H), 7.44(s,2H), 7.24(d,2H), 2.40(s,6H,2CH_3)	147.7, 137.6, 133.2, 131.9, 129.6, 128.9, 127.6, 126.1, 114.8, 114.5, 21.8	530 $M^{\circ+}$(2), 492 $M^{\circ+}$-Cl (10), 454 $M^{\circ+}$-2Cl (5), 418 $M^{\circ+}$-3Cl (2), 338 $M^{\circ+}$-$TiCl_4$ (50)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
43		8.27(t,2H), 8.03(d,2H), 7.64(d,2H), 7.54(s,2H), 7.36(d,2H), 2.49(s,6H,2CH_3)	147.2, 136.2, 133.8, 133.5, 133.3, 131.8, 127.8, 124.7, 114.7, 114.43, 21.9	571 $M^{\circ+}$(1), 498 $M^{\circ+}$-2Cl (1), 464 $M^{\circ+}$-3Cl (1), 429 $M^{\circ+}$-4Cl (1), 338 $M^{\circ+}$-$ZrCl_4$ (100)
44		n.d.	n.d.	495 $M^{\circ+}$(2), 425 $M^{\circ+}$-2Cl (1), 388 $M^{\circ+}$-3Cl (1), 338 $M^{\circ+}$-VCl_3 (100)
45		8.22(d,2H), 7.92(t,2H), 7.74(s,2H), 7.69(d,2H), 7.43(d,2H)	151.0, 136.6, 134.5, 132.4, 132.1, 129.3, 126.6, 125.3, 116.8, 115.1	568 $M^{\circ+}$(1), 481 $M^{\circ+}$-2Cl-NH (2), 462 $M^{\circ+}$-3Cl (10), 426 $M^{\circ+}$-4Cl (2), 378 $M^{\circ+}$-$TiCl_4$ (100)
46		8.08(d,2H), 7.76(t,2H), 7.67(s,2H), 7.61(d,2H), 7.25(d,2H)	151.7, 137.7, 135.4, 131.9, 128.7, 127.7, 124.6, 123.4, 116.8, 115.3	611 $M^{\circ+}$(2), 541 $M^{\circ+}$-2Cl (3), 503 $M^{\circ+}$-3Cl (2), 467$M^{\circ+}$-4Cl (5), 378 $M^{\circ+}$-$ZrCl_4$ (100)
47		n.d.	n.d.	535 $M^{\circ+}$(1), 464 $M^{\circ+}$-2Cl (2), 428 $M^{\circ+}$-3Cl (5), 378 $M^{\circ+}$-VCl_3 (100)
48		8.13(d,1H), 7.70-7.67(m,4H), 7.45-7.44(m,6H), 2.51(s,3H,CH_3)	149.2, 143.1, 135.1, 134.5, 133.1, 132.7, 126.0, 125.5, 125.3, 122.9, 115.3, 115.2, 21.6	516 $M^{\circ+}$ (2), 443 $M^{\circ+}$-2Cl (2), 409 $M^{\circ+}$-3Cl (2), 372 $M^{\circ+}$-4Cl (2), 324 $M^{\circ+}$-$TiCl_4$ (40)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
49		8.13(d,1H), 7.69-7.63(m,4H), 7.42-7.39(dd,4H), 7.38(s,1H), 7.37(d,1H), 2,51(s,3H,CH_3)	149.8, 142.5, 135.9, 135.1, 132.5, 132.2, 127.0, 125.1, 124.8, 123.6, 115.4, 115.2, 21.6	557 $M^{\circ+}$(1) 542 $M^{\circ+}$-CH_3 (5), 414 $M^{\circ+}$-4Cl (20), 324 $M^{\circ+}$-$ZrCl_4$ (100)
50		n.d.	n.d.	481 $M^{\circ+}$(2) 466 $M^{\circ+}$-CH_3 (5), 445 $M^{\circ+}$-Cl (3), 374 $M^{\circ+}$-3Cl (3), 324 $M^{\circ+}$-VCl_3 (100)
51		8.27(d,2H), 7.92(d,1H), 7.74(d,2H), 7.63(s,2H), 7.45(d,2H), 2.65(s,6H,2CH_3), 2.61(s,3H,CH_3)	147.0, 146.9, 144.3, 136.6, 136.5, 134.7, 134.1, 133.6, 133.5, 131.6, 131.4, 129.9, 129.2, 128.1, 126.3, 124.2, 121.5, 114.8, 114.7, 114.5, 22.1, 21.9	542 $M^{\circ+}$ (2), 468 $M^{\circ+}$-2Cl (2), 433 $M^{\circ+}$-3Cl (3), 371 $M^{\circ+}$-4Cl -2CH_3 (3), 352 $M^{\circ+}$-$TiCl_4$ (100)
52		8.16(d,2H), 7.82(d,1H), 7.63(d,2H), 7.53(s,2H), 7.34(d,2H), 2.47(s,6H,2CH_3), 2.30(s,3H,CH_3)	147.6, 147.2 143.5, 135.8, 134.2, 133.7, 133.4, 133.2, 132.2, 131.8, 129.6, 128.9, 127.5, 126.0, 124.9, 122.0, 114.7, 114.6, 114.4, 114.3, 21.9, 21.6	585 $M^{\circ+}$ (2), 514 $M^{\circ+}$-2Cl (3), 478 $M^{\circ+}$-3Cl (5), 413 $M^{\circ+}$-4Cl -2CH_3 (3), 352 $M^{\circ+}$-$ZrCl_4$ (100)
53		n.d.	n.d.	511 $M^{\circ+}$ (10), 439 $M^{\circ+}$-2Cl (3), 403 $M^{\circ+}$-3Cl (5), 373 $M^{\circ+}$-3Cl -2CH_3 (3), 352 $M^{\circ+}$-VCl_3 (70)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
54		8.06(s,1H), 8.04 (s,2H) 7.70-7.61(m,4H), 7.39-7.34(m,2H), 2.45(s,3H,CH_3)	151.2, 142.7, 137.0, 136.3, 134.8, 134.1, 132.7, 132.5, 132.1, 132.1, 126.8, 125.9, 125.3, 125.1, 123.5, 116.7, 116.6, 115.2, 115.0, 21.5	582 $M^{\circ+}$(2), 565 $M^{\circ+}$-CH_3 (5), 545 $M^{\circ+}$-Cl (2), 508 $M^{\circ+}$-2Cl (2), 472 $M^{\circ+}$-3Cl (5), 458 $M^{\circ+}$-4Cl-CH_3 (5), 392 $M^{\circ+}$-$TiCl_4$ (100)
55		8.10(s,1H), 8.07 (s,2H), 7.75-7.64(m,4H), 7.42-7.37(m,2H), 2.51(s,3H,CH_3)	151.6, 142.4, 137.6, 136.9, 135.4, 134.7, 132.4, 132.0, 131.5, 128.9, 128.7, 127.3, 127.1, 124.9, 124.8, 116.8, 116.7, 115.3, 115.1, 21.6	626 $M^{\circ+}$(2), 611 $M^{\circ+}$-CH_3 (5), 590 $M^{\circ+}$-Cl (2), 553 $M^{\circ+}$-2Cl (2), 517 $M^{\circ+}$-3Cl (3), 469 $M^{\circ+}$-4Cl-CH_3 (5), 392 $M^{\circ+}$-$ZrCl_4$ (100)
56		n.d.	n.d.	550 $M^{\circ+}$(3), 535 $M^{\circ+}$-CH_3 (3), 514 $M^{\circ+}$-Cl (2), 478 $M^{\circ+}$-2Cl (5), 428 $M^{\circ+}$-3Cl-CH_3 (5), 392 $M^{\circ+}$-VCl_3 (100)

3. Synthesis of bis(benzothiazolyl) and bis(benzoxazolyl) complexes

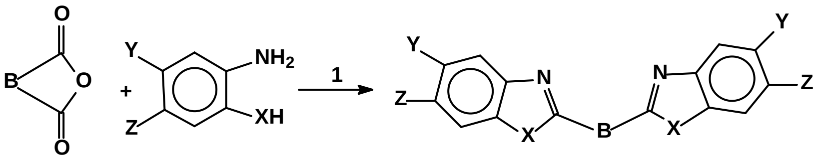
3.1. General remarks

Benzothiazole has a heterocyclic sulphur 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 their complexes with late transition metals are reported[63, 81-85]. Also, the nickel(II), cobalt(II) and copper(II) coordination chemistry of some tetradentate ligands involving benzothiazole functional groups has been published[86]. In all cases involving benzothiazoles as functional groups the ligands behave as nitrogen donors, except in a few cases involving bridging benzothiazole[87] 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[88,89] has been shown to behave as an N-3 donor in its complexes with manganese(II), iron(II) and nickel(II). Herein novel complexes of early transition metals (titanium(IV), zirconium(IV) and vanadium(III)) with 1,2-bis(benzothiazolyl, benzoxazolyl)benzene, 1,2-bis(benzothiazolyl, benzoxazolyl)ethane, 1,2-bis(benzothiazolyl, benzoxazolyl)methane and 2,6-bis(benzothiazolyl, benzoxazolyl)pyridine ligands are reported. After activation with methylaluminoxane (MAO) the complexes were used as catalysts for ethylene polymerization reactions.

3.2. Synthesis of the organic compound 57-75

The ligand precursors **57-75** were synthesized according to published procedures[90] using polyphosphoric acid as condensation medium (Scheme 20). Low product yields were obtained from the reaction of oxalic acid dihydrate and malonic acid with amino-thiophenole, most probably due to a side reaction which resulted in the formation of compound **127**, which is fully characterized as bis-(2-aminophenyl)disulphide. The ^{1}H NMR spectrum of **127** (Scheme 21) shows five sets of signals. The triplet at δ = 7.03 ppm [$J_{H,H}$ = 7.4 Hz] can be assigned to two aromatic protons (H4), the doublet at δ = 6.96 ppm [$J_{H,H}$ = 7.4 Hz] is assigned to two protons H3, and the doublet at δ = 6.68 ppm [$J_{H,H}$ = 7.4 Hz] can be assigned to H6. The triplet at δ = 6.38 ppm [$J_{H,H}$ = 7.4 Hz] corresponds to H5. At δ = 5.35 ppm the amino protons (H7) are located.

The ^{13}C NMR of compound **127** (Scheme 22) shows six signals, each signal is equivalent to two aromatic carbon atoms. The signal at δ = 150.7 ppm corresponds to C2, the signal at δ = 135.9 ppm is assigned to C4. The signal at δ = 132.0 ppm can be assigned to C1, the signal at δ = 117.1 ppm assigned to C5. Finally, the signals at δ = 116.9 and 115.1 ppm can be assigned to C6 and C3.



1= polyphosphoric acid, 175°C

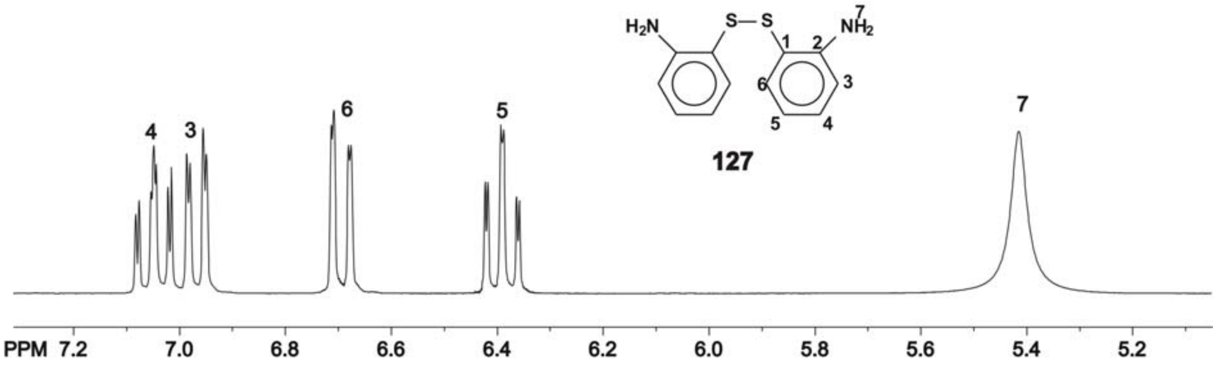
B= 0, CH_2, CH_2CH_2, 1,2-phenylene, 4-methyl-1,2-phenylene

X=O,S

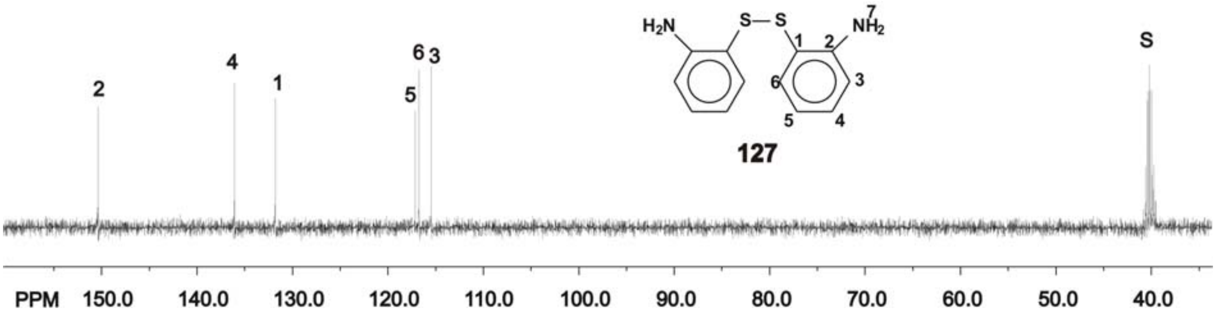
Y= H, CH_3

Z=H,CH_3

Scheme 20. Synthesis of bis-(benzothiazole) and bis-(benzoxazole) compounds.

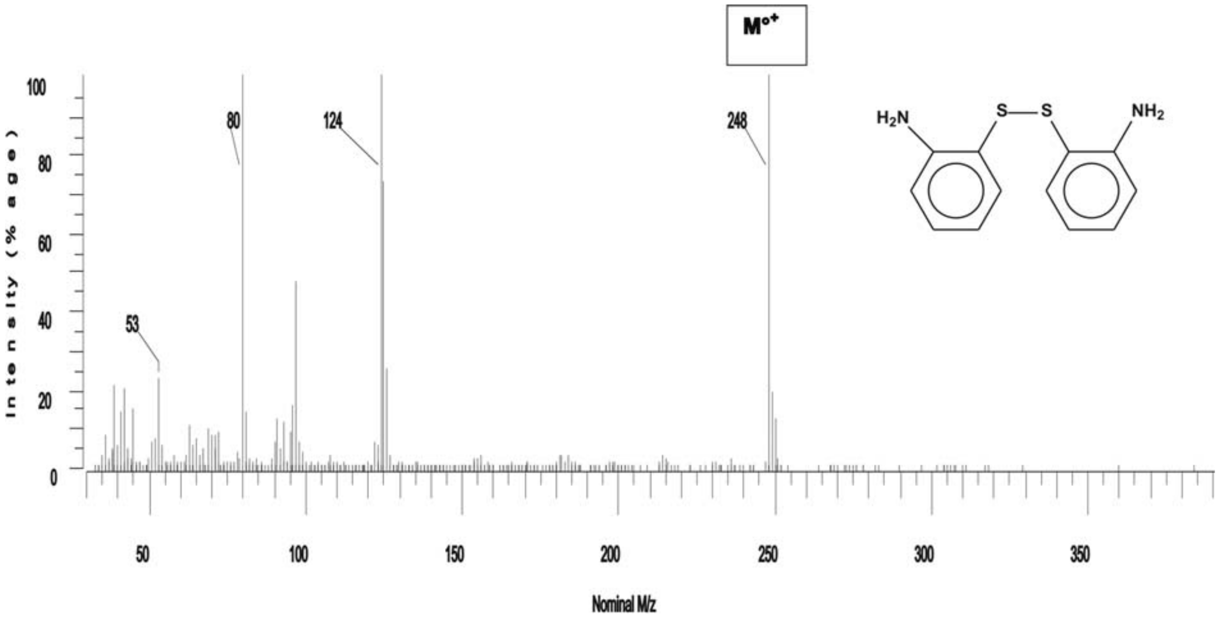


Scheme 21. ^{1}H NMR spectrum of compound **127.**



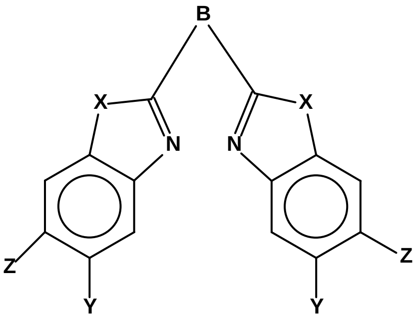
Scheme 22. ^{13}C NMR spectrum of compound **127.**

The mass spectrum of compound **127** (see Scheme 23), shows the molecular ion peak at m/z = 248.



Scheme 23. Mass spectrum of compound **127.**

All attempts to condense oxalic acid dihydrate with 2-aminophenol and methyl substituted 2-amino phenols failed.



X=S,O, Y and Z = H, CH_3

Table 5. The synthesized bis-benzothiazole and bis-benzoxazole compounds.

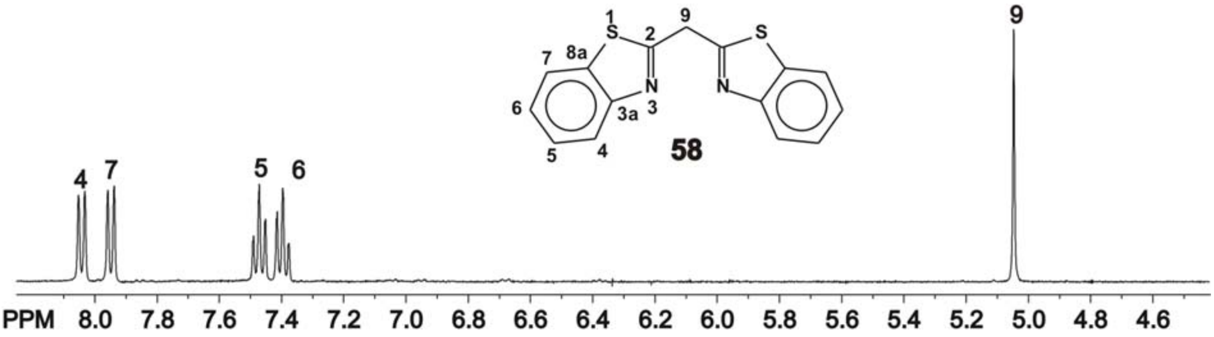
No.	Bridging unit (B)	X	Y	Z
57	-	S	H	H
58	CH_2	S	H	H
59	CH_2CH_2	S	H	H
60	1,2-phenylene	S	H	H
61	4-Me-1,2-phenylene	S	H	H
62	2,6-pyridyl	S	H	H
63	-	O	H	H
64	CH_2	O	H	H
65	CH_2	O	CH_3	H
66	CH_2	O	H	CH_3
67	CH_2CH_2	O	H	H
68	CH_2CH_2	O	H	CH_3
69	CH_2CH_2	O	CH_3	H
70	1,2-phenylene	O	H	H
71	1,2-phenylene	O	CH_3	H
72	1,2-phenylene	O	H	CH_3
73	4-Me-1,2-phenylene	O	H	H
74	2,6-pyridyl	O	H	H
75	2,6-pyridyl	O	CH_3	H

3.3. Characterization of the organic compounds 57-75

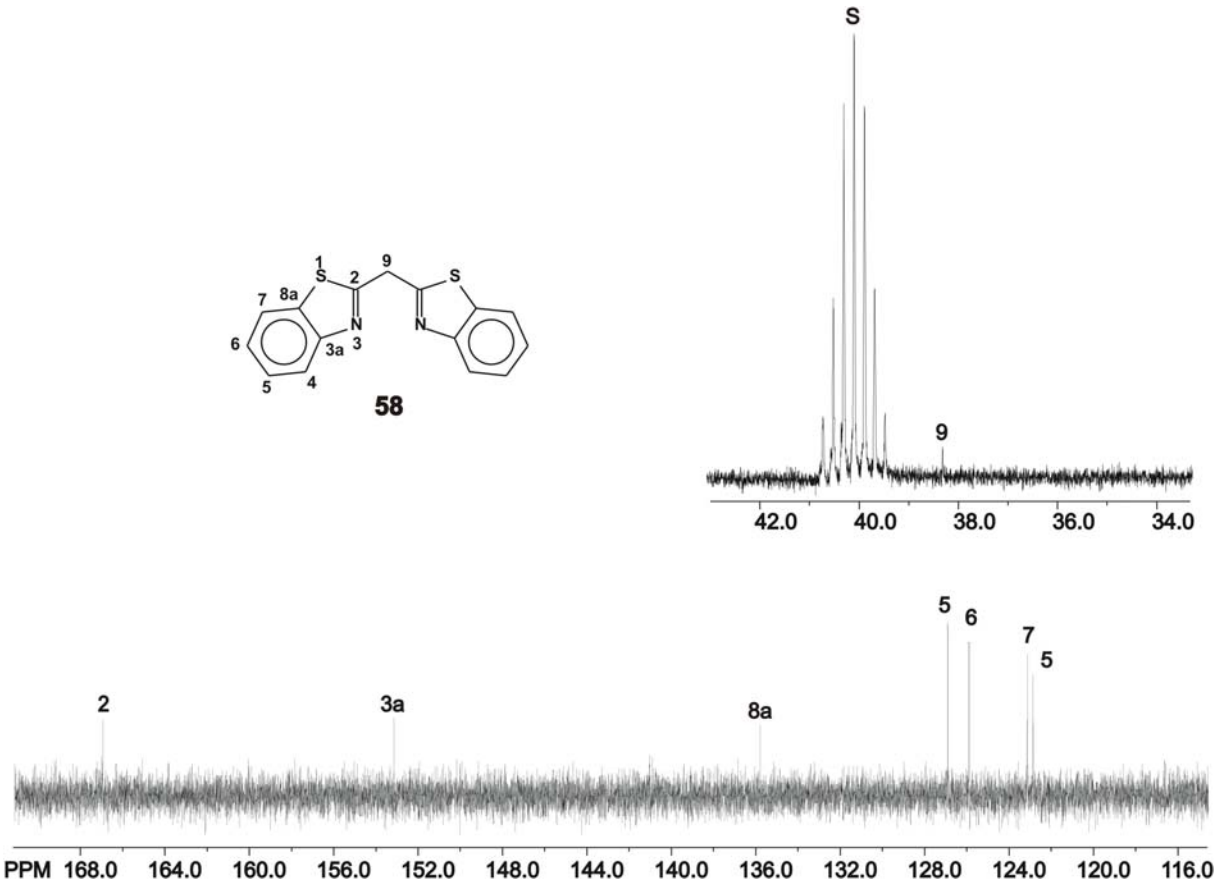
3.3.1. NMR spectroscopy

The ligand precursors **57-75** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of compound **58** (see Scheme 24) shows five sets of resonance signals: a doublet at δ = 8.04 [$J_{H,H}$ = 7.8 Hz] ppm assigned to the two aromatic protons H4, the doublet at δ = 7.95 ppm [d, 2H, $J_{H,H}$ = 7.8 Hz] assigned to the aromatic protons H7. At δ = 7.47 ppm a [dd, $J_{H,H}$ = 7.8 Hz] can be assigned to two protons of the aromatic ring (H5), the double doublet at δ = 7.43 ppm [$J_{H,H}$ = 7.8 Hz] assigned to two aromatic protons (H6). At δ = 5.05 ppm a singlet corresponds to the protons of the bridging methylene group H9.

The ^{13}C NMR spectrum of compound **58** (Scheme 25) shows eight resonance signals: at δ = 167.0 ppm the to two carbon atoms C2 appear. The signal at δ = 153.2 ppm is assigned to the carbon atoms C3a. The signal at δ = 135.9 ppm represents the carbon atoms C8a. At δ = 127.0 and 125.9 ppm the carbon atoms C5 and C6 appear. The signals at δ = 123.2 ppm and 122.9 ppm can be assigned to C7 and C5, while the signal at δ = 38.5 ppm corresponds to the carbon atom of the bridging CH_2 unit.



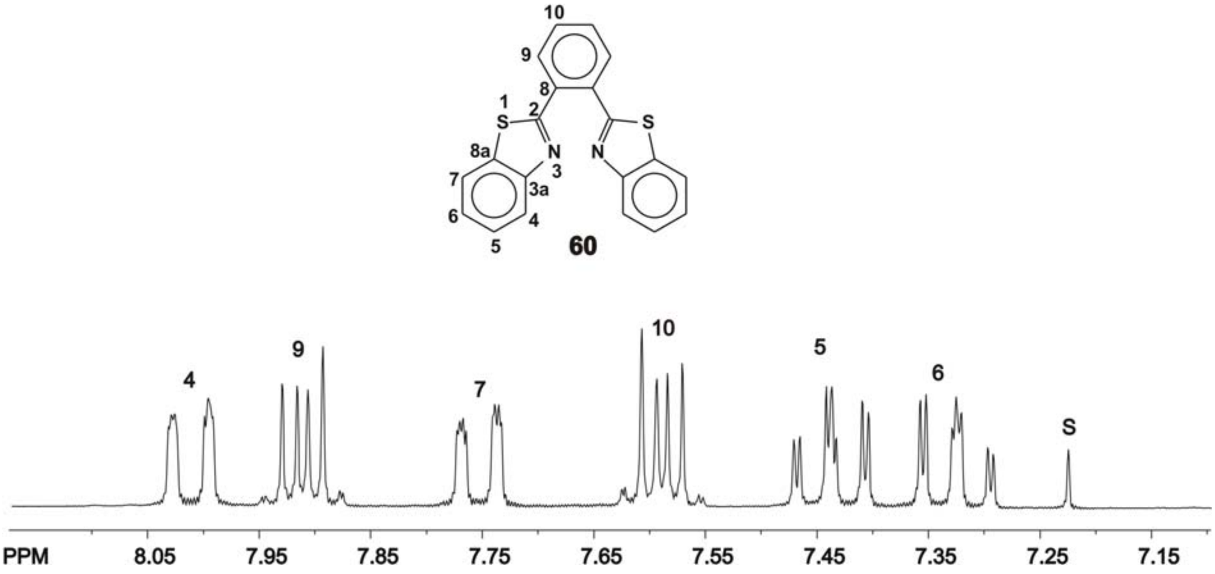
Scheme 24. ^{1}H NMR spectrum of compound **58.**



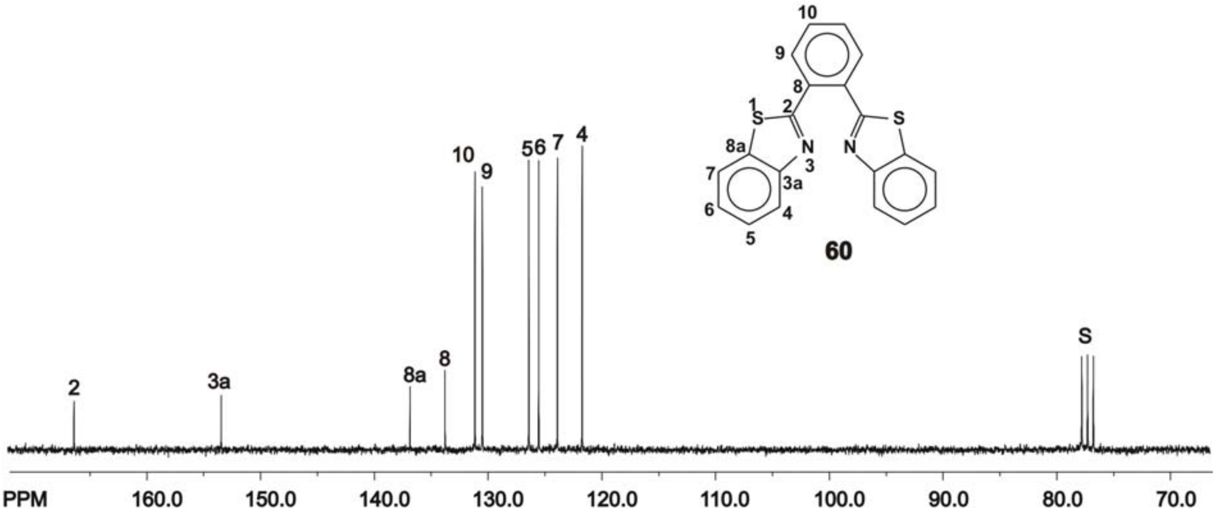
Scheme 25. ^{13}C NMR spectrum of compound **58.**

The ^{1}H NMR spectrum of compound **60** (see Scheme 26) shows six resonance signals: the double doublet at δ = 8.01 [$J_{H,H}$ = 7.6 Hz] ppm assigned to two protons of the benzothiazole phenyl ring H4, the multiplet at δ = 7.93-7.90 ppm corresponding to two protons of the connecting phenyl ring H9. The double doublet at δ = 7.76 ppm [$J_{H;H}$ = 7.6 Hz] assigned to the protons H7, the multiplet at δ = 7.61-7.58 ppm correspond to H10, at δ = 7.47-7.41 ppm a multiplet assigned to H5, and at δ = 7.36-7.30 ppm a second multiplet assigned to the protons H6.

The ^{13}C NMR spectrum for compound **60** (Scheme 27) shows ten resonance signals each equivalent to 2 carbon atoms: at δ = 166.4 (C2), 153.4 (C3a), 136.6 (C8a), 133.5 (C8), 131.6 (C10), 131.5 (C9), 127.2 (C5), 126.3 (C6), 123.8 (C7) and 121.9 ppm (C4).

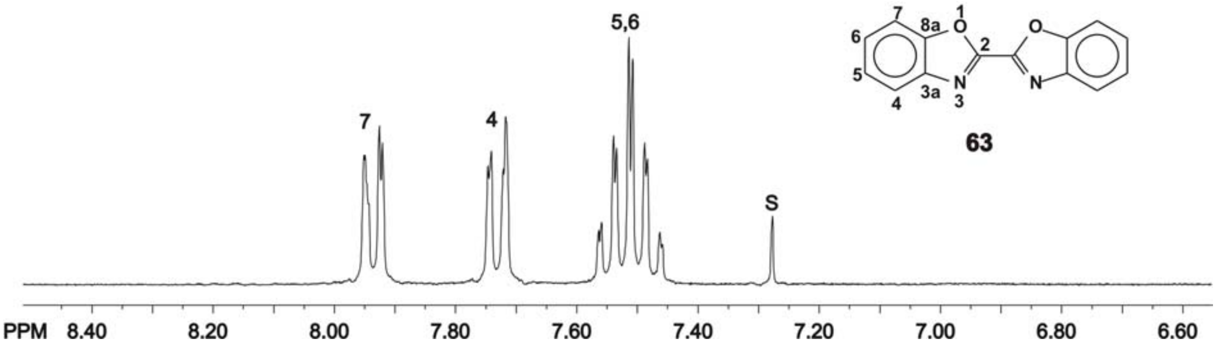


Scheme 26. ^{1}H NMR spectrum of compound **60.** **$CDCl_3$**



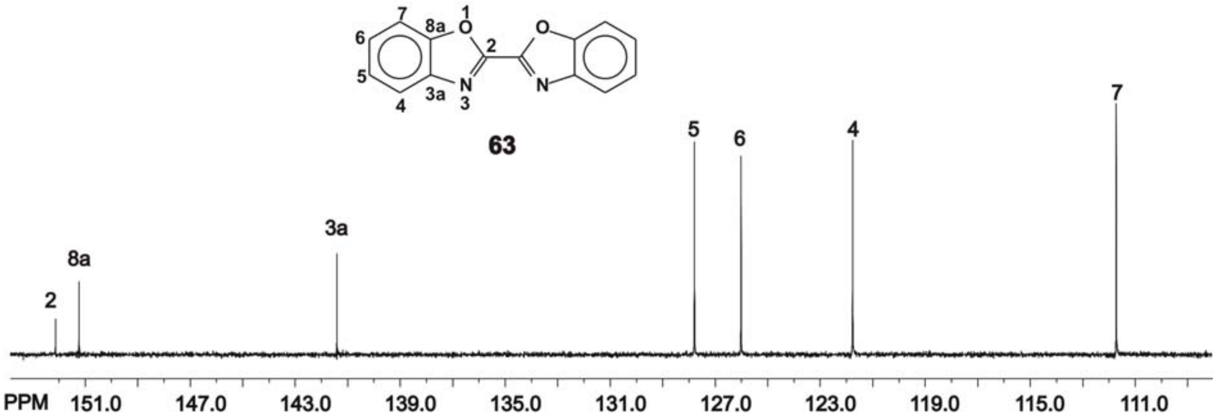
Scheme 27. ^{13}C NMR spectrum of compound **60.**

The ^{1}H NMR spectrum of **63** (see Scheme 28) shows three sets of resonance signals: at δ = 7.93 ppm [dd, 2H, $J_{H,H}$ = 7.6 Hz] which can be assigned to the aromatic protons H7, a second double doublet at δ = 7.74 ppm [2H, $J_{H,H}$ = 7.6 Hz] corresponding to the aromatic protons H4, and a multiplet at δ = 7.56-7.46 ppm for the four aromatic protons H5 and H6.



Scheme 28. ^{1}H NMR spectrum of compound **63.**

The ^{13}C NMR spectrum of compound **63** (Scheme 29) shows seven signals each equivalent to 2 carbon atoms at $\delta = 152.1$ (C2), 151.2 (C8a), 141.4 (C3a), 127.8 (C5), 126.0 (C6), 121.8 (C4), and 111.7 ppm (C7).

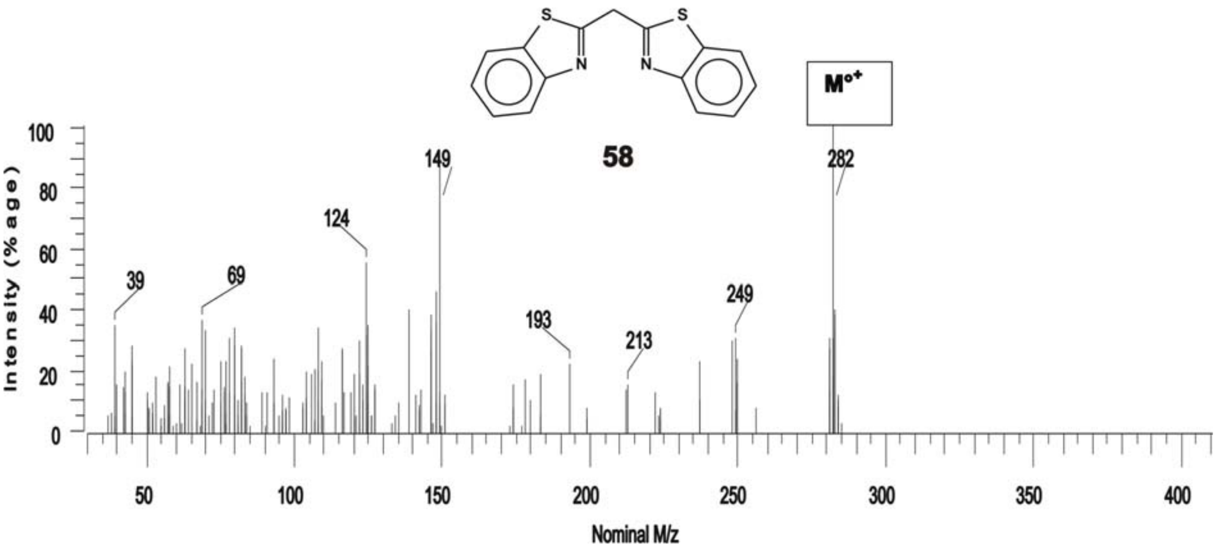


Scheme 29. ^{13}C NMR spectrum of compound **63.**

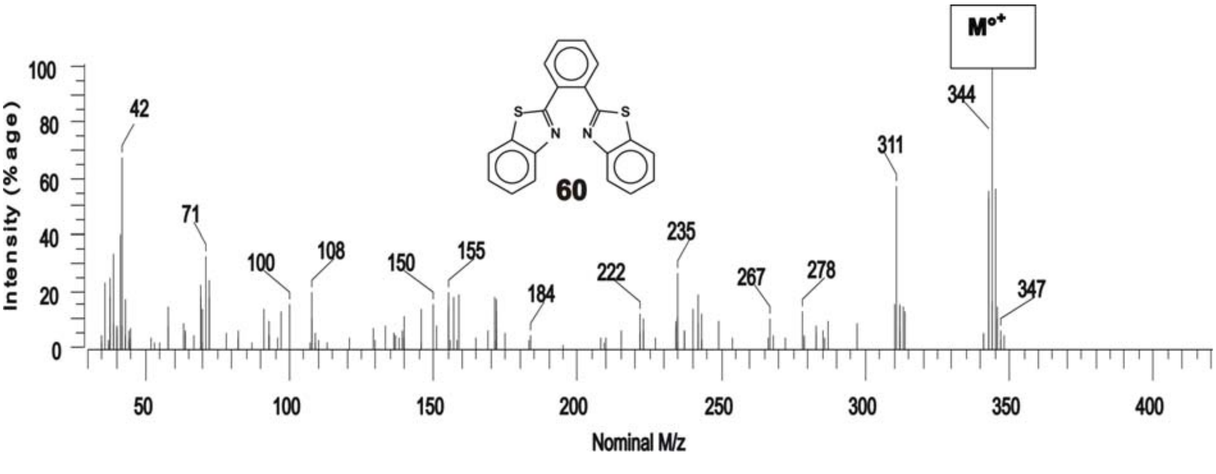
3.3.2. Mass spectroscopy

The compounds **57-75** were characterized, in addition to their NMR spectra, by mass spectroscopy. The mass spectrum of compound **58** (Scheme 30) shows the molecular ion peak at m/z = 282. The peak with m/z = 192 represents the loss of C_6H_4N. The loss of one benzothiazole unit results in a fragment with m/z = 148. Scheme 31 shows the mass spectrum of compound **60**. It shows the molecular ion peak with m/z = 344. The loss of one -SH results in an ion with m/z = 312, the ion with m/z = 280 corresponds to the loss of two sulphur atoms, the peak with m/z = 222 is assigned to ($M^{\circ+}$- C_6H_4NS). The ion with m/z = 110 can be assigned to the fragment C_6H_4S.

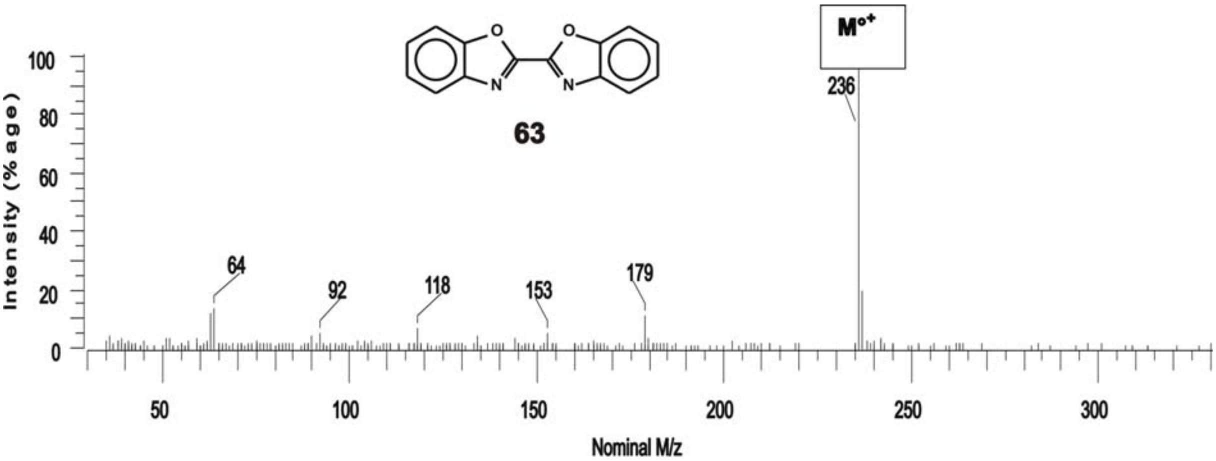
The mass spectrum of compound **63** (Scheme 32) shows a peak with m/z = 236 corresponding to the molecular ion. The peak with m/z = 118 corresponds to the benzoxazole unit C_7H_4NO. The data for other compounds are given in Table 5, in which only the molecular ion mass is shown.



Scheme 30. Mass spectrum of compound **58.**

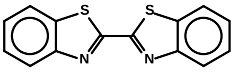
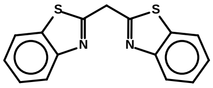
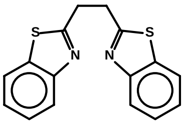
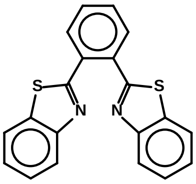
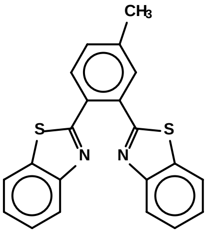


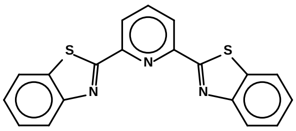
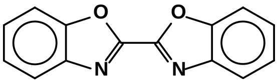
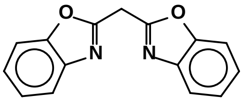
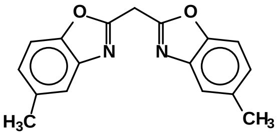
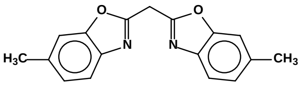
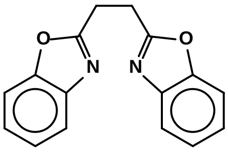
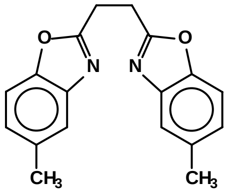
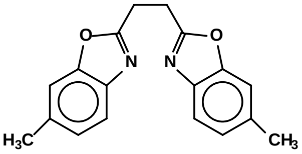
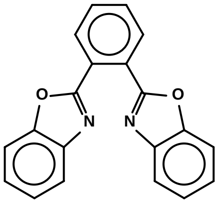
Scheme 31. Mass spectrum of compound **60.**

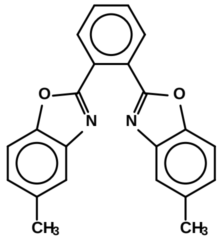
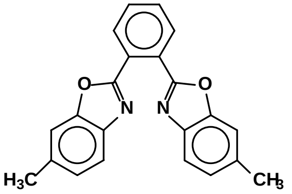
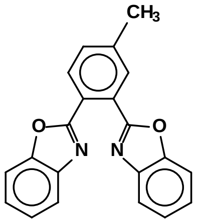
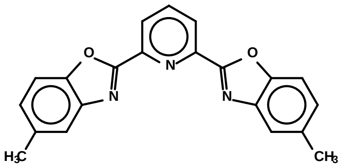
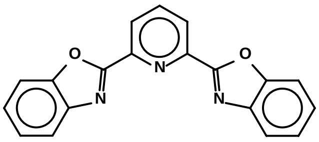


Scheme 32. Mass spectrum of compound **63.**

Table 6. NMR and mass spectral data for compounds **57-75.**

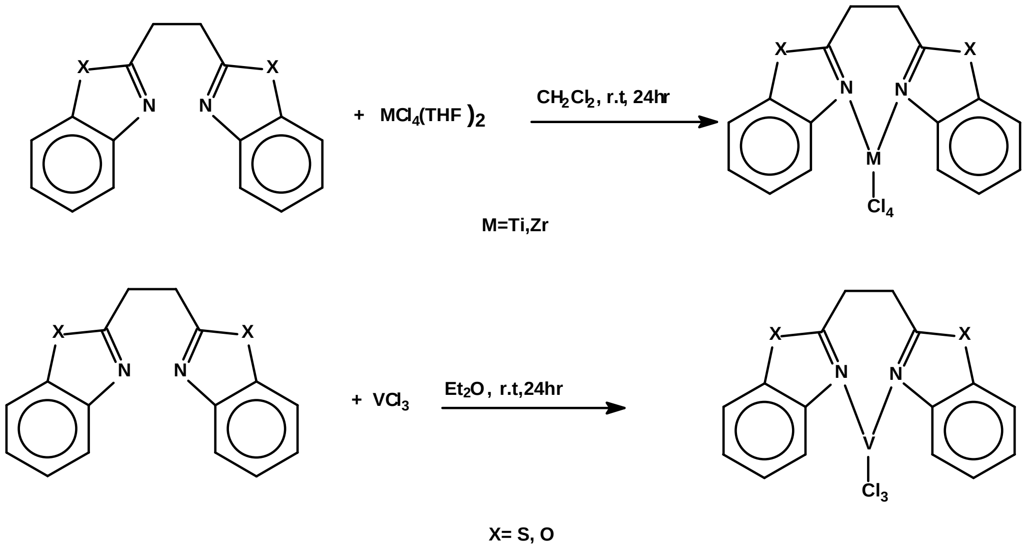
No.	**compound**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**Mass m/z(%)**
57		8.15(d,2H), 7.96(d,2H), 7.54(t,2H), 7.47(t,2H)	n.d.	268 $M^{\circ+}$ (100)
58		8.04(d,2H), 7.95(d,2H), 7.47(t,2H), 7.43(t,2H), 5.05(s,2H,CH_2)	167.0, 153.2, 135.9, 127.0, 125.9, 123.2, 122.9, 38.5	282 $M^{\circ+}$ (100)
59		7.98(d,2H), 7.82(d,2H), 7.44(t,2H), 7.37(t,2H), 3.74(s,4H, 2CH_2)	169.6, 153.5, 135.5, 126.4, 125.3, 123.0, 121.9, 33.6	296 $M^{\circ+}$ (100)
60		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	344 $M^{\circ+}$ (100)
61		8.01-7.95(m,2H), 7.84-7.79(m,3H), 7.74(s,1H), 7.48-7.44(m,3H), 7.38-7.33(m,2H), 2.50(s,3H, CH_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	358 $M^{\circ+}$ (100)

No.	compound	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
62		8.41(d,2H), 8.09(d,2H), 8.00-7.95(m,3H), 7.51(t,2H), 7.42(t,2H)	168.8, 154.5, 151.5, 138.4, 136.6, 126.6, 126.15, 124.0, 122.2, 122.1	345 $M^{\circ+}$ (100)
63		7.93(d,2H), 7.73(d,2H), 7.51(t,4H)	152.1, 151.2, 141.4, 127.8, 126.0, 121.8, 111.7	236 $M^{\circ+}$ (100)
64		7.70(d,2H), 7.50 (d,2H), 7.31(t,4H), 4.62(s,2H, CH_2)	159.5, 151.5, 141.3, 125.5, 124.8, 120.4, 110.9, 29.6	250 $M^{\circ+}$ (100)
65		7.60(d,2H), 7.52(s,2H), 7.21(d,2H), 4.84(s,2H,CH_2), 2.41(s,6H, 2CH_3)	161.4, 149.5, 141.5, 134.7, 126.9, 120.2, 110.9, 29.4, 21.6	278 $M^{\circ+}$ (100)
66		7.59(d,2H), 7.52(s,2H), 7.19(d,2H), 4.82(s,2H,CH_2), 2.46(s,6H,2CH_3)	160.8, 151.5, 139.2, 136.0, 126.4, 119.7, 111.5, 29.3, 21.9	278 $M^{\circ+}$ (100)
67		7.65(t,2H), 7.46(t,2H), 7.28(d,4H), 3.56(s,4H)	165.2, 151.2, 141.6, 125.2, 124.7, 120.2, 110.9, 25.7	264 $M^{\circ+}$ (100)
68		7.46(s,2H), 7.41(d,2H), 7.16(d,2H), 3.55(s,4H,2CH_2), 2.47(s,6H,2CH_3)	165.5, 149.4, 141.8, 134.3, 125.9, 119.7, 109.9, 25.7, 21.3	292 $M^{\circ+}$ (100)
69		7.53(d,2H), 7.35(s,2H), 7.16(d,2H), 3.54(s,4H,2CH_2), 2.50(s,6H,2CH_3)	164.8, 151.5, 139.3, 135.4, 125.5, 119.1, 110.7, 25.6, 21.6	292 $M^{\circ+}$ (100)
70		8.07(t,2H), 7.81(t,2H), 7.72(t,2H), 7.53(d,2H), 7.35(d,4H)	162.2, 151.0, 141.9, 132.5, 131.7, 127.4, 126.5, 125.5, 120.7, 111.5	312 $M^{\circ+}$ (100)

No.	compound	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
71		8.13(t,2H), 7.84(d,2H), 7.52(s,2H), 7.44(d,2H), 7.19(d,2H), 2.40(s,6H,2CH$_3$)	162.3, 149.4, 142.2, 134.9, 132.4, 131.6, 127.6, 127.4, 120.5, 110.9, 21.6	340 M$^{\circ+}$ (100)
72		8.12-8.09(m,2H), 7.85-7.82(m,2H), 7.60(d,2H), 7.37(s,2H), 7.20(d,2H), 2.41(s,6H, 2CH$_3$)	161.8, 151.4, 139.8, 136.5, 132.3, 131.7, 127.5, 126.7, 120.2, 111.4, 21.9	340 M$^{\circ+}$ (100)
73		7.97(d,1H), 7.89(s,1H), 7.64(d,2H), 7.59(d,1H), 7.49(d,2H), 7.31(t,4H), 2.37(s,3H,CH$_3$)	162.7, 162.6, 151.2, 151.1, 142.2, 142.1, 142.1, 132.1, 131.9, 131.19, 127.5, 125.5, 125.4, 124.9, 124.6, 124.5, 120.4, 120.2, 110.7, 110.6, 21.4	326 M$^{\circ+}$ (100)
74		8.40-8.38(d,2H), 7.98(t,1H), 7.56-7.51(m,4H), 7.17(d,2H), 2.43(s,6H)	161.2, 149.7, 147.0, 142.2, 138.4, 135.2, 128.0, 125.0, 120.8, 111.2, 21.8	341 M$^{\circ}$+ (100)
75		8.49(d,2H), 8.08(t,1H), 7.84(d,2H), 7.70(d,2H), 7.44-7.37(m,4H)	160.9, 151.5, 146.9, 141.9, 138.5, 126.6, 125.3, 125.3, 121.0, 111.8	313 M$^{\circ+}$ (100)

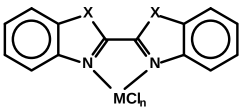
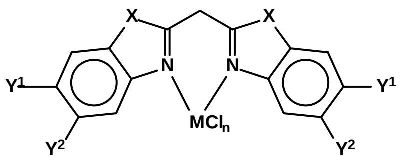
3.4. Synthesis of the complexes 76-126

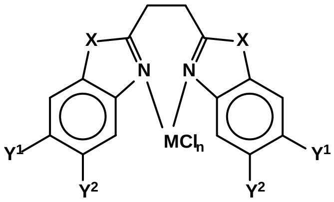
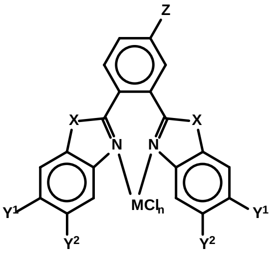
The complexes **76-127** were synthesized according to the protocol used for the preparation of complexes **94-105** (Scheme 33). By dissolving the metal chloride (VCl$_3$) or the tetrahydrofuran adducts of titanium tetrachloride or zirconium tetrachloride in an appropriate solvent followed by the addition of the potential ligand, the mixture was stirred overnight, and the products were obtained in good yields (70-85%).

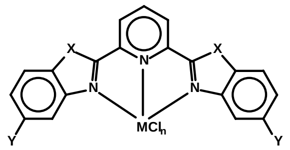


Scheme 33. Synthesis of complexes **94-105.**

Table 7. The synthesized bis(benzothiazole) and bis(benzoxazole) transition metal complexes.

Structure	Complex No.	X	Y^1	Y^2	Z	M
	**76**	S	-	-	-	Ti
	77	S	-	-	-	Zr
	78	S	-	-	-	V
	79	O	-	-	-	Ti
	80	O	-	-	-	Zr
	81	O	-	-	-	V
	**82**	S	H	H	-	Ti
	83	S	H	H	-	Zr
	84	S	H	H	-	V
	85	O	H	H	-	Ti
	86	O	H	H	-	Zr
	87	O	H	H	-	V
	88	O	H	CH_3	-	Ti

Structure	Complex No.	X	Y^1	Y^2	Z	M
	89	O	H	CH_3	-	Zr
	90	O	H	CH_3	-	V
	91	O	CH_3	H	-	Ti
	92	O	CH_3	H	-	Zr
	93	O	CH_3	H	-	V
	**94**	S	H	H	-	Ti
	95	S	H	H	-	Zr
	96	S	H	H	-	V
	97	O	H	H	-	Ti
	98	O	H	H	-	Zr
	99	O	H	H	-	V
	100	O	H	CH_3	-	Ti
	101	O	H	CH_3	-	Zr
	102	O	H	CH_3	-	V
	103	O	CH_3	H	-	Ti
	104	O	CH_3	H	-	Zr
	105	O	CH_3	H	-	V
	**106**	S	H	H	H	Ti
	107	S	H	H	H	Zr
	108	S	H	H	H	V
	109	S	H	H	CH_3	Ti
	110	S	H	H	CH_3	Zr
	111	S	H	H	CH_3	V
	112	O	H	H	H	Ti
	113	O	H	H	H	Zr
	114	O	H	H	H	V
	115	O	H	H	H	Ti
	116	O	H	H	H	Zr
	117	O	H	H	H	V
	118	O	CH_3	H	H	Ti
	119	O	CH_3	H	H	Zr
	120	O	CH_3	H	H	V

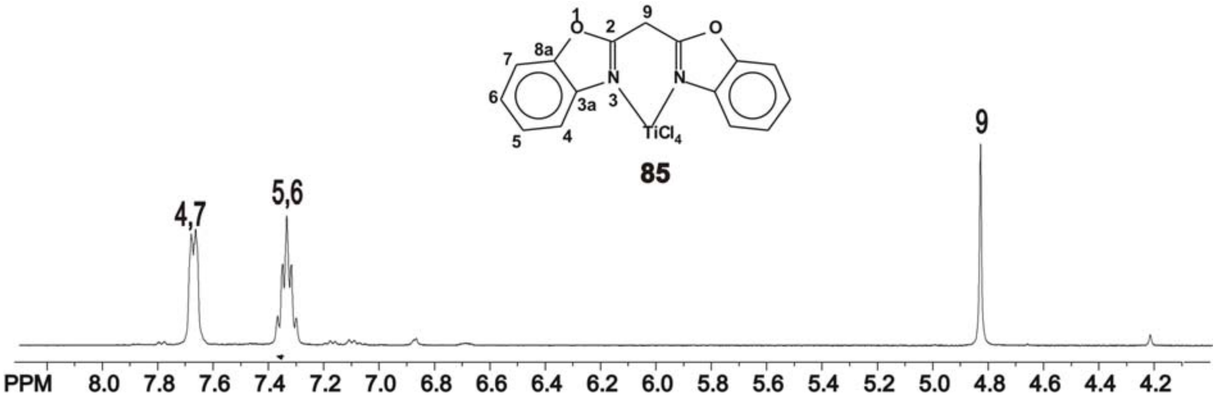
Structure	Complex No.	X	Y^1	Y^2	Z	M
	121	O	H	H	CH_3	Ti
	122	O	H	H	CH_3	Zr
	123	O	H	H	CH_3	V
	**124**	S	H	-	-	V
	125	O	H	-	-	V
	126	O	CH_3	-	-	V

3.5. Characterization of the complexes 76-126

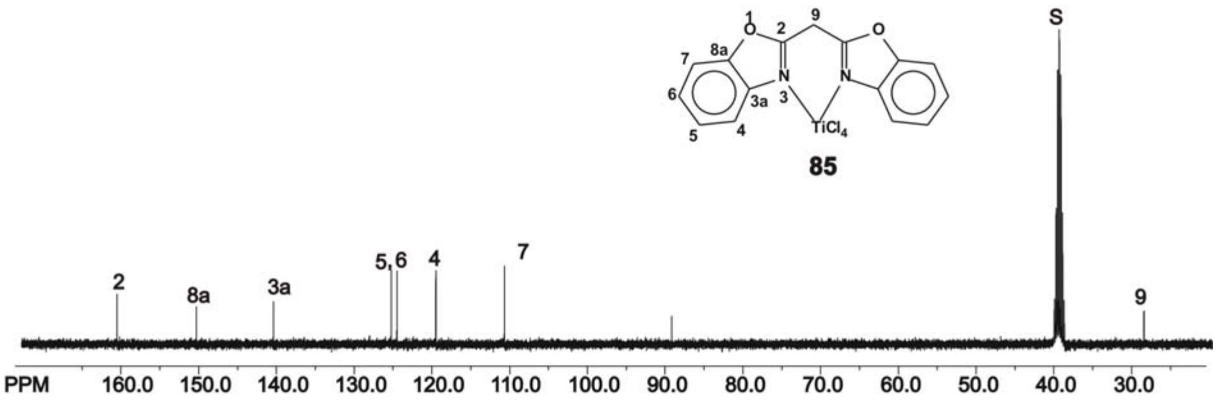
3.5.1. NMR spectroscopy

The titanium and zirconium complexes with the corresponding ligands were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of complex **85** (Scheme 34) shows three resonance signals at δ = 7.69 ppm [d, $J_{H,H}$ = 7.8 Hz] assigned to four protons H4, H7, at δ = 7.37-7.34 ppm (multiplet corresponding to four protons (H5, H6)), at δ = 4.85 ppm (a singlet assigned to the methylene protons).

The ^{13}C NMR spectrum of complex **85 (**Scheme 35), displays eight resonance signals: the signal at δ = 161.4 ppm is equivalent to the 2 carbon atoms C2 which is slightly shifted downfield compared to the same carbon atom of the free ligand. The signal at δ = 151.2 ppm is equivalent to the 2 carbon atoms C8a, at δ = 141.3 ppm to C3a, at δ = 126.1 ppm to C5, at δ = 125.4 ppm to C6, at δ = 120.4 ppm to C4, at δ = 111.5 ppm to C7 and at δ = 29.3 ppm to carbon atom C9.



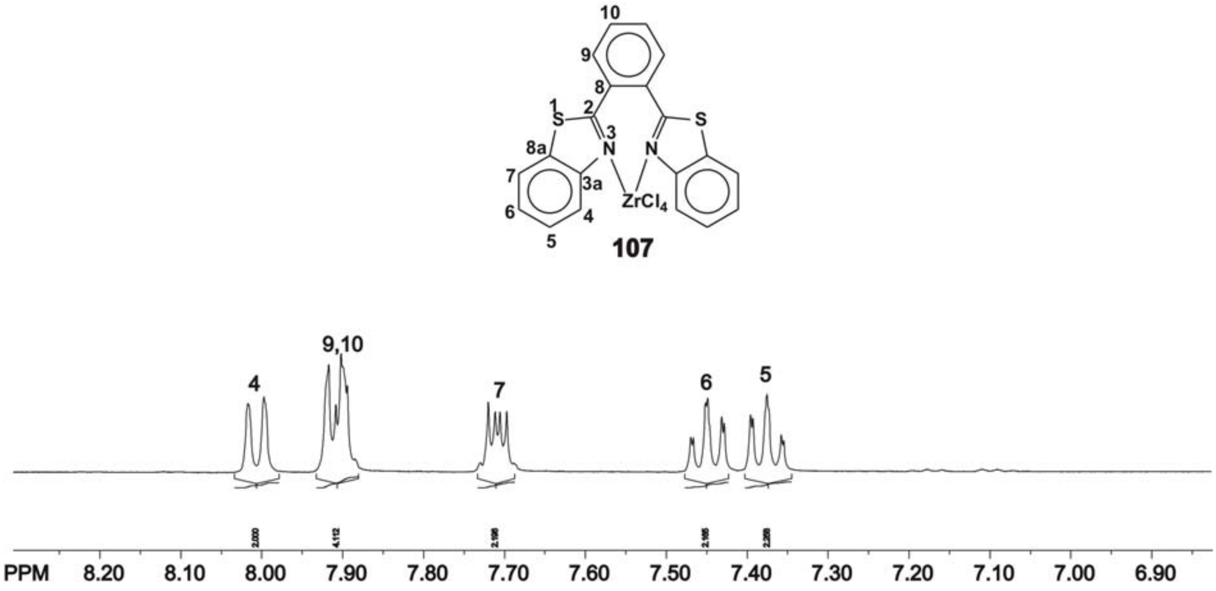
Scheme 34. ^{1}H NMR spectrum of complex **85.**



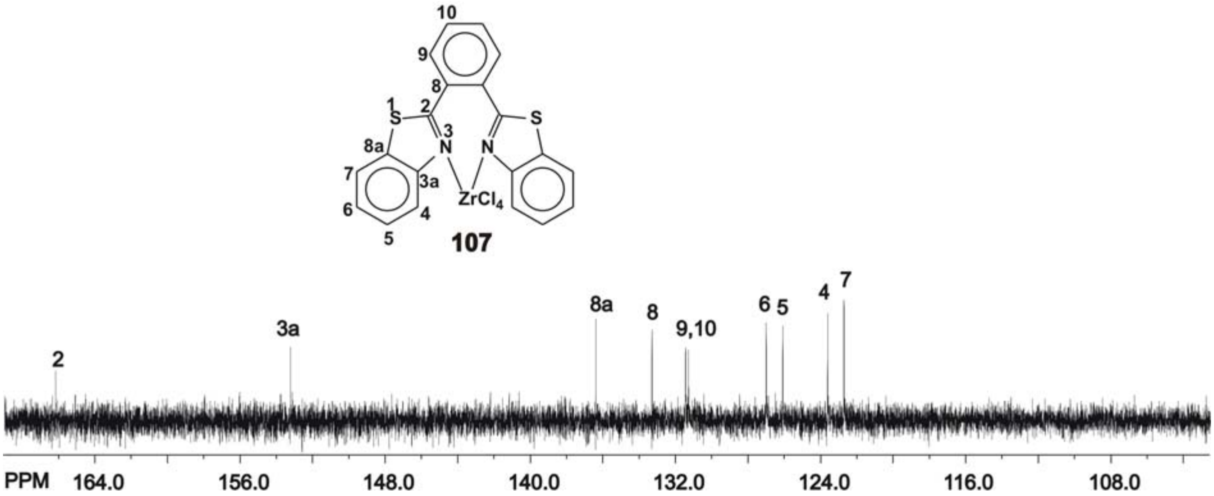
Scheme 35. ^{13}C NMR spectrum of complex **85.**

The ^{1}H NMR spectrum of complex **107** (Scheme 36) shows five sets of resonance signals. The doublet [2H,$J_{H,H}$ = 7.8 Hz] at δ = 8.01ppm can be assigned to the protons H4, the multiplet at δ = 7.92-7.90 ppm can be assigned to the protons H9 and H10, the doublet of doublet signal at δ = 7.71 ppm is assigned to the protons H7. The two triplets at δ = 7.45 ppm [2H, $J_{H,H}$ = 7.8 Hz] and 7.38 ppm [2H, $J_{H,H}$ = 7.8 Hz] are assigned to the protons H6 and H5.

Scheme 37 shows the ^{13}C NMR spectrum of complex **107**. There are ten resonance signals each corresponding to two carbon atoms. The signal at δ = 166.4 ppm can be assigned to C2. Further signals appear at δ = 153.4 (C3a), 136.6 (C8a), 133.5 (C8), 131.6 (C9), 131.5 (C10), 127.2 (C6), 126.3 (C5) and at δ = 123.8 ppm (C4). The signal at δ = 122.9 ppm corresponds to C7.



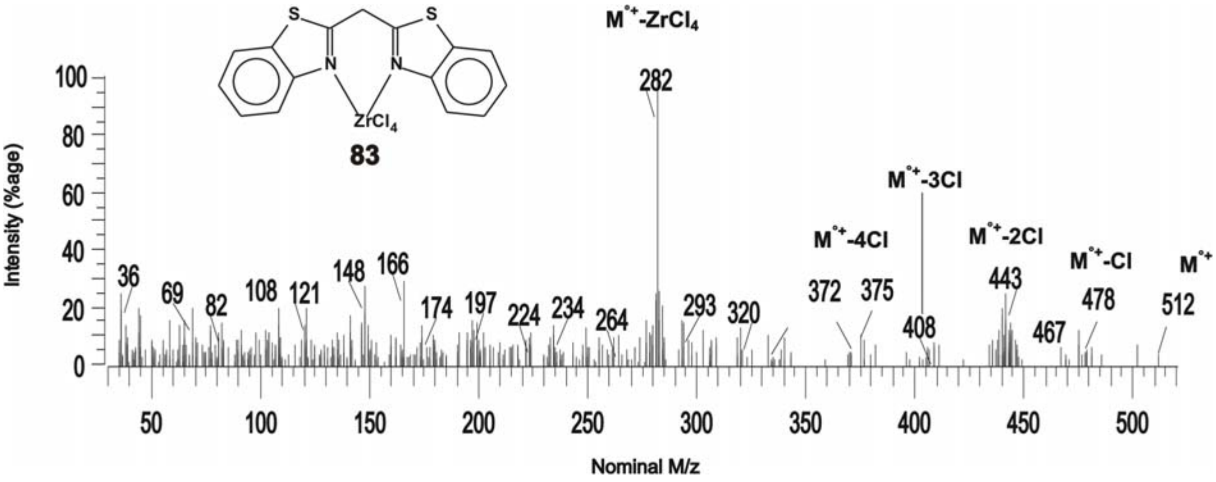
Scheme 36. ^{1}H NMR spectrum of complex **107.**



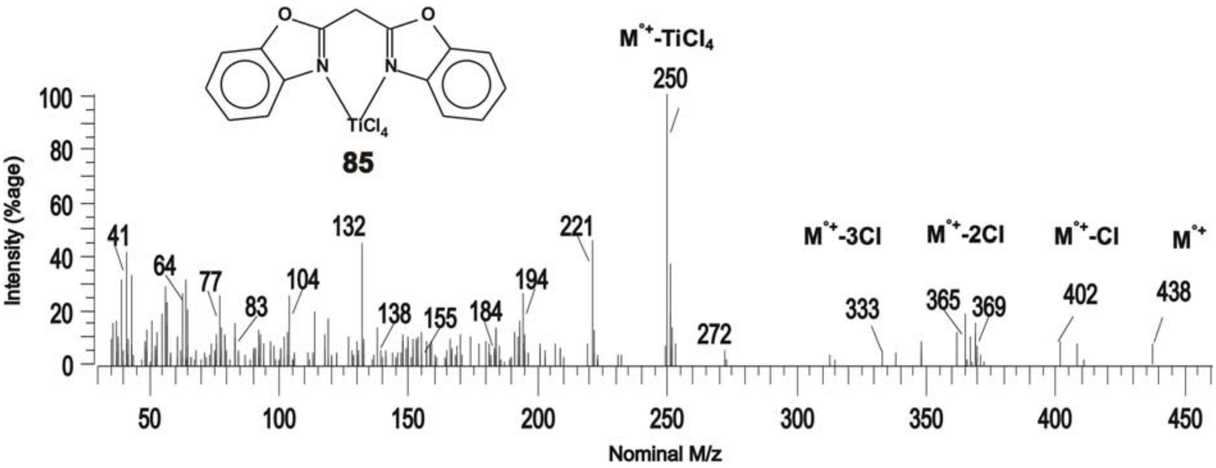
Scheme 37. ^{13}C NMR spectrum of complex **107.**

3.5.2. Mass spectroscopy

Benzothiazole and benzoxazole transition metal complexes were characterized by mass spectroscopy. The mass spectrum of complex **83** (see Scheme 38) shows m/z = 512 for the molecular ion. Further peaks appear at m/z = 478 representing the loss of one chlorine atom (M^+ - Cl), m/z = 443 representing the ions from the loss of two chlorine atoms (M^+ - 2Cl), and at m/z = 408 (M^+ - 3Cl). The base peak can be found at m/z = 282 (ligand mass). The mass spectrum of complex **85** (Scheme 39) shows the following peaks: at m/z = 438 for the molecular ion, at m/z = 368 (M^+ - 2Cl). The peak at m/z = 333 represents the ion resulting from the loss of three chlorides (M^+ - 3Cl). The base peak appears at m/z = 250 (ligand mass).

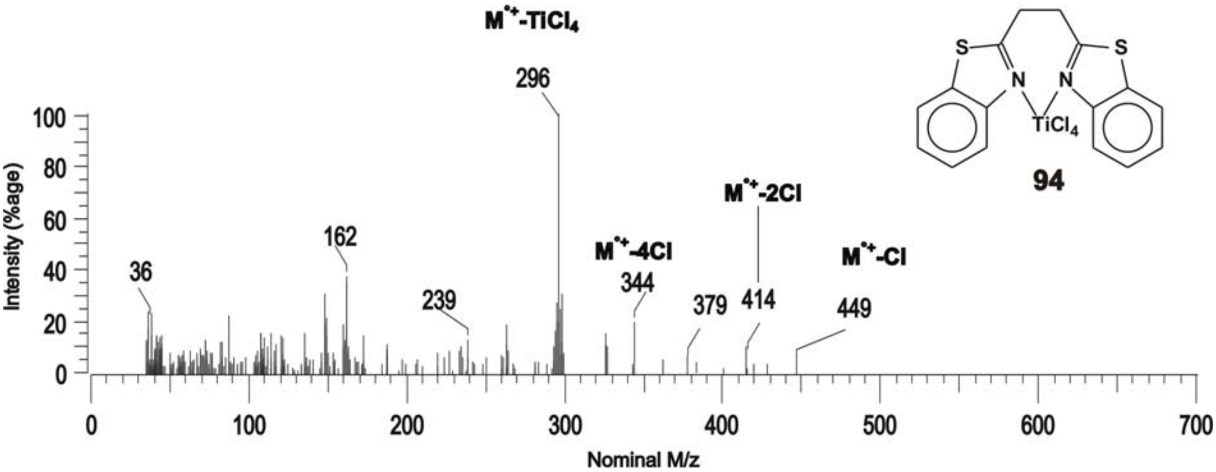


Scheme 38. Mass spectrum of complex **83.**

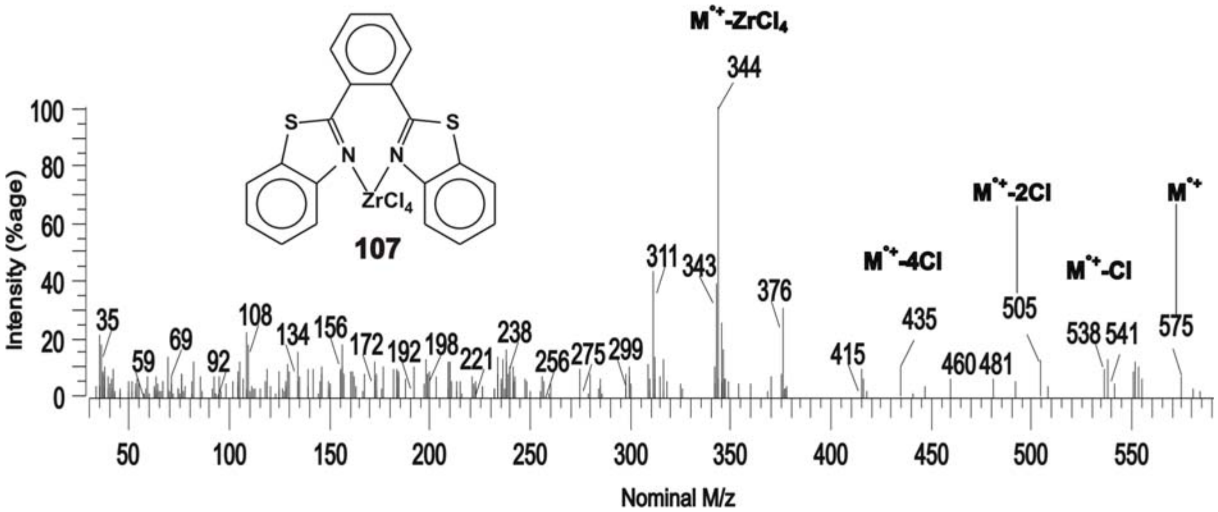


Scheme 39. Mass spectrum of complex **85.**

Scheme 40 shows the mass spectrum of complex **94**. The ion with m/z = 449 represents the loss of one chloride, the ions with m/z = 414 and m/z = 344 result from the loss of two and four chlorine atoms respectively. The ion with m/z = 296 represents the mass of the free ligand. The mass spectrum of complex **107** (see Scheme 41) shows the molecular ion peak at m/z = 575. The ion resulting from the loss of two and four chlorine atoms can be found at m/z = 505 and m/z = 435 respectively. The base peak appears at m/z = 344 representing the mass of the free ligand. Generally, it can be observed that the week dative bonds involved in the formation of the complexes is responsible for relatively low intensities of the fragmentation pattern. The data for the other complexes are given in Table 6.

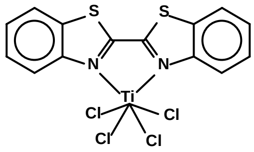
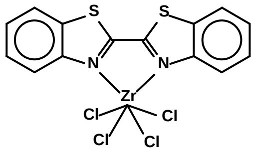
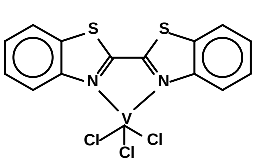
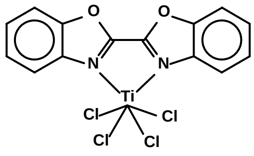


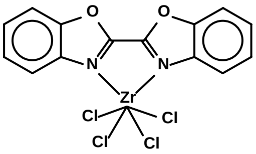
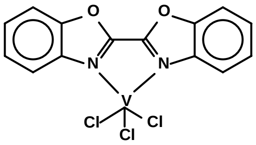
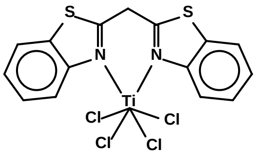
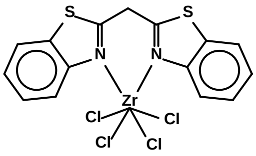
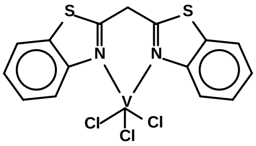
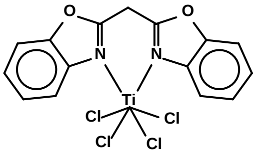
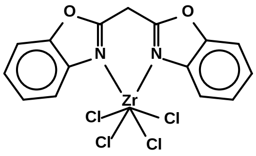
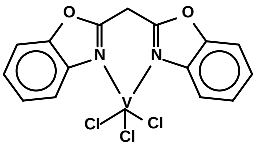
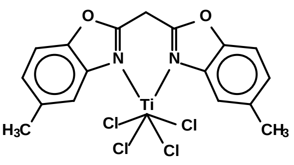
Scheme 40. Mass spectrum of complex **94.**

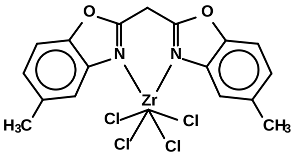
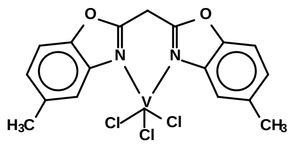
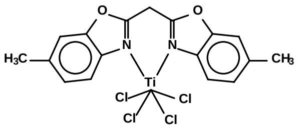
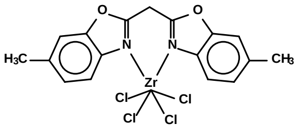
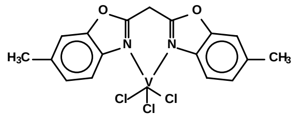
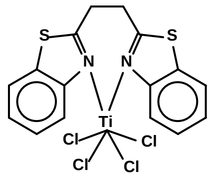
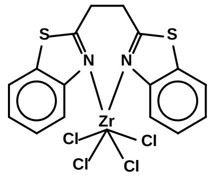
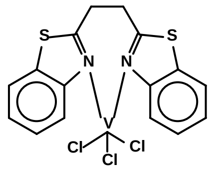
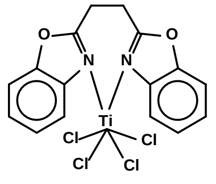


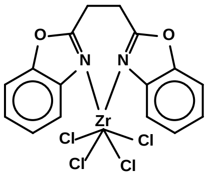
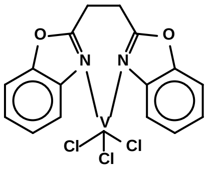
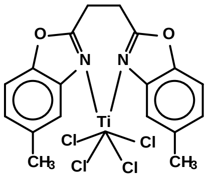
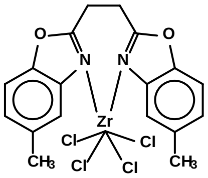
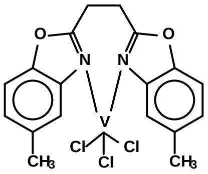
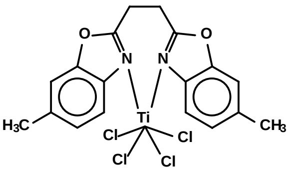
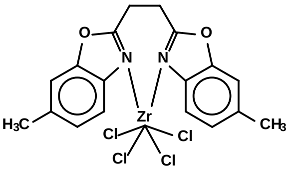
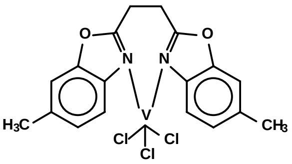
Scheme 41. Mass spectrum of complex **107.**

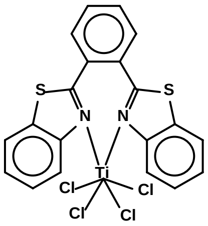
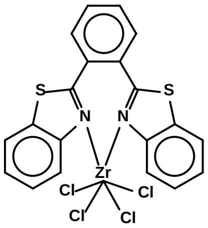
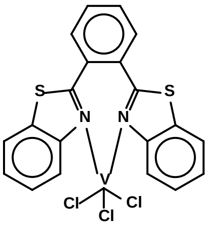
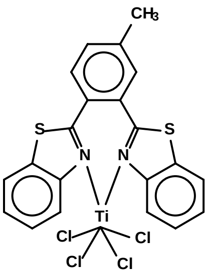
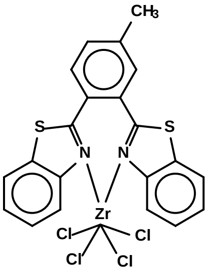
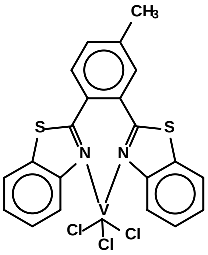
Table 8. NMR and mass spectroscopic data for complexes **76-126.**

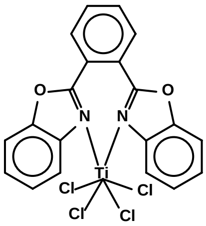
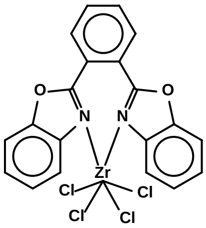
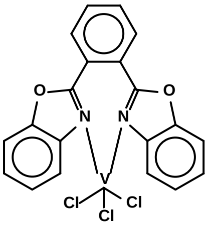
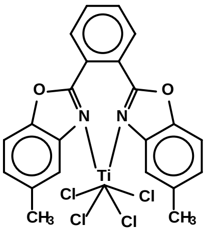
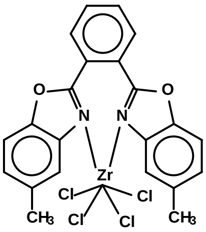
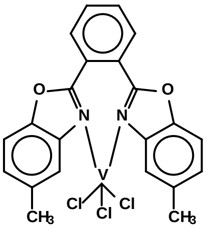
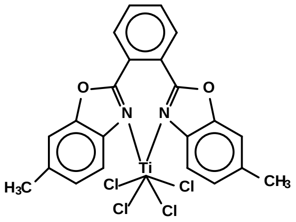
No.	**complex**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**Mass m/z (%)**
76		n.d.	n.d.	458 $M^{\circ+}$(2), 422 $M^{\circ+}$-Cl (1), 387 $M^{\circ+}$-2Cl (5), 317 $M^{\circ+}$-4Cl (2), 268 $M^{\circ+}$-$TiCl_4$ (100)
77		n.d.	n.d.	501 $M^{\circ+}$(1), 465 $M^{\circ+}$-Cl (3), 429 $M^{\circ+}$-2Cl (5), 358 $M^{\circ+}$-4Cl (3), 268 $M^{\circ+}$-$ZrCl_4$ (100)
78		n.d.	n.d.	425 $M^{\circ+}$(2), 390 $M^{\circ+}$-Cl (4), 355 $M^{\circ+}$-2Cl (2) 319 $M^{\circ+}$-3C l(2), 268 $M^{\circ+}$-VCl_3 (100)
79		7.95(d,4H), 7.60-7.56(m,4H)	152.3, 150.9, 141.3, 128.5, 126.7, 121.8, 112.4	425 $M^{\circ+}$(2), 390 $M^{\circ+}$-Cl (4), 355 $M^{\circ+}$-2Cl (2), 319 $M^{\circ+}$-3Cl (2), 236 $M^{\circ+}$-$TiCl_4$ (100)

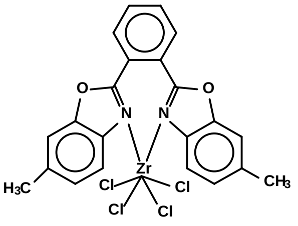
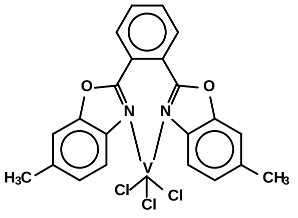
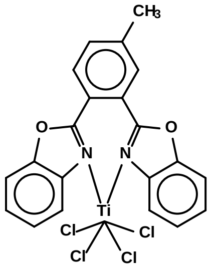
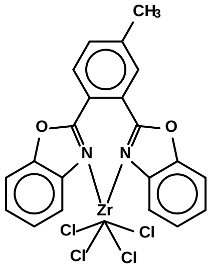
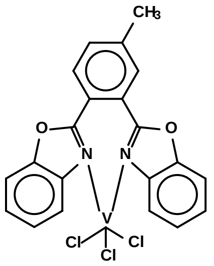
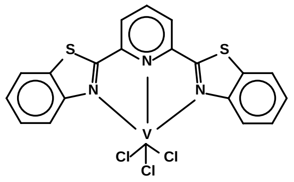
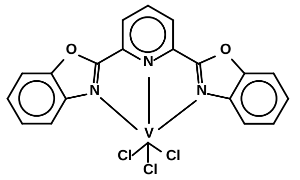
No.	complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
80		7.96(d,4H), 7.62-7.55(m,4H)	152.2, 150.9, 141.3, 128.6, 126.8, 121.8, 111.9	469 $M^{\circ+}$(2), 433 $M^{\circ+}$-Cl (5), 397 $M^{\circ+}$-2Cl (3), 361 $M^{\circ+}$-3Cl (5), 236 $M^{\circ+}$-$ZrCl_4$ (100)
81		n.d.	n.d.	398 $M^{\circ+}$(20), 360 $M^{\circ+}$-Cl (15), 287 $M^{\circ+}$-3Cl (10), 236 $M^{\circ+}$-VCl_3 (100)
82		8.02(d,2H), 7.92(d,2H), 7.45(t,2H), 7.38(t,2H), 5.02(s,2H,CH_2)	167.0, 153.2, 135.8, 127.0, 125.9, 123.2, 122.9, 38.4	472 $M^{\circ+}$(2), 436 $M^{\circ+}$-Cl (5), 401 $M^{\circ+}$-2Cl (10), 365 $M^{\circ+}$-3Cl (5), 282 $M^{\circ+}$-$TiCl_4$ (100)
83		8.10(d,2H), 8.01(d,2H), 7.53(t,2H), 7.45t,2H), 5.10(s,2H,CH_2)	167.1, 153.4, 135.9, 127.0, 126.0, 123.3, 123.0, 38.5	513 $M^{\circ+}$(1), 478 $M^{\circ+}$-Cl (10), 443 $M^{\circ+}$-2Cl (20), 408 $M^{\circ+}$-3Cl (5), 282 $M^{\circ+}$-$ZrCl_4$ (100)
84		n.d.	n.d.	439 $M^{\circ+}$(2), 402 $M^{\circ+}$-Cl (5), 366 $M^{\circ+}$-2Cl (5), 331 $M^{\circ+}$-3Cl (10), 282 $M^{\circ+}$-VCl_3 (100)
85		7.69(d,4H), 7.36(t,4H), 4.85(s,2H,CH_2)	161.4, 151.2, 141.3, 126.1, 125.4, 120.4, 111.5, 29.3	438 $M^{\circ+}$(5), 402 $M^{\circ+}$-Cl (5), 368 $M^{\circ+}$-2Cl (10), 333 $M^{\circ+}$-3Cl(10), 250 $M^{\circ+}$-$TiCl_4$ (100)
86		7.76(d,4H), 7.47(t,4H), 4.99(s,2H,CH_2)	161.78, 151.4, 151.2, 141.5, 141.1, 126.6, 126.4, 125.7, 125.6, 120.7, 120.6, 111.8, 29.6	483 $M^{\circ+}$(2), 447 $M^{\circ+}$-Cl (5), 411 $M^{\circ+}$-2Cl (5), 375 $M^{\circ+}$-3Cl (10), 250 $M^{\circ+}$-$ZrCl_4$ (100)
87		n.d.	n.d.	407 $M^{\circ+}$(3), 371 $M^{\circ+}$-Cl (5), 335 $M^{\circ+}$-2Cl (10), 300 $M^{\circ+}$-3Cl (5), 250 $M^{\circ+}$-VCl_3 (100)
88		7.61(d,2H), 7.53(s,2H), 7.23(d,2H), 4.84(s,2H,CH_2), 2.41(s,6H,2CH_3)	161.5, 149.4, 141.5, 134.8, 127.0, 120.2, 111.0, 29.4, 21.7	468 $M^{\circ+}$(5), 432 $M^{\circ+}$-Cl (2),361 $M^{\circ+}$-3Cl (3), 296 $M^{\circ+}$-4Cl-2CH_3 (5), 278 $M^{\circ+}$-$TiCl_4$ (100)

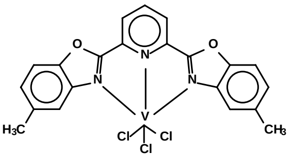
No.	complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
89		7.57(d,2H), 7.51(s,2H), 7.20(d,2H), 4.82(s,2H,CH_2), 2.40(s,6H,2CH_3)	161.4, 149.4, 141.5, 134.7, 127.0, 120.2, 110.9, 29.4, 21.6	511 $M^{\circ+}$(3), 474 $M^{\circ+}$-Cl (2), 404 $M^{\circ+}$-3Cl (1), 340 $M^{\circ+}$-4Cl-2CH_3 (3), 278 $M^{\circ+}$-$ZrCl_4$ (100)
90		n.d.	n.d.	435 $M^{\circ+}$(1), 399 $M^{\circ+}$-Cl (3), 363 $M^{\circ+}$-2Cl (3), 300 $M^{\circ+}$-3Cl-2CH_3 (5), 278 $M^{\circ+}$-VCl_3 (100)
91		7.60(d,2H), 7.54(s,2H), 7.21(d,2H), 4.82(s,2H,CH_2), 2.44(s,6H,2CH_3)	160.8, 151.5, 139.1, 136.1, 126.5, 119.8, 111.5, 29.3, 21.9	468 $M^{\circ+}$(2), 432 $M^{\circ+}$-Cl (3), 361 $M^{\circ+}$-3Cl (2), 296 $M^{\circ+}$-4Cl-2CH_3 (2), 278 $M^{\circ+}$-$TiCl_4$ (100)
92		7.58(d,2H), 7.52(s,2H), 7.19(d,2H), 4.81(s,2H,CH_2), 2.42(s,6H,2CH_3)	160.8, 151.5, 139.1, 136.0, 126.4, 119.7, 111.5, 29.3, 21.9	511 $M^{\circ+}$(1), 474 $M^{\circ+}$-Cl (3), 404 $M^{\circ+}$-3Cl (3), 340 $M^{\circ+}$-4Cl-2CH_3 (2), 278 $M^{\circ+}$-$ZrCl_4$ (100)
93		n.d.	n.d.	435 $M^{\circ+}$(2), 399 $M^{\circ+}$-Cl (5), 363 $M^{\circ+}$-2Cl (3), 300 $M^{\circ+}$-3Cl-2CH_3 (3), 278 $M^{\circ+}$-VCl_3 (100)
94		8.02(d,2H), 7.99(d,2H), 7.44-7.35(m,4H), 3.68(s,4H,2CH_2)	170.6, 153.3, 135.3, 126.9, 125.8, 123.1, 122.9, 33.1	449 $M^{\circ+}$-Cl (10), 414 $M^{\circ+}$-2Cl (10), (10), 344 $M^{\circ+}$-4Cl (80), 296 $M^{\circ+}$-$TiCl_4$ (75)
95		8.03(d,2H), 7.92(d,2H), 7.49-7.35(m,4H), 3.71(s,4H,2CH_2)	170.7, 152.8, 135.3, 126.7, 125.7, 122.9, 122.7, 33.0	530 $M^{\circ+}$(1), 493 $M^{\circ+}$-Cl (5), 456 $M^{\circ+}$-2Cl (5), 389 $M^{\circ+}$-4Cl (20), 296 $M^{\circ+}$-$ZrCl_4$(100)
96		n.d.	n.d.	454 $M^{\circ+}$(5), 416 $M^{\circ+}$-Cl (2), 383 $M^{\circ+}$-2Cl (3) 296 $M^{\circ+}$-VCl_3 (70)
97		7.59(t,2H), 7.26(t,2H), 7.16(d,2H), 7.09(d,2H), 3.47(s,4H,2CH_2)	166.1, 150.9, 141.4, 125.5, 124.9, 112.0, 111.2, 25.3	454 $M^{\circ+}$(2), 418 $M^{\circ+}$-Cl (5), 381 $M^{\circ+}$-2Cl (2), $312^{\circ+}$-4Cl (5), 264 $M^{\circ+}$-$TiCl_4$ (100)

No.	complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
98		7.68-7.64(m,4H), 7.35-7.31(m,4H), 3.55(s,4H,2CH$_2$)	166.2, 150.9, 141.4, 125.5, 125.0, 120.0, 111.3, 25.3	497 $M^{\circ+}$(2), 462 $M^{\circ+}$-Cl (2), 426 $M^{\circ+}$-2Cl (5), 354 $M^{\circ+}$-4Cl (10), 264 $M^{\circ+}$-ZrCl$_4$ (100)
99		n.d.	n.d.	422 $M^{\circ+}$(1), 386 $M^{\circ+}$-Cl(5), 348 $M^{\circ+}$-2Cl (2), 315 $M^{\circ+}$-3Cl (5), 264 $M^{\circ+}$-VCl$_3$ (100)
100		7.53(s,2H), 7.48(d,2H), 7.24(d,2H), 3.76(s,4H,2CH$_2$), 2.39(s,6H,2CH$_3$)	167.2, 149.7, 142.3, 136.0, 127.6, 119.5, 111.2, 25.6, 21.4	486 $M^{\circ+}$(2), 419 $M^{\circ+}$-Cl-2CH$_3$ (3), 414 $M^{\circ+}$-2Cl (5), 378 $M^{\circ+}$-3Cl (3), 296 $M^{\circ+}$-TiCl$_4$ (100)
101		7.53(d,2H), 7.44(s,2H), 7.15(d,2H), 3.50(s,4H,2CH$_2$), 2.38(s,6H,2CH$_3$)	166.2, 149.4, 141.3, 134.3, 126.4, 119.9, 110.7, 25.4, 21.6	526 $M^{\circ+}$(3), 460 $M^{\circ+}$-Cl-2CH$_3$ (5), 453 $M^{\circ+}$-2Cl (5), 417 $M^{\circ+}$-3Cl (2), 381 $M^{\circ+}$-4Cl (1), 296 $M^{\circ+}$-ZrCl$_4$ (100)
102		n.d.	n.d.	453 $M^{\circ+}$(3), 423 $M^{\circ+}$-2CH$_3$ (5), 382 $M^{\circ+}$-2Cl (2), 352 $M^{\circ+}$-2Cl-2CH$_3$ (5), 345 $M^{\circ+}$-3Cl (3), 296 $M^{\circ+}$-VCl$_3$ (100)
103		7.52(s,2H), 7.49(d,2H), 7.14(d,2H), 3.49(s,4H,2CH$_2$), 2.42(s,6H,2CH$_3$)	165.5, 151.2, 139.3, 135.4, 126.0, 119.4, 111.3, 25.3, 21.9	486 $M^{\circ+}$(2), 449 $M^{\circ+}$-Cl (3) 421 $M^{\circ+}$-Cl-2CH$_3$ (5), 414 $M^{\circ+}$-2Cl (2), 378 $M^{\circ+}$-3Cl (3), 296 $M^{\circ+}$-TiCl$_4$ (100)
104		7.51(s,2H), 7,46(d,2H), 7.12(d,2H), 3.48(s,4H,2CH$_2$), 2.40(s,6H,2CH$_3$)	165.5, 151.2, 139.2, 135.4, 126.0, 119.4, 111.3, 25.3, 21.8	526 $M^{\circ+}$(3), 460 $M^{\circ+}$-Cl-2CH$_3$ (2), 453 $M^{\circ+}$-2Cl (3), 417 $M^{\circ+}$-3Cl (2), 381 $M^{\circ+}$-4Cl (1), 296 $M^{\circ+}$-ZrCl$_4$ (100)
105		n.d.	n.d.	453 $M^{\circ+}$(2), 417 $M^{\circ+}$-Cl (5), 382 $M^{\circ+}$-2Cl (2), 352 $M^{\circ+}$-2Cl-2CH$_3$ (3), 345 $M^{\circ+}$-3Cl (3), 296 $M^{\circ+}$-VCl$_3$ (100)

No.	complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
106		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	534 $M^{\circ+}$(3), 498 $M^{\circ+}$-Cl (2), 463 $M^{\circ+}$-2Cl (2), 427 $M^{\circ+}$-3Cl (1), 344 $M^{\circ+}$-$TiCl_4$ (100)
107		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	575 $M^{\circ+}$(10), 540 $M^{\circ+}$-Cl (3), 505 $M^{\circ+}$-3Cl (5), 435 $M^{\circ+}$-4Cl (5), 344 $M^{\circ+}$-$ZrCl_4$ (100)
108		n.d.	n.d.	501 $M^{\circ+}$(1), 465 $M^{\circ+}$-Cl (3), 430 $M^{\circ+}$-2Cl (2), 394 $M^{\circ+}$-3Cl (1), 344 $M^{\circ+}$-VCl_3 (100)
109		8.02(t,2H), 7.92(t,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	548 $M^{\circ+}$(1), 512 $M^{\circ+}$-Cl (2), 496 $M^{\circ+}$-Cl-CH_3 (5), 441 $M^{\circ+}$-3Cl (3), 405 $M^{\circ+}$-4Cl (2), 358 $M^{\circ+}$-$TiCl_4$ (100)
110		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	593 $M^{\circ+}$(3), 558 $M^{\circ+}$-Cl (2), 522 $M^{\circ+}$-2Cl (5), 485 $M^{\circ+}$-3Cl (2), 471 $M^{\circ+}$-3Cl-CH_3 (2), 450 $M^{\circ+}$-4Cl (5), 358 $M^{\circ+}$-$ZrCl_4$ (100)
111		n.d.	n.d.	515 $M^{\circ+}$(2), 478$M^{\circ+}$-Cl (1), 464 $M^{\circ+}$-Cl-CH_3 (3), 443 $M^{\circ+}$-2Cl (3), 407 $M^{\circ+}$-3Cl (3), 392 $M^{\circ+}$-3Cl-CH_3 (2), $M^{\circ+}$-358 $M^{\circ+}$-VCl_3 (100)

No.	complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
112		8.12-8.09(dd,2H), 7.83-7.81(dd,2H), 7.69(t,2H), 7.54(t,2H), 7.35-7.33(m,4H)	162.2, 151.0, 141.9, 132.5, 131.7, 127.4, 126.5, 125.5, 120.7, 111.5	502 $M^{\circ+}$(1), 466 $M^{\circ+}$-Cl (2), 429 $M^{\circ+}$ -2Cl (3), 312 $M^{\circ+}$ -$TiCl_4$ (100)
113		8.11-8.09(dd,2H), 7.83-7.81(dd,2H), 7.68(t,2H), 7.53(t,2H), 7.35-7.33(m,4H)	162.2, 151.0, 141.9, 132.5, 131.7, 127.4, 126.5, 125.5, 120.7, 111.5	545 $M^{\circ+}$(1), 509 $M^{\circ+}$-Cl (2), 472 $M^{\circ+}$ -2Cl (5), 312 $M^{\circ+}$ -$ZrCl_4$ (100)
114		n.d.	n.d.	469 $M^{\circ+}$(3), 433 $M^{\circ+}$-Cl (1), 398 $M^{\circ+}$ -2Cl (5), 361 $M^{\circ+}$-3Cl (2) 312 $M^{\circ+}$-VCl_3 (100)
115		8.12(d,2H), 7.85(t,2H), 7.53(s,2H), 7.46(d,2H), 7.21(d,2H), 2.42(s,6H,2CH_3)	162.3, 149.3, 142.2, 134.9, 132.4, 131.6, 127.5, 127.4, 120.5, 110.9, 21.6	530 $M^{\circ+}$(1), 464 $M^{\circ+}$-Cl-2CH_3 (2), 459 $M^{\circ+}$-2Cl (5), 423 $M^{\circ+}$ -3Cl (3), 388 $M^{\circ+}$-4Cl (1), 340 $M^{\circ+}$-$TiCl_4$ (100)
116		8.24-8.21(dd,2H), 7.97(t,2H), 7.63(s,2H), 7.57(d,2H), 7.31(d,2H), 2.52(s,6H,2CH_3)	162.6, 149.6, 142.4, 135.2, 132.7, 131.9, 127.8, 127.7, 120.8, 111.2, 21.9	573 $M^{\circ+}$(1), 506 $M^{\circ+}$-Cl-2CH_3 (1), 501 $M^{\circ+}$-2Cl (3), 465 $M^{\circ+}$ -3Cl (3), 431 $M^{\circ+}$-4Cl (2), 340 $M^{\circ+}$-$ZrCl_4$ (100)
117		n.d.	n.d.	497 $M^{\circ+}$(3), 432 $M^{\circ+}$-Cl-2CH_3 (2), 426 $M^{\circ+}$ -2Cl (5), 390 $M^{\circ+}$-3Cl (2) 340 $M^{\circ+}$-VCl_3 (100)
118		8.14-8.11(dd,2H), 7.87-7.84(dd,2H), 7.62(d,2H), 7.41(s,2H), 7.22(d,2H), 2.43(s,6H,2CH_3)	161.8, 151.4, 139.8, 136.6, 132.4, 131.7, 127.5, 126.7, 120.2, 111.5, 21.9	530 $M^{\circ+}$(3), 494 $M^{\circ+}$-Cl (2), 430 $M^{\circ+}$-2Cl-2CH_3 (5), 423 $M^{\circ+}$ -3Cl (1), 389 $M^{\circ+}$-4Cl (2), 340 $M^{\circ+}$-$TiCl_4$ (100)

No.	complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
119		8.13-8.10(dd,2H), 7.86-7.83(dd,2H), 7.61(d,2H), 7.40(s,2H), 7.21(d,2H), 2.42(s,6H,2CH_3)	161.8, 151.4, 139.8, 136.5, 132.4, 131.7, 127.5, 126.7, 120.2, 111.5, 21.9	573 $M^{\circ+}$(3), 537 $M^{\circ+}$-Cl (2), 472 $M^{\circ+}$-2Cl-2CH_3 (3), 467 $M^{\circ+}$ -3Cl (2), 431 $M^{\circ+}$-4Cl (2), 340 $M^{\circ+}$-$ZrCl_4$ (100)
120		n.d.	n.d.	497 $M^{\circ+}$(2), 432 $M^{\circ+}$-Cl-2CH_3 (2), 426 $M^{\circ+}$ -2Cl (3), 390 $M^{\circ+}$-3Cl(5) 340 $M^{\circ+}$-VCl_3 (100).
121		7.98(d,1H), 7.91(s,1H), 7.68-7.64(m,2H), 7.61(d,1H), 7.53-7.49(dd,2H), 7.32(t,4H), 2,45(s,3H,CH_3)	162.3, 162.3, 151.0, 150.9, 142.8, 141.9, 141.8, 133.0, 132.1, 131.6, 127.3, 126.4, 126.3, 125.5, 125.4, 124.6, 120.7, 120.6, 111.5, 111.4, 21.5	516 $M^{\circ+}$, 480 $M^{\circ+}$-Cl (3), 444 $M^{\circ+}$-2Cl (2), 408 $M^{\circ+}$ -2Cl(1), 372 $M^{\circ+}$-4Cl (2), 326 $M^{\circ+}$-$TiCl_4$ (100)
122		8.00(d,1H), 7.92(s,1H), 7.69-7.65(m,2H), 7.62(d,1H), 7.54-7.50(m,2H), 7.34(t,4H), 2.45(s,3H,CH_3)	162.3, 162.2, 151.0, 150.9, 142.8, 141.9, 141.8, 133.0, 132.2, 131.5, 127.3, 126.4, 126.3, 125.5, 125.4, 124.7, 120.7, 120.6, 111.5, 111.4, 21.5	560 $M^{\circ+}$(1), 524 $M^{\circ+}$-Cl (2), 474 $M^{\circ+}$-2Cl-CH_3 (3), 452 $M^{\circ+}$ -3Cl (2), 417 $M^{\circ+}$-4Cl (2), 326 $M^{\circ+}$-$ZrCl_4$ (100)
123		n.d.	n.d.	483 $M^{\circ+}$(5), 444 $M^{\circ+}$-Cl(5), 407 $M^{\circ+}$ -2Cl (1), 357 $M^{\circ+}$-3Cl (5), 326 (100)
124		n.d.	n.d.	501 $M^{\circ+}$ (1), 465 $M^{\circ+}$-Cl (2), 430 $M^{\circ+}$-2Cl(2), 393 $M^{\circ+}$-3Cl (2), 345 $M^{\circ+}$-VCl_3 (60)
125		n.d.	n.d.	472 $M^{\circ+}$ (5), 401 $M^{\circ+}$-2Cl (20), 361 $M^{\circ+}$-3Cl (5), 313 $M^{\circ+}$-VCl_3 (10)

No.	complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
126		n.d.	n.d.	498 $M^{\circ+}$, 462 $M^{\circ+}$-Cl (30), 390 $M^{\circ+}$-3Cl (10), 341 (100)

4. Synthesis of (2-benzimidazolyl)pyridine, (2-benzothiazolyl)pyridine, and (2-benzoxazolyl)pyridine transition metal complexes

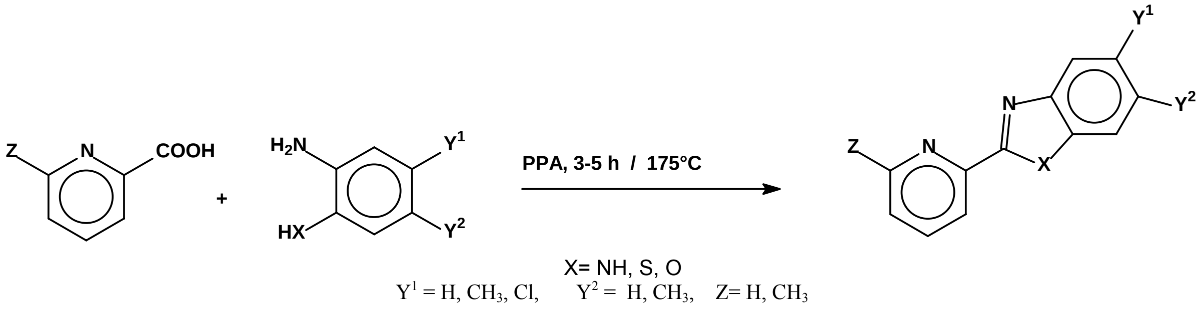
4.1. General remarks

2,6-Bis(benzimidazolyl)pyridine[91-95], 2,6-bis(benzothiazolyl)pyridine[89] and 2,6-bis (benzoxazolyl)pyridine[96] derivatives have been reported as ligands for transition metals in order to investigate the complexes for their structures and properties. Ceniceros-Gomez[97] reported on the preparation of (2-benzimidazolyl)pyridine chromium(III) complexes. For (2-benzothiazolyl)pyridines and (2-benoxazolyl)pyridines, no data were reported in the literature concerning the above mentioned compounds or their complexes with transition metals.

Herein the first titanium(IV), zirconium(IV) and vanadium(III) complexes with the titled ligands are reported together with their use as catalysts for olefin polymerization after activation with methylaluminoxane (MAO).

4.2. Synthesis of the pyridine derivatives 128-135

The compounds **128-135** were synthesized via the polyphosphoric acid method[90]. Condensation reactions of 2-pyridine carboxylic acid, or 6-methyl-2-pyridine carboxylic acid with 2-aminothiophenol, o-phenylene diamine, 3-methyl-o-phenylene, diamine 2-amino-4-methylphenol, and 2-amino-5-methylphenol were performed. The products were obtained in high yields (≥85%). The Phillip's modified method[79,80] failed to give any of the desired products. Table 9 summarizes the prepared compounds, and Table 10 gives their spectroscopic data.



Scheme 42. Synthesis of the ligand precursors **128-135.**

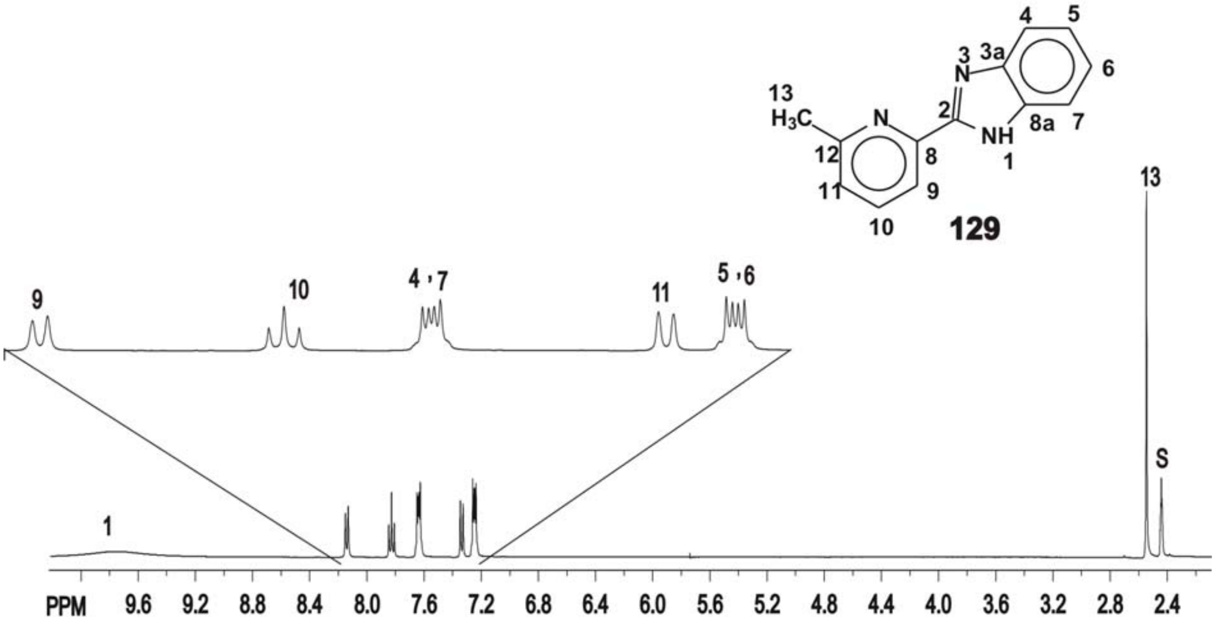
Table 9. Synthesized (2-benzimidazolyl)pyridine, (2-benzoxazolyl)pyridine and (2-benzothiazolyl)pyridine compounds **128-135.**

No.	**X**	**Y^1**	**Y^2**	**Z**
128	NH	H	H	H
129	NH	H	H	CH_3
130	NH	CH_3	H	H
131	NH	Cl	H	H
132	S	H	H	H
133	O	H	H	H
134	O	CH_3	H	H
135	O	H	CH_3	H

4.3. Characterization of the compounds 128-135

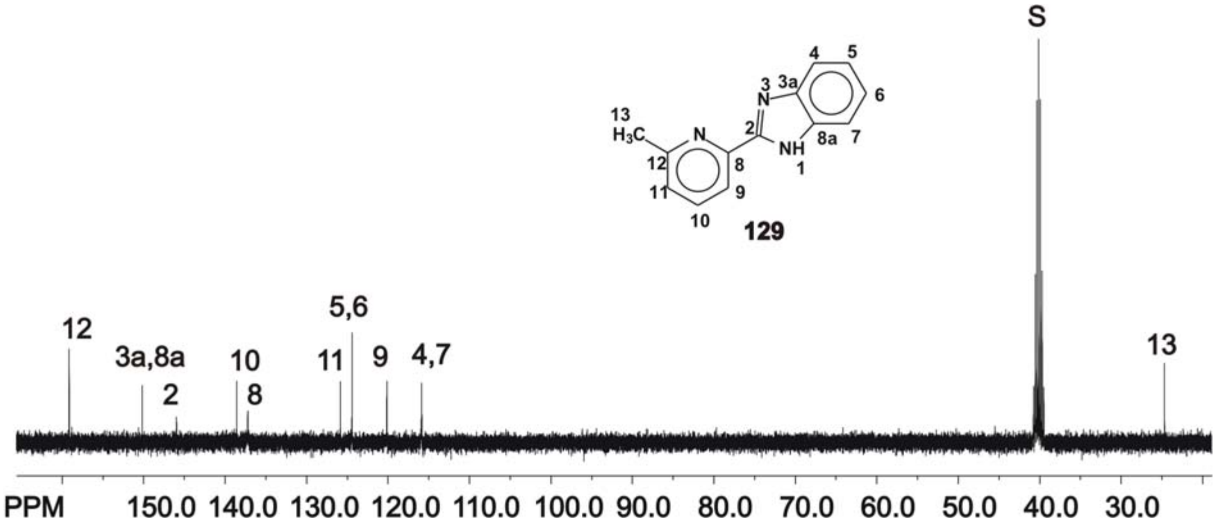
4.3.1. NMR spectroscopy

The compounds **128-135** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR of compound **129** (Scheme 43) shows seven sets of signals. The broad signal with low intensity downfield at δ = 9.88 ppm is assigned to the NH proton, a doublet at δ = 8.25 ppm [1H, $J_{H,H}$ = 7.5 Hz] can be assigned to the pyridine ring proton H9. The triplet at δ = 7.82 ppm [1H, $J_{H,H}$ = 7.5 Hz] is assigned to H10, the multiplet at δ = 7.72-7.68 ppm can be assigned to the phenyl protons H4 and H7. H11 appears at δ = 7.38 ppm [d, 1H, $J_{H,H}$ = 7.5 Hz]. The multiplet at δ = 7.27-7.25 ppm is assigned to the protons H5 and H6, and the methyl group protons are found as singlet a at δ = 2.58 ppm.



Scheme 43. ^{1}H NMR spectrum of compound **129.**

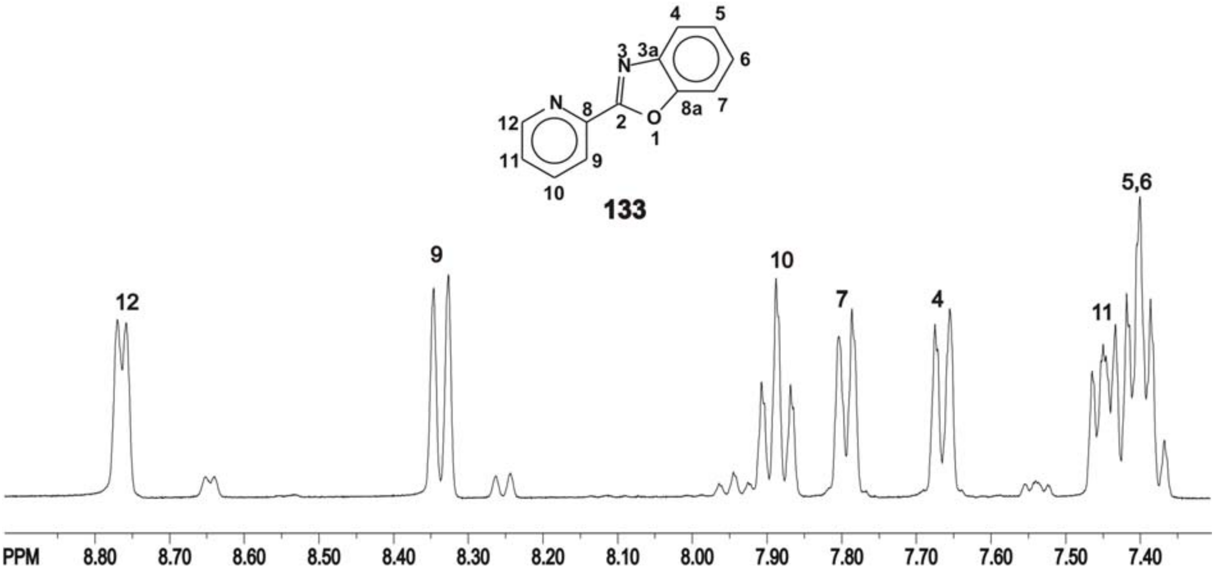
The ^{13}C NMR spectrum of compound **129** (Scheme 44) shows ten signals. The signal at δ = 159.1 ppm corresponds to carbon atom C1, the signal appearing at δ = 150.2 ppm is assigned to carbon atom C5, the signals at δ = 146.0 and 138.6 ppm can be assigned to C12 and C3. The signal at δ = 137.2 ppm arises from the two carbon atoms of the phenyl ring (C6,C11). The carbon atom C2 of the pyridine ring appears at δ=125.9 ppm. The carbon atoms C8 and C9 appear at δ = 124.4 ppm, the signal at δ = 120.1 ppm corresponds to C4, while C7 and C10 appear at δ = 115.9 ppm. At δ = 24.7 ppm, the methyl group carbon atom (C13) can be detected.



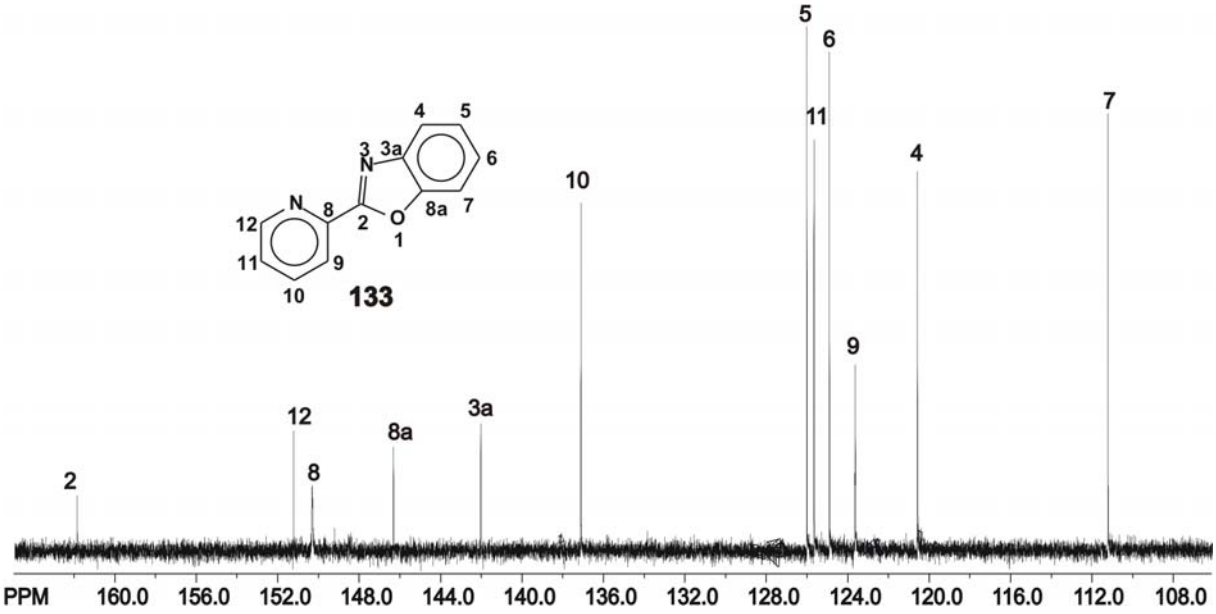
Scheme 44. ^{13}C NMR spectrum of compound **129.**

The ^{1}H NMR spectrum of compound **133** (Scheme 45) shows six resonance signals. The doublet at δ = 8.77 ppm [$J_{H,H}$ = 5.8 Hz] is assigned to H12 of the pyridine ring. The doublet at δ = 8.34 ppm [$J_{H,H}$ = 7.7 Hz] corresponds to proton H9, at δ = 7.88 ppm [$J_{H,H}$ = 7.7 Hz] a triplet is assigned to H10. The two doublets at δ = 7.80 ppm [$J_{H,H}$ = 7.7 Hz] and δ = 7.67 ppm [$J_{H,H}$ = 7.7 Hz] can be assigned to H7 and H4. The triplet at δ = 7.46 ppm [$J_{H,H}$ = 5.8 Hz] corresponds to H11. The aromatic protons H5 and H6 appear as triplet at δ =7.39 ppm [$J_{H,H}$ = 7.7 Hz].

The ^{13}C NMR spectrum of compound **133** (see Scheme 46) shows twelve resonance signals each corresponding to one carbon atom. The signal at δ = 161.9 ppm is assigned to C2. The five signals at δ = 151.3, 150.4, 146.4, 142.1, 137.2 ppm can be assigned to C12, C8, C8a, C3a and C10. The signal at δ = 126.1 ppm corresponds to C5, the signals at δ = 125.7 and 125.0 ppm can be assigned to C11 and C6. The three signals at δ = 123.7, 120.6, 111.3 ppm correspond to C9, C4 and C7. The data for the other compounds are listed in Table 10.



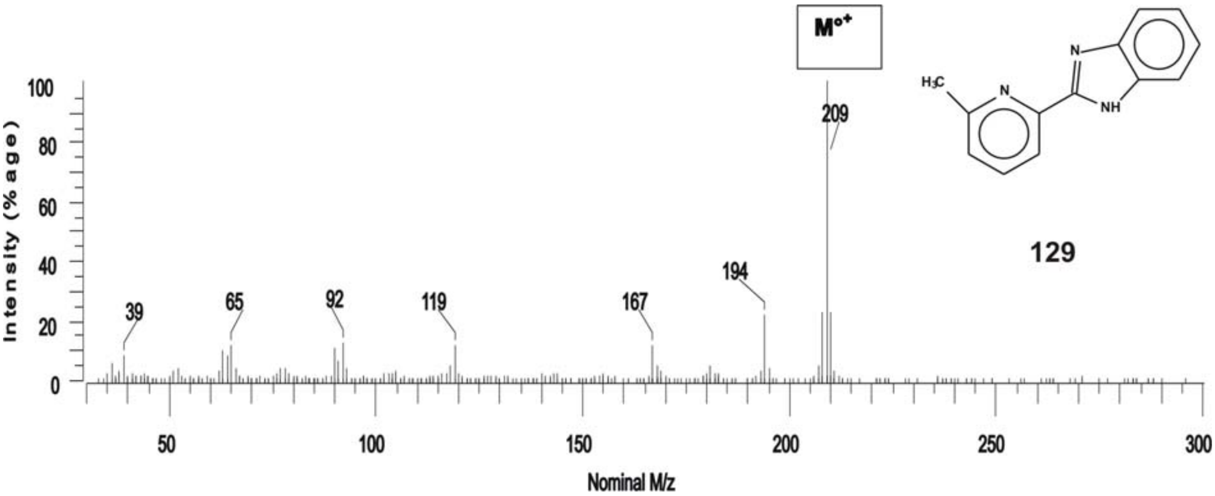
Scheme 45. ^{1}H NMR spectrum of compound **133.**



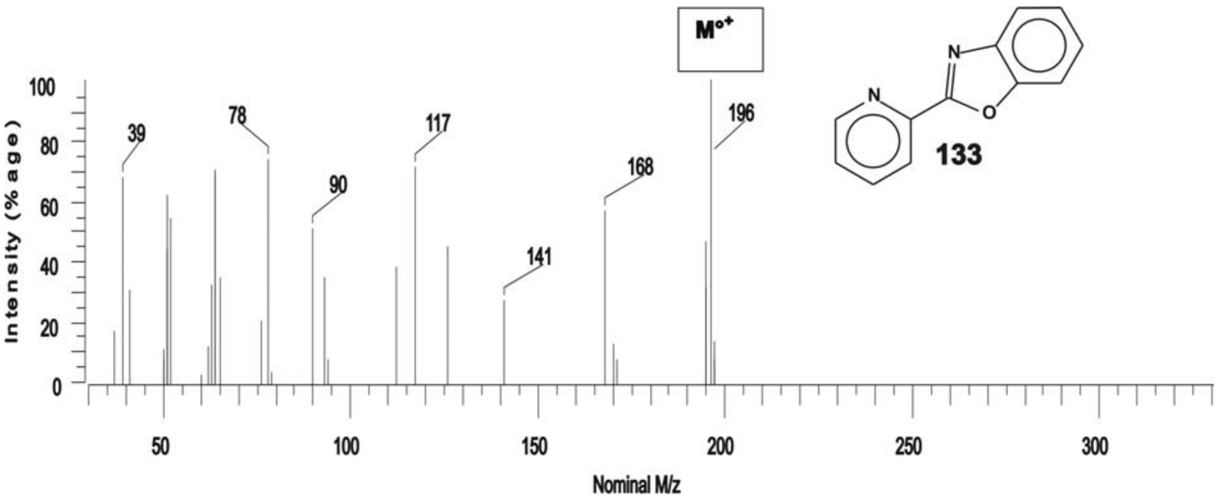
Scheme 46. ^{13}C NMR spectrum of compound **133.**

4.3.2. Mass spectroscopy

The compounds **128-135** in addition to their ^{1}H NMR and ^{13}C NMR spectra, were characterized by mass spectroscopy. The mass spectrum of compound **129** shows the molecular ion at m/z = 209. The ion resulting from the loss of a methyl group is represented by m/z = 194 (the full fragmentation pattern is shown in Scheme 47). Another example, the mass spectrum of the compound **133** shows the molecular ion with m/z = 196 as the base peak, while the fragment with mass m/z = 117 represents one benzoxazole unit. The full fragmentation pattern is shown in Scheme 48.

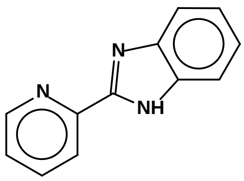
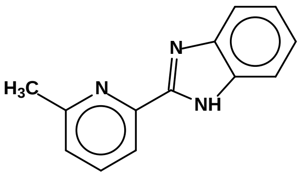
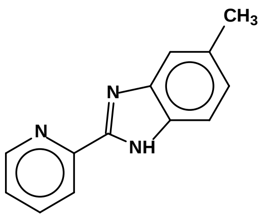
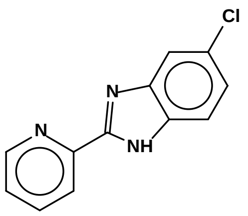


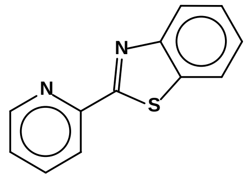
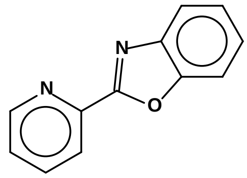
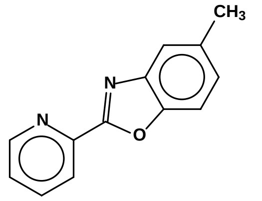
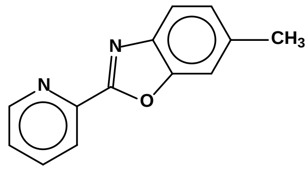
Scheme 47. Mass spectrum of compound **129.**



Scheme 48. Mass spectrum of compound **133.**

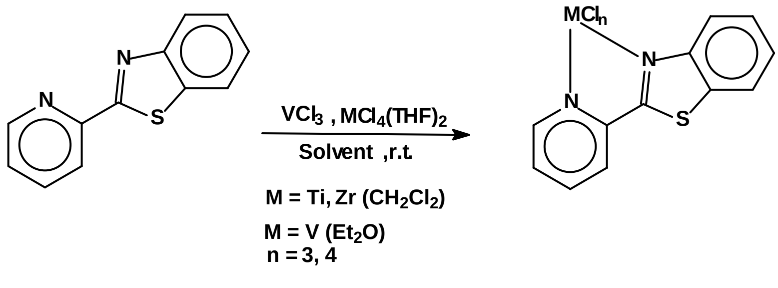
Table 10. NMR and mass spectroscopic data for the compounds **128-135.**

No.	**compound**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**Mass m/z (%)**
128		8.69(d,1H), 8.29(d,1H), 7.95(t,1H), 7.59-7.57(m,2H), 7.48(t,1H), 7.19-7.17(m,2H)	151.3, 150.0, 149.1, 138.2, 125.4, 123.2, 122.1	195 M$^{\circ+}$ (100)
129		8.24(d,1H), 7.82(t,1H), 7.72-7.68(m,2H), 7.38(d,1H), 7.27-7.25(m,2H), 2.58(s,3H,CH_3)	159.1, 150.2, 145.9, 138.6, 137.2, 125.8, 124.4, 120.1, 115.9, 24.7	209 M$^{\circ+}$ (100)
130		8.71(d,1H), 8.32(d,1H), 7.98(t,1H), 7.50(d,2H), 7.41(s,1H), 7.05(d,1H), 2.42(s,3H, CH_3)	150.4, 149.0, 145.5, 138.7, 135.8, 134.7, 134.5, 126.5, 126.4, 123.3, 115.6, 114.8, 21.9	209 M$^{\circ+}$ (100)
131		8.75(d,1H), 8.33(d,1H), 8.02(t,1H), 7.78(s,1H), 7.55(d,2H), 7.26(t,1H)	150.2, 148.7, 138.4, 125.8, 124.0, 123.0, 122.3, 121.3, 119.4, 114.1, 112.4	231 M$^{\circ+}$ (100)

No.	compound	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z (%)
132		8.68(d,1H), 8.27(d,1H), 8.11(d,1H), 8.05(d,1H), 7.99(t,1H), 7.53-7.49(m,2H), 7.45(t,1H)	169.7, 154.4, 151.0, 150.6, 138.5, 136.1, 127.3, 126.8, 126.6, 124.0, 123.2, 121.0	212 $M^{\circ+}$ (100)
133		8.77(d,1H), 8.34(d,1H), 7.89(t,1H), 7.80(d,1H), 7.67(d,1H), 7.46-7.39(m,3H)	161.9, 151.3, 150.4, 146.4, 142.1, 137.2, 126.1, 125.7, 125.0, 123.7, 120.6, 111.3	196 $M^{\circ+}$ (100)
134		8.79(d,1H), 8.31(d,1H), 8.04(t,1H), 7.70(d,1H), 7.64(s,1H), 7.61(t,1H), 7.29(d,1H), 2.44(s,3H,CH_3)	162.1, 150.9, 149.4, 146.0, 142.1, 138.3, 135.2, 128.0, 126.8, 124.2, 120.7, 111.4, 21.7	210 $M^{\circ+}$ (100)
135		8.78(d,1H), 8.29(d,1H), 8.15(t,1H), 7.72(d,1H), 7.62(s,1H), 7.59(t,1H), 7.25(d,1H), 2.53(s,3H,CH_3)	161.5, 151.4, 150.8, 146.1, 139.8, 138.3, 137.1, 127.0, 126.7, 124.0, 120.4, 111.9, 22.0	210 $M^{\circ+}$ (100)

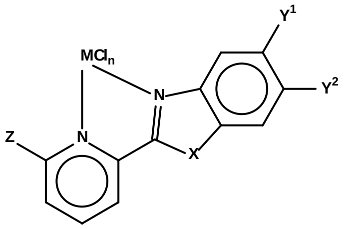
4.4. Synthesis of complexes 136-159

The complexes **136-159** were synthesized according to Scheme 49 by mixing the organic compounds and the corresponding metal salt (VCl_3) or the tetrahydrofuran adducts of zirconium and titanium tetrachloride in an appropriate solvent and stirring the mixture overnight. The products were obtained in very good yields, except in the cases of **148-150**.



Scheme 49. Synthesis of complexes **148-150.**

Table 11. The synthesized 2-(benzimidazolyl)pyridine , 2-(benzothiazolyl)pyridine and 2-(benzoxazolyl)pyridine transition metal complexes.



n=3 or 4

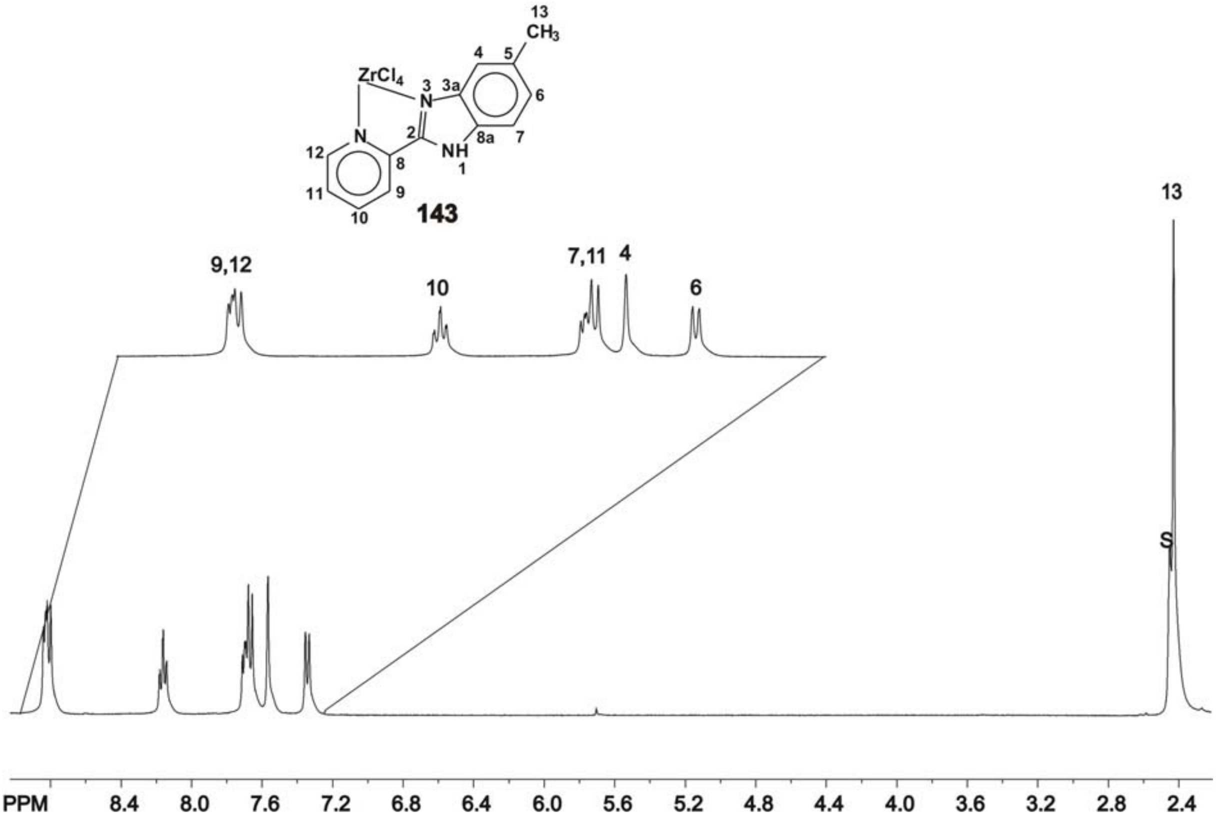
Complex No.	X	Y^1	Y^2	Z	M
136	NH	H	H	H	Ti
137	NH	H	H	H	Zr
138	NH	H	H	H	V
139	NH	H	H	CH_3	Ti
140	NH	H	H	CH_3	Zr
141	NH	H	H	CH_3	V
142	NH	CH_3	H	H	Ti
143	NH	CH_3	H	H	Zr
144	NH	CH_3	H	H	V
145	NH	Cl	H	H	Ti
146	NH	Cl	H	H	Zr
147	NH	Cl	H	H	V
148	S	H	H	H	Ti
149	S	H	H	H	Zr
150	S	H	H	H	V
151	O	H	H	H	Ti
152	O	H	H	H	Zr
153	O	H	H	H	V
154	O	CH_3	H	H	Ti
155	O	CH_3	H	H	Zr
156	O	CH_3	H	H	V
157	O	H	CH_3	H	Ti
158	O	H	CH_3	H	Zr
159	O	H	CH_3	H	V

4.5. Characterization of the complexes 136-159

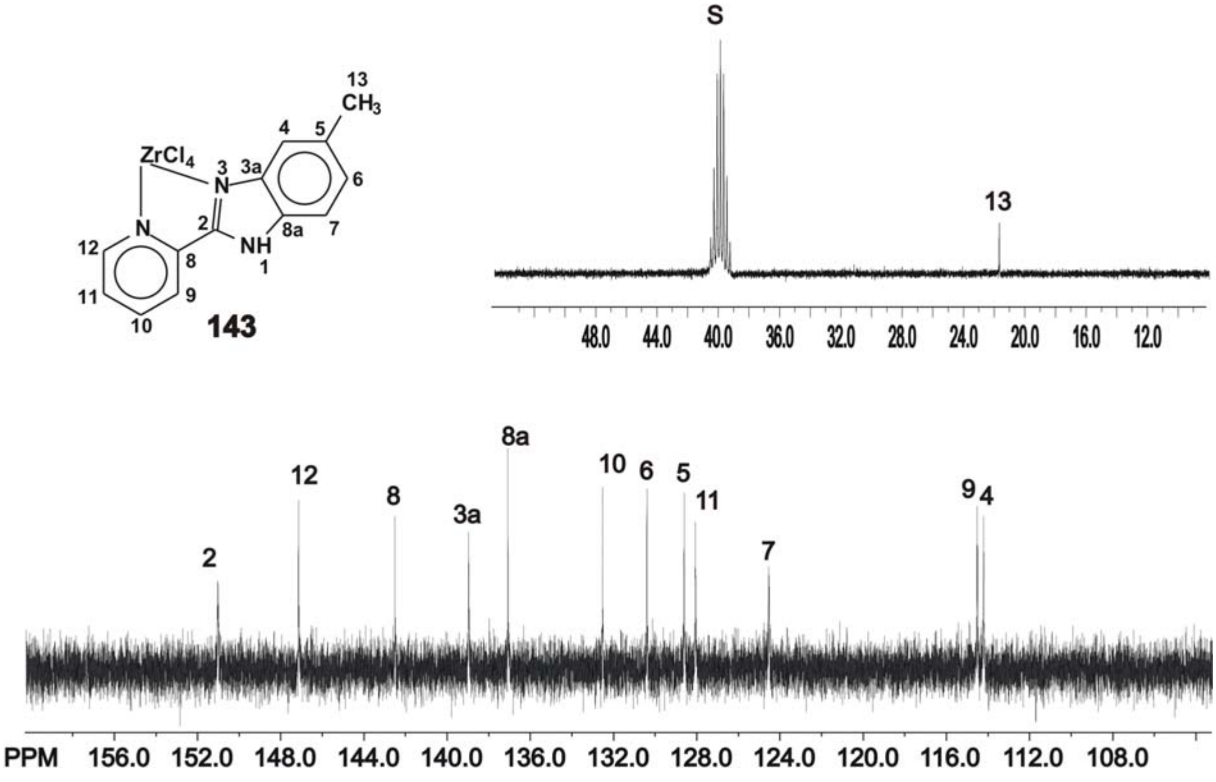
4.5.1. NMR spectroscopy

The complexes **136-159** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of complex **143** (Scheme 50) shows six resonance signals: the signal at δ = 8.84 ppm corresponds to H9, H12. The triplet at δ = 8.19 ppm [$J_{H,H}$ = 7.5Hz] is assigned to H10. The multiplet at δ = 7.71 ppm can be assigned to the protons H7 and H11, and the singlet at δ = 7.56 ppm is assigned to H4. At δ = 7.35 ppm [$J_{H,H}$ = 8.5Hz], H6 appears as doublet. The protons of the methyl group appear at δ = 2.02 ppm.

The ^{13}C NMR spectrum of complex **143** (Scheme 51) shows 13 resonance signals assigned to the 13 carbon atoms as follows: δ = 151.1 (C2), 147.2 (C12), 142.6 (C8), 139.0 (C3a), 137.2 (C8a), 133.6 (C10), 130.5 (C6), 128.7 (C5), 128.1 (C11), 124.6 (C7), 114.6 (C9), 114.3 (C4) and δ = 21.9 ppm (C13).



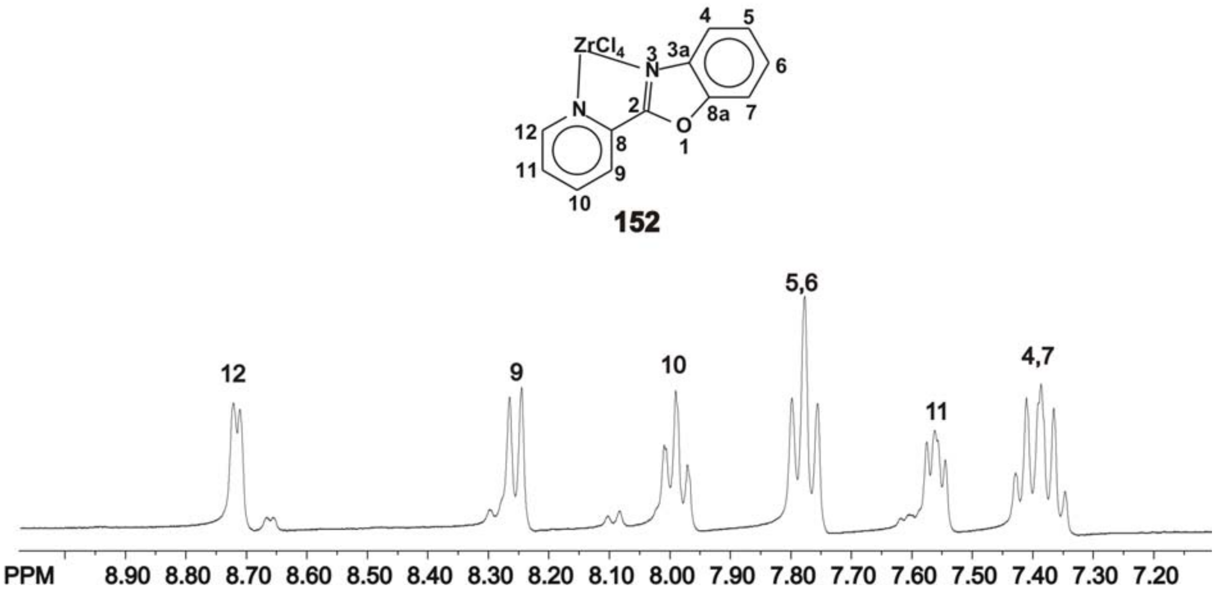
Scheme 50. ^{1}H NMR spectrum of complex **143.**



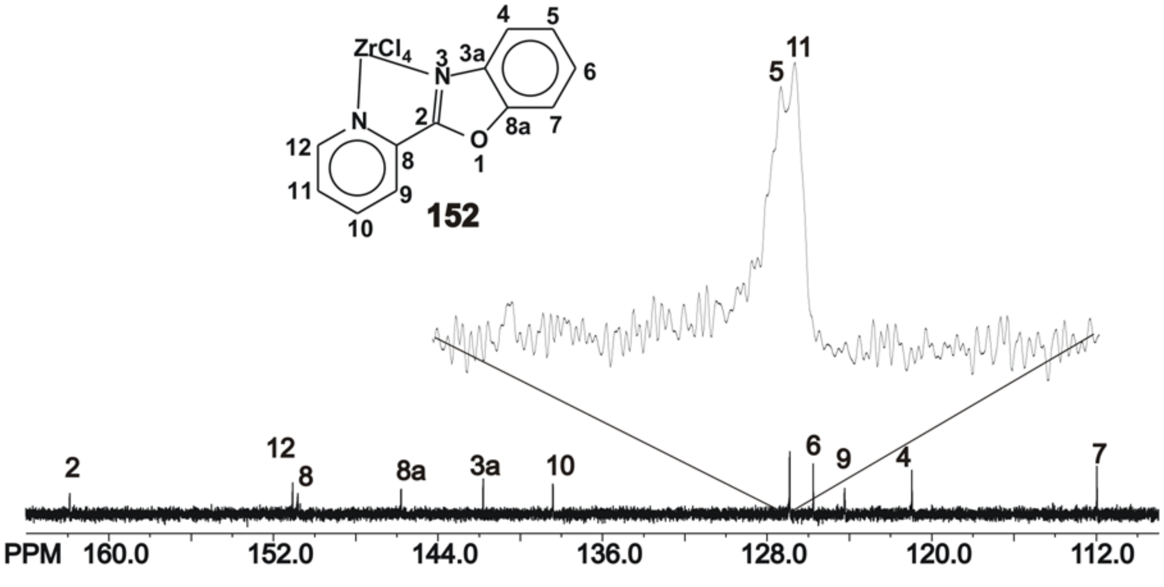
Scheme 51. ^{13}C NMR spectrum of complex **143.**

The ^{1}H NMR spectrum of complex **152** (Scheme 52) shows six resonance signals: at δ = 8.72 ppm [1H, $J_{H,H}$ = 6.1 Hz] a doublet is assigned to proton H12, at δ = 8.26 ppm [d,1H, $J_{H,H}$ = 7.6 Hz] for H9, at δ = 8.04 ppm [1H, $J_{H,H}$ = 7.6 Hz] a triplet assigned to H10. H5, H6 appear as triplet [2H, $J_{H,H}$ = 7.6 Hz] at δ = 7.78 and H11 as triplet at δ = 7.57 ppm [1H,$J_{H,H}$ = 6.1 Hz]. The multiplet at δ = 7.43-7.35 (m,2H) can be assigned to the protons H4 and H7.

The ^{13}C NMR spectrum of complex **152** (Scheme 53) shows 12 resonance signals which can be assigned as follows: δ = 161.9 (C2), 151.1 (C12), 150.8 (C8), 145.8 (C8a), 141.8 (C3a), 138.4 (C10), the signa at δ = 126.9 ppm (assigned to 2 carbon atoms (C5, C11), 125.8 (C6), 124.2 (C9), 121.0 (C4), and 111.9 ppm (C7). The NMR data of the other complexes are given in Table 12.



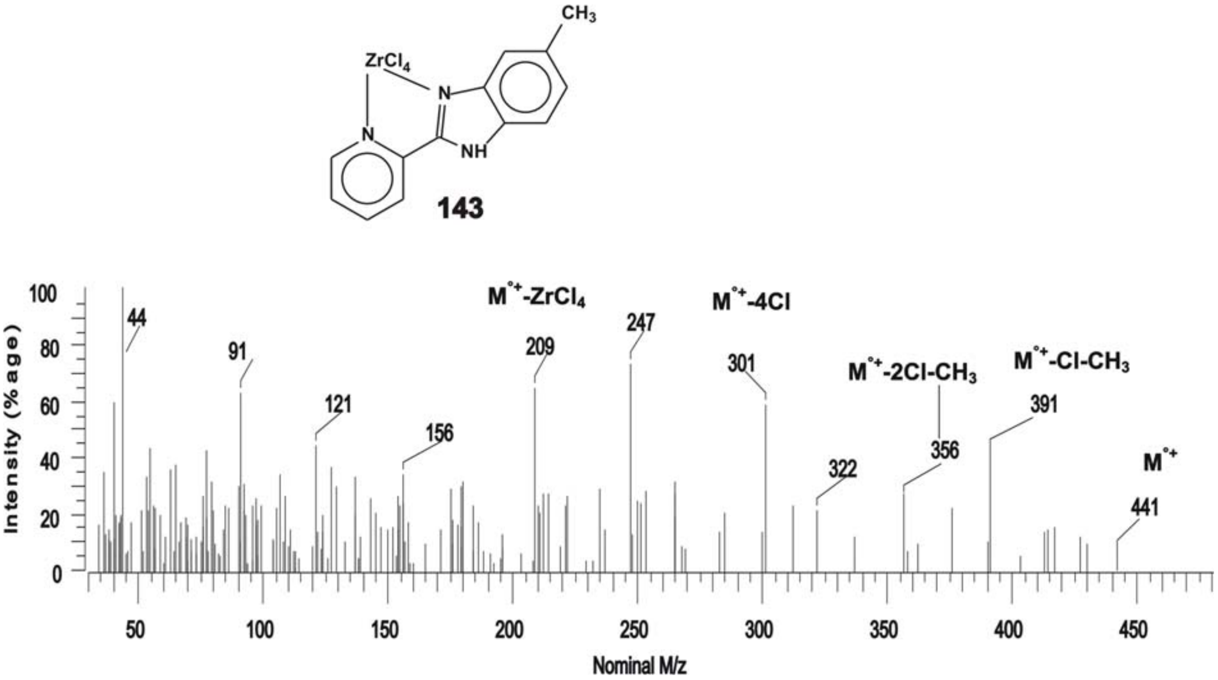
Scheme 52. ^{1}H NMR spectrum of complex **152.**



Scheme 53. ^{13}C NMR spectrum of complex **152.**

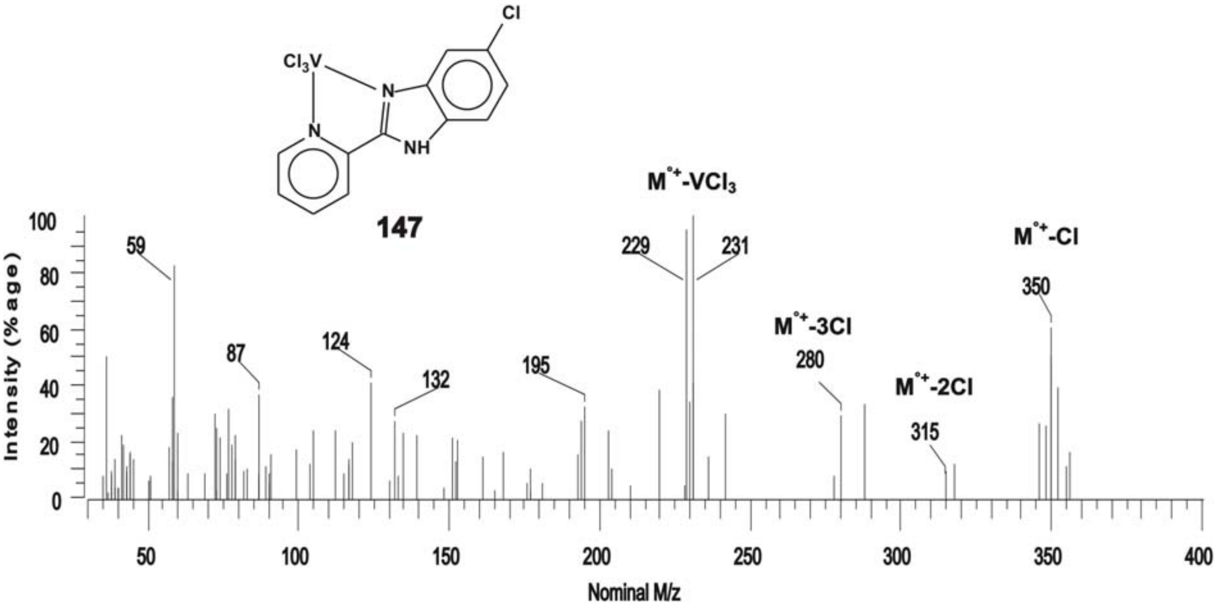
4.5.2. Mass spectroscopy

In addition to their NMR spectra, the complexes **136-159** were characterized by mass spectroscopy. The mass spectrum of complex **143** (Scheme 54) shows the molecular ion at m/z = 441. The peaks at m/z = 391 and m/z = 356 represent the ions [$M^{\circ+}$ - Cl-CH_3], and [$M^{\circ+}$ - 2Cl-CH_3], the peak at m/z = 301 represents the ion [$M^{\circ+}$ - 4Cl]. The peak at m/z = 209 can be assigned to the free ligand.


143

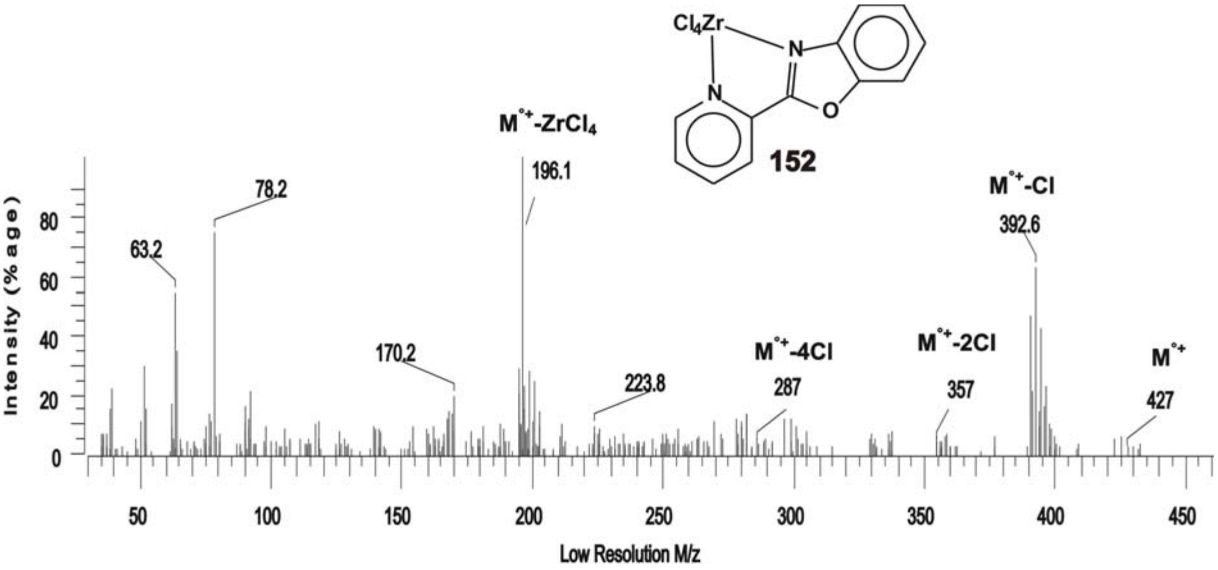
Scheme 54. Mass spectrum of complex **143.**

The mass spectrum of complex **147** (Scheme 55) shows the peak with the mass m/z = 350 ($M^{\circ+}$- Cl). The loss of 2 chloride ions results in a peak with m/z = 315 ($M^{\circ+}$-2Cl). The peak with m/z = 229/231 represents the free ligand.


147

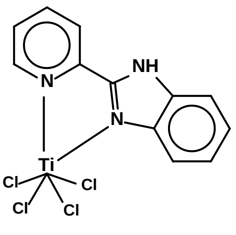
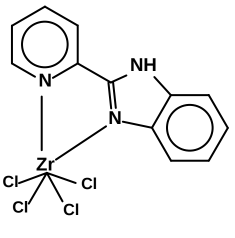
Scheme 55. Mass spectrum of complex **147.**

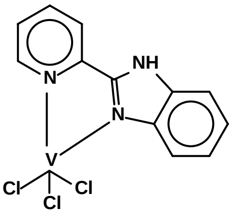
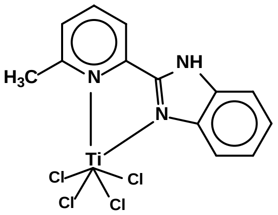
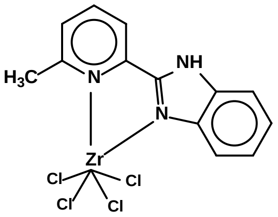
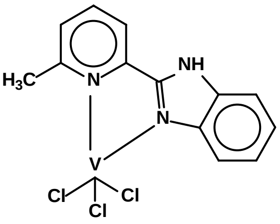
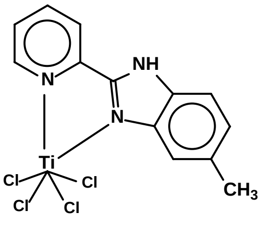
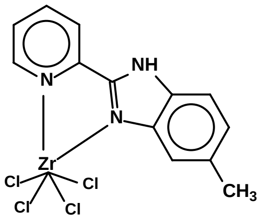
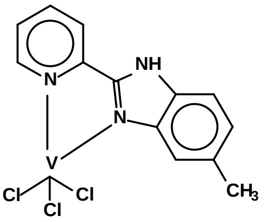
The mass spectrum of complex **152** (Scheme 56) shows the molecular ion peak ($M^{\circ+}$) at m/z = 426. The loss of one chloride ion results in a peak with m/z = 393 ($M^{\circ+}$-Cl). The peak with m/z = 196 represents the free ligand. The mass spectroscopic data of the other complexes are given in Table 12.

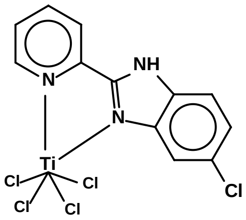
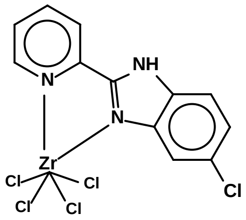
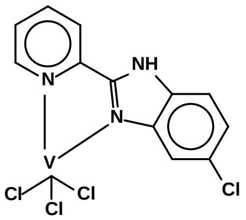
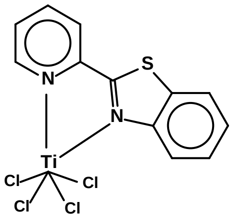
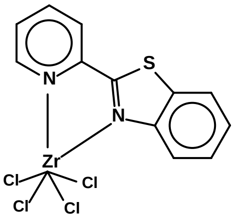
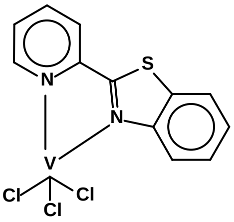


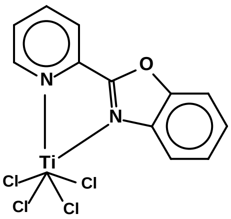
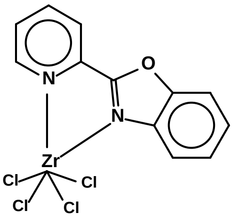
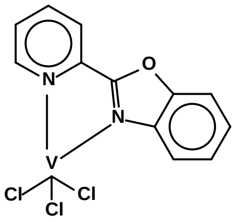
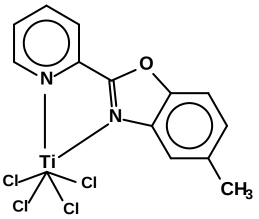
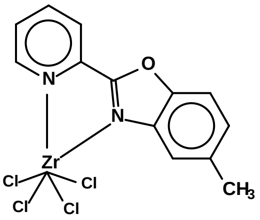
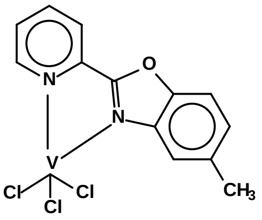
Scheme 56. Mass spectrum of complex **152.**

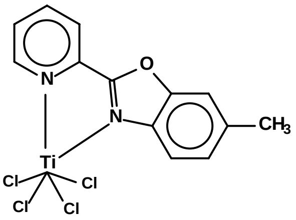
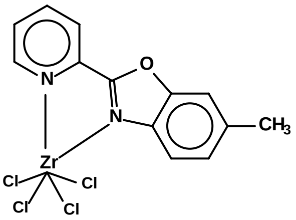
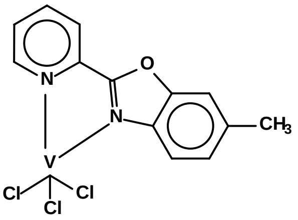
Table 12. NMR and Mass spectroscopic data for the complexes **136-159**

No.	**Complex**	**^{1}H NMR** **δ [ppm]**	**^{13}C NMR** **δ [ppm]**	**Mass** **m/z(%)**
136		8.93-8.90(dd,2H), 8.24(t,1H), 7,88-7.85(dd,2H), 7.80-7.75(dd,1H), 7.61-7.58(dd,2H)	151.2, 147.8, 142.8, 139.1, 132.6, 128.3, 127.1, 124.8, 115.1	385 $M^{\circ+}$(5), 349 $M^{\circ+}$-Cl (10), 312 $M^{\circ+}$ -2Cl (5), 276 $M^{\circ+}$ -3Cl (15), 243 $M^{\circ+}$ -4Cl (5) 195 $M^{\circ+}$-$TiCl_4$ (100)
137		8.79(d,1H), 8.50(d,1H), 8.08(t,1H), 7.71-7.68(dd,2H), 7.62-7.59(dd,1H), 7.38-7.36(dd,2H)	150.8, 148.9, 144.2 138.8, 134.3, 127.3, 125.8, 123.9, 115.5	428 $M^{\circ+}$(2), 392 $M^{\circ+}$-Cl (15), 355 $M^{\circ+}$ -2Cl (20), 320 $M^{\circ+}$ -3Cl (5), 284 $M^{\circ+}$ -4Cl (5), 195 $M^{\circ+}$-$ZrCl_4$ (100)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
138		n.d.	n.d.	352 $M^{\circ+}$(5), 316 $M^{\circ+}$-Cl (20), 281 $M^{\circ+}$ -2Cl (10), 195 $M^{\circ+}$-VCl_3 (100)
139		8.53(d,1H), 8.10-8.06(t,1H), 7.84 (br,2H), 7.61-7.59(d,1H), 7.58-7.56(m,2H), 2.5(s,3H,CH_3)	160.5, 148.2, 142.2, 139.5, 133.0, 128.1, 127.0, 122.0, 115.2, 24.8	401 $M^{\circ+}$(5), 364 $M^{\circ+}$-Cl (5), 328 $M^{\circ+}$ -2Cl (5), 254 $M^{\circ+}$ -4Cl (5), 209 $M^{\circ+}$-$TiCl_4$ (100)
140		8.87 (br,1H), 8. 25 (br,1H), 8.02(br,2H), 7.74(br,3H), 2.42(s,3H,CH_3)	160.5, 148.1, 142.1, 139.4, 132.7, 128.4, 127.3, 122.5, 115.4, 25.0	442 $M^{\circ+}$(5), 405 $M^{\circ+}$-Cl (10), 368 $M^{\circ+}$ -2Cl (10), 329 $M^{\circ+}$ -3Cl (20) 209 $M^{\circ+}$-$ZrCl_4$ (100)
141		n.d.	n.d.	366 $M^{\circ+}$(5), 329 $M^{\circ+}$-Cl (10), 295 $M^{\circ+}$ -2Cl (15), 259 $M^{\circ+}$ -3Cl (20) 209 $M^{\circ+}$-VCl_3 (100)
142		8.86(d,1H), 8.67(d,1H), 8.17(t,1H), 7.70(t,2H), 7.57(s,1H), 7.33(d,1H), 2.47(s,3H,CH_3)	151.0, 148.0, 143.7, 139.0, 136.4, 133.9, 131.9, 128.0, 127.7, 124.1, 115.0, 114.5, 22.0	402 $M^{\circ+}$(5), 364 $M^{\circ+}$-Cl (5), 328 $M^{\circ+}$ -2Cl(5), 254 $M^{\circ+}$ -4Cl (5), 209 $M^{\circ+}$-$TiCl_4$ (100)
143		8.84-8.80(m,2H), 8.17(t,1H), 7.71-7.66(m,2H), 7.57(s,1H), 7.34(d,1H), 2.02(s,3H,CH_3)	151.1, 147.2, 142.6, 139.0, 137.2, 133.6, 130.5, 128.7, 128.1, 124.6, 114.6, 114.3, 21.9	442 $M^{\circ+}$(5), 428 $M^{\circ+}$-CH_3 (10) 405 $M^{\circ+}$-Cl (10), 368 $M^{\circ+}$ -2Cl (10), 329 $M^{\circ+}$ -3Cl (20), 300 $M^{\circ+}$ -4Cl (20) 209 $M^{\circ+}$-$ZrCl_4$ (100)
144		n.d.	n.d.	366 $M^{\circ+}$(5), 330 $M^{\circ+}$-Cl (10), 316$M^{\circ+}$-Cl-CH_3 (5), 294 $M^{\circ+}$ -2Cl (15), 260 $M^{\circ+}$ -3C l(20) .209 $M^{\circ+}$-

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
				VCl_3 (100)
145		8.86(d,1H), 8.70(d,1H), 8.19(t,1H), 7.82(s,1H), 7.77(d,1H), 7.71(t,1H), 7.54-7.50(dd,1H)	150.9, 15.0, 144.2, 139.0, 135.6, 133.6, 130.2, 127.8, 126.4, 124.2, 117.0, 115.1	384 $M^{\circ+}$-Cl (10), 349 $M^{\circ+}$ -2Cl (7), 229 $M^{\circ+}$-$TiCl_4$ (50)
146		8.75(d,1H), 8.46(d,1H), 8.04(t,1H), 7.69(d,1H), 7.65(s,1H), 7.58(t,1H), 7.35-7.32(dd,1H)	151.2, 150.5, 146.3, 138.667, 136.0, 132.7, 128.9, 126.8, 125.0, 123.2, 117.2, 115.4	468 $M^{\circ+}$(10), 426 $M^{\circ+}$-Cl (40), 387 $M^{\circ+}$ -2Cl (50), 229 $M^{\circ+}$-$ZrCl_4$ (100)
147		n.d.	n.d.	386 $M^{\circ+}$(7), 350 $M^{\circ+}$-Cl (20), 315 $M^{\circ+}$ -2Cl (30), 279 $M^{\circ+}$-3Cl (5), 229 $M^{\circ+}$-VCl_3 (100)
148		8.70(t,1H), 8.30(d,1H), 8.14(d,1H), 8.07(d,1H), 8.01(t,1H), 7.57(t,2H), 7.53-7.46(m,2H)	169.6, 154.4, 150.9, 150.577, 138.6, 136.1, 127.3, 126.8, 126.7, 124.0, 123.3, 121.1	403 $M^{\circ+}$(3), 366 $M^{\circ+}$-Cl (15), 329 $M^{\circ+}$ -2Cl (20), 293 $M^{\circ+}$ -3Cl (10), 212 $M^{\circ+}$ -$TiCl_4$ (100)
149		8.73(t,1H), 8.33(d,1H), 8.18(d,1H), 8.11(d,1H), 8.05(t,1H), 7.60(t,2H), 7.54-7.47(m,2H)	169.7, 154.4, 151.0, 150.7, 138.6, 136.1, 127.4, 126.9, 126.7, 124.0, 123.3, 121.1	445 $M^{\circ+}$(2), 408 $M^{\circ+}$-Cl (20), 372 $M^{\circ+}$ -2Cl (10), 300 $M^{\circ+}$ -4Cl (20), 212 $M^{\circ+}$ -$ZrCl_4$ (100)
150		n.d.	n.d.	370 $M^{\circ+}$(5), 334 $M^{\circ+}$-Cl (10), 297 $M^{\circ+}$ -2Cl (15), 263 $M^{\circ+}$ -3Cl (5), 212 $M^{\circ+}$ -VCl_3 (100)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
151		8.75(d,1H), 8.29(d,1H), 8.03(t,1H), 7.81(t,2H), 7.60(t,1H), 7.46-7.37(m,2H)	161.8, 151.1, 150.7, 145.7, 141.8, 138.6, 127.0, 126.9, 125.8, 124.3, 121.0, 112.0	386 $M^{\circ+}$(2), 333 $M^{\circ+}$-Cl-O (30), 297 $M^{\circ+}$-2Cl-O (30), 245 $M^{\circ+}$-4Cl (5), 196 $M^{\circ+}$- $TiCl_4$ (100)
152		8.72(d,1H), 8.26(d,1H), 8.04(t,1H), 7.78(t,2H), 7.57(t,1H), 7.43-7.35(m,2H)	161.9, 151.1, 150.8, 145.8, 141.8, 138.4, 126.9(2C), 125.8, 124.2, 121.0, 111.9	429 $M^{\circ+}$(2), 392 $M^{\circ+}$-Cl (50), 376 $M^{\circ+}$-Cl-O (5), 356 $M^{\circ+}$-2Cl (5), 289 $M^{\circ+}$-4Cl (5), 196 $M^{\circ+}$- $ZrCl_4$ (100)
153		n.d.	n.d.	353 $M^{\circ+}$(2), 317 $M^{\circ+}$-Cl (30), 283 $M^{\circ+}$-2Cl (5), 266 $M^{\circ+}$-Cl-O (7), 196 $M^{\circ+}$- VCl_3 (100)
154		8.77(d,1H), 8.29(d,1H), 8.05(t,1H), 7.69(d,1H), 7.63(s,1H), 7.60(t,1H), 7.28(d,1H), 2.44(s,3H,CH_3)	162.0, 150.8, 149.4, 145.9, 142.1, 138.5, 135.3, 128.0, 126.9, 124.2, 120.7, 111.4, 21.7	399 $M^{\circ+}$(2), 349 $M^{\circ+}$-Cl-CH_3 (5) 325 $M^{\circ+}$-2Cl (5), 293 $M^{\circ+}$-3Cl (7), 258 $M^{\circ+}$-4Cl (5), 210 $M^{\circ+}$-$TiCl_4$ (100)
155		8.76(d,1H), 8.30(d,1H), 8.05(t,1H), 7.69(d,1H), 7.63(s,1H), 7.61(t,1H), 7.28(d,1H), 2.43(s,3H,CH_3)	162.0, 150.8, 149.4, 145.9, 142.1, 138.4, 135.3, 127.9, 126.9, 124.2, 120.7, 111.4, 21.7	443 $M^{\circ+}$(5), 407 $M^{\circ+}$-Cl (5), 393 $M^{\circ+}$-Cl-CH_3 (10), 370 $M^{\circ+}$2Cl (10), 301 $M^{\circ+}$-4Cl (5), 210 $M^{\circ+}$- $ZrCl_4$ (100)
156		n.d.	n.d.	367 $M^{\circ+}$(5), 331 $M^{\circ+}$-Cl (10), 316 $M^{\circ+}$-Cl-CH_3 (3) 296 $M^{\circ+}$-2Cl (5), 280 $M^{\circ+}$-2Cl-O (5), 210 $M^{\circ+}$- VCl_3 (100)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
157		8.80(d,1H), 8.33(d,1H), 8.09(t,1H), 7.72(s,1H), 7.66(d,2H), 7.30(d,1H), 2.45(s,3H,CH_3)	161.8, 150.6, 149.4, 145.7, 142.1, 138.8, 135.3, 128.1, 126.9, 124.3, 120.7, 111.4, 21.7	400 $M^{\circ+}$(3), 349 $M^{\circ+}$-Cl-CH_3 (5) 325 $M^{\circ+}$-2Cl (5), 293 $M^{\circ+}$-3Cl (10, 258 $M^{\circ+}$-4Cl (10), 210 $M^{\circ+}$-$TiCl_4$ (100)
158		8.80(d,1H), 8.34(d,1H), 8.08(t,1H), 7.73(s,1H), 7.67(d,2H), 7.31(d,1H), 2.46(s,3H,CH_3)	161.9, 150.7, 149.4, 145.8, 142.1, 138.6, 135.3, 128.1, 126.9, 124.3, 120.8, 111.4, 21.7	443 $M^{\circ+}$(2), 407 $M^{\circ+}$-Cl (7), 393 $M^{\circ+}$-Cl-CH_3 (5), 370 $M^{\circ+}$2Cl (10), 301 $M^{\circ+}$-4Cl (5), 210 $M^{\circ+}$- $ZrCl_4$ (100)
159		n.d.	n.d.	367 $M^{\circ+}$(3), 331 $M^{\circ+}$-Cl (5), 317 $M^{\circ+}$-Cl-CH_3 (3) 296 $M^{\circ+}$-2Cl (5), 210 $M^{\circ+}$- VCl_3 (100)

5. Synthesis of N-allyl substituted bis-benzimidazoles and N-allyl substituted 2-benzimidazolyl pyridine transition metal complexes

5.1. General remarks

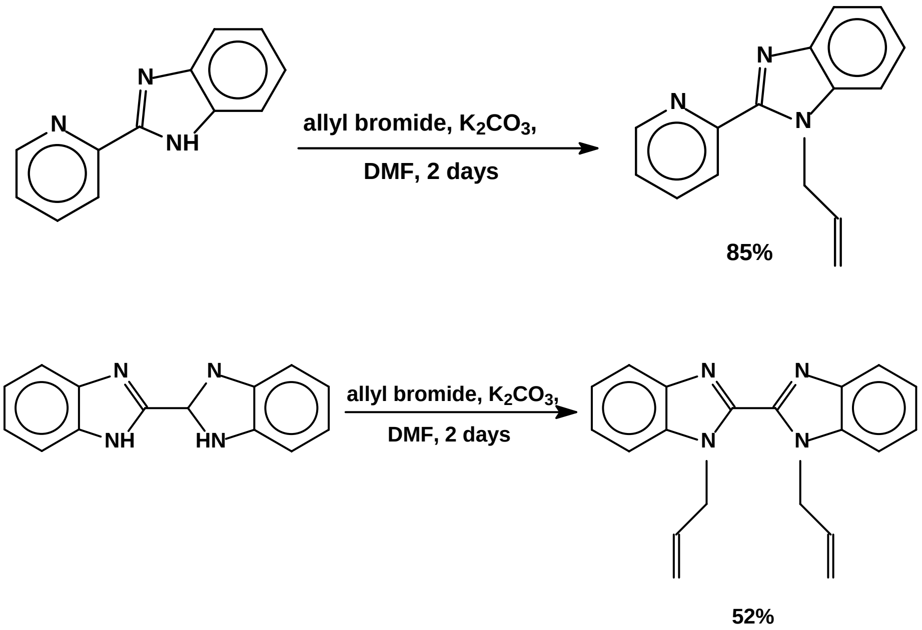
One elegant route used in catalytic olefin polymerization to get rid of the so-called reactor fouling is the self - immobilization concept introduced by Alt and coworkers[8,98]. As an analogous approach, alkenyl groups should be introduced into benzimidazole containing compounds. Kikugawa[99] reported the use of powdered potassium hydroxide for N-alkylation of imidazoles and benzimidazoles. Xianjin[100] recently reported the synthesis of 2,6-bis(N-allylbenzimidazolyl)pyridine copper (II) complexes.

Wenjuan[74] reported the use of N-alkylated 2-(benzimidazolyl)pyridine and 2,6-bis(benzimidazolyl)pyridine chromium(III) complexes in ethylene polymerization and oligomerization reactions.

Herein, the preparation and characterization of N-allyl substituted 2-(benzimidazolyl)pyridine, 1,2-bis(benzimidazolyl)benzene, 1,2-bis(benzimidazolyl)ethane 1,1-bis(benzimidazolyl)methane, and 2,6-bis(benzimidazolyl)pyridine along with their titanium, zirconium and vanadium complexes and their use in ethylene polymerization reactions after activation with methylaluminoxane is reported.

5.2. Synthesis of the allyl substituted imidazoles 160-165

N-allyl substituted bis-benzimidazoles were prepared according to a published procedure[101]. In the presence of potassium carbonate, the N-allylation proceeded readily to give the desired product in aprotic solvents, especially DMF under mild conditions. However, the reaction of allyl bromide with 2-(benzimidazolyl) pyridine is more productive. Generally, the introduction of one allyl group is much easier compared with double allylation. This is clearly shown from the yield of each reaction under the same conditions.



Scheme 57. Preparation of N-allyl substituted imidazoles.

5.3. Characterization

5.3.1. NMR spectroscopy

The compounds **160-165** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy.

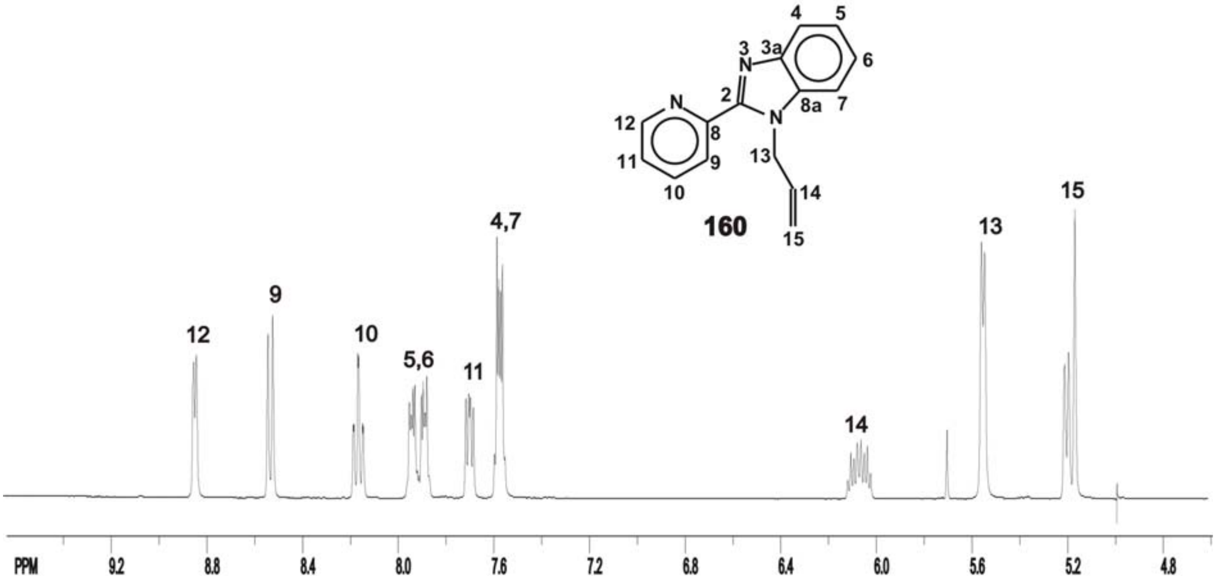
The ^{1}H NMR of compound **160** (Scheme 58) shows ten sets of resonance signals. The doublet at δ = 8.84 ppm [$J_{H,H}$ = 5.4 Hz] is assigned to H12. H9 appears as doublet at δ = 8.52 ppm[$J_{H,H}$ = 7.9 Hz]. The triplet at δ = 8.15 ppm [$J_{H,H}$ = 7.9 Hz] is assigned to H10. The two multiplets at δ = 7.93 and 7.88 ppm can be assigned to H5 and H6. The triplet at δ = 7.69 ppm [$J_{H,H}$ = 5.4 Hz] is assigned to H11, the multiplet at δ = 7.56 ppm corresponds to H4 and H7. The multiplet at δ = 6.10-6.01 ppm represents the CH proton of the allyl group. The multiplet at δ = 5.53-5.52 ppm corresponds to the methylene protons H13. The signal at δ = 5.20-5.15 ppm corresponds to the protons of the terminal CH_2 group of the double bond.

The ^{13}C NMR spectrum of complex **160** (Scheme 59) shows 15 resonance signals each equivalent to one carbon atom of the molecule: at δ = 150.9 (C8), 149.9 (C2), 148.8 (C3a), 143.0 (C12) , 137.4 (C8a), 137.0 (C10), 133. 9 (CH of the allyl group C14), 124.7 (C11), 123.9 (C6), 123.4 (C9), 122.6 (C5), 120.1 (C4), 116.6 ppm (terminal CH_2 of the allyl group C15), 110.7 ppm (C7) and at δ = 48.1 ppm (CH_2 of the allyl group C13).

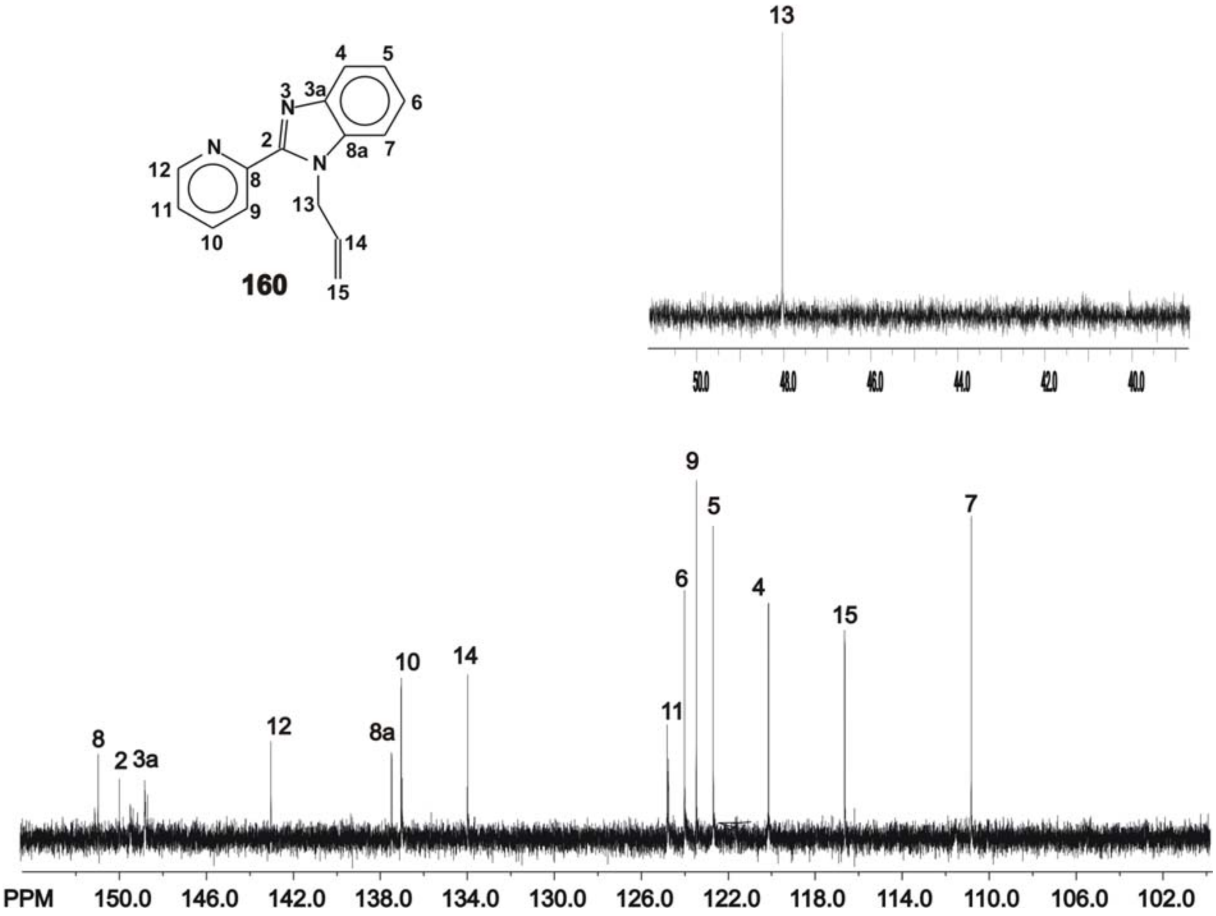
The ^{1}H NMR spectrum of compound **165** (Scheme 60) shows four sets of resonance signals. The signal at δ = 7.19 ppm corresponds to eight aromatic protons (H4-H7), the resonance signal at δ = 5.90-5.94 ppm represents the CH protons of the allyl group. The signal at δ =

5.25-5.18 ppm corresponds to protons of the terminal CH_2 group of the double bond, and the signal at $\delta = 4.82$ ppm corresponds to the methylene protons (H9).

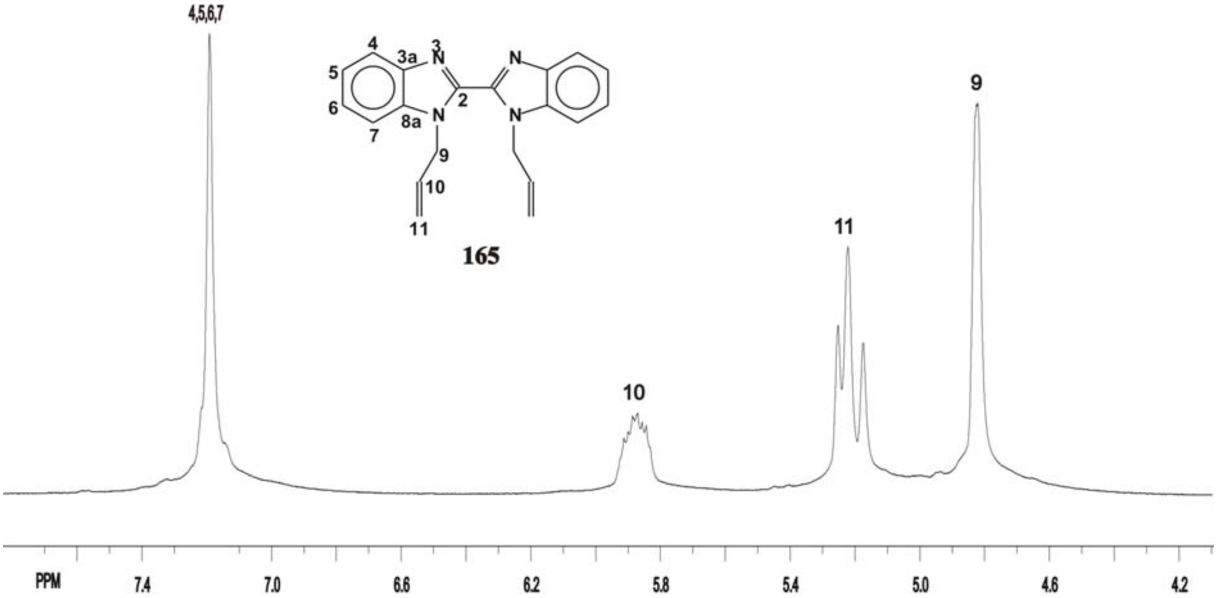
The ^{13}C NMR spectrum of compound **165** (Scheme 61) shows seven resonance signals. The signal at $\delta = 154.2$ ppm is assigned to the carbon atom C2, further signals appear at $\delta = 130.6$ (C10), 126.8 (C3a,8a), 124.4 (C5,6), 118.5 (C4,7), 115.9 (C11) and at $\delta = 45.7$ ppm (C9).



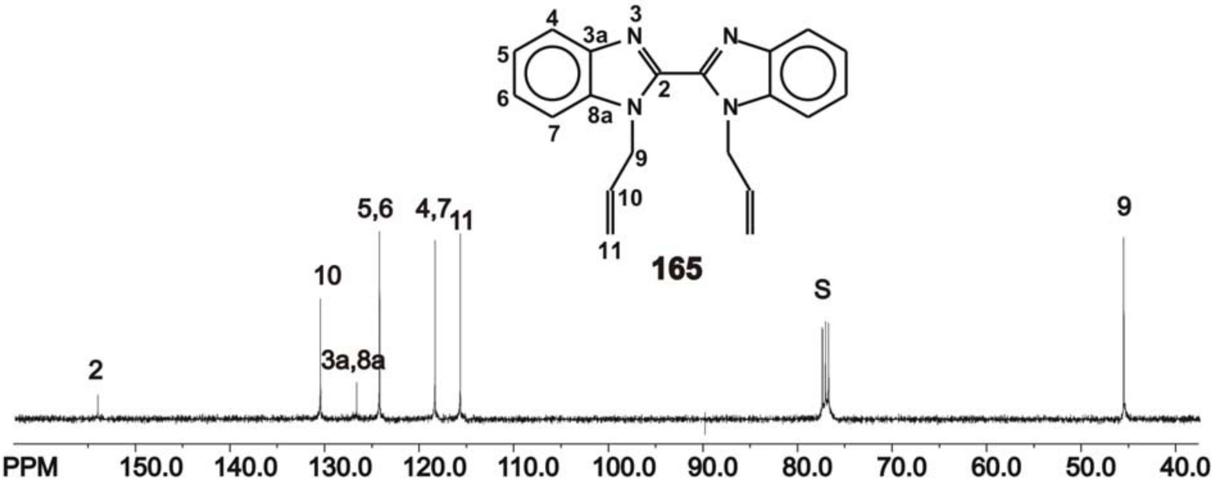
Scheme 58. ^1H NMR spectrum of compound **160.**



Scheme 59. ^{13}C NMR spectrum of compound **160.**



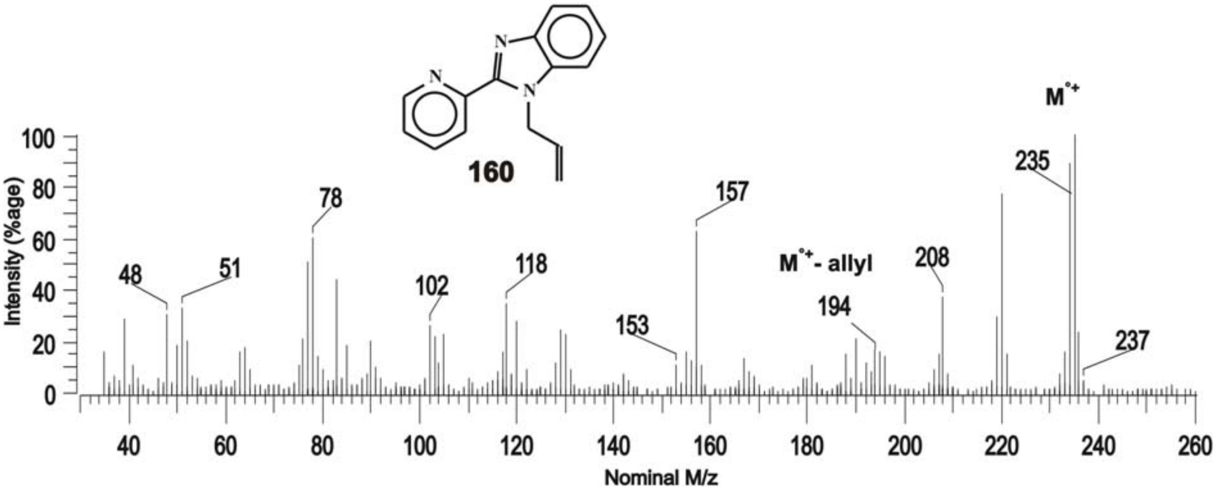
Scheme 60. ^{1}H NMR spectrum of compound **165.**



Scheme 61. ^{13}C NMR spectrum of compound **165.**

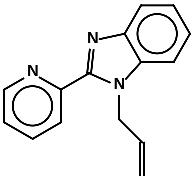
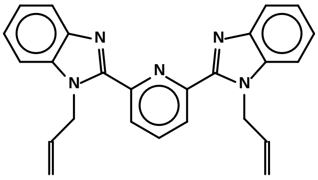
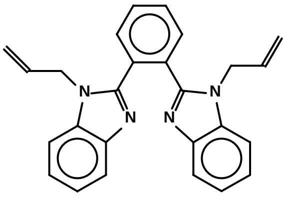
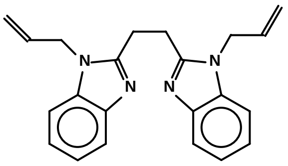
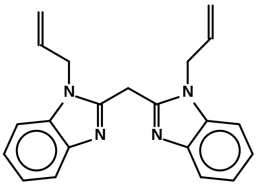
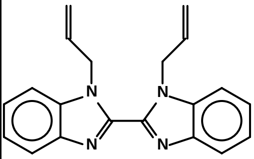
5.3.2. Mass spectroscopy

The mass spectrum of compound **160** (Scheme 62) shows the molecular ion peak ($M^{\circ+}$) with m/z = 234. The peak with m/z = 195 represents the loss of the allyl group ($M^{\circ+}$-allyl).



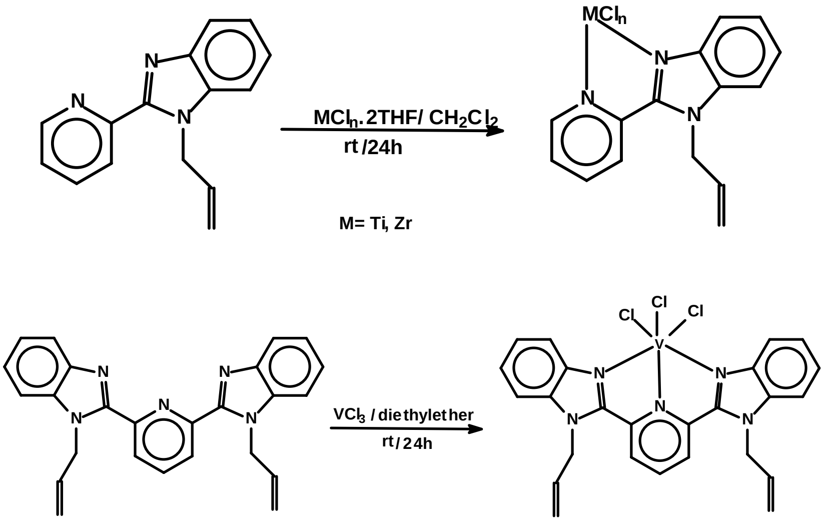
Scheme 62. Mass spectrum of compound **160.**

Table 13. Spectroscopic data for the compounds **160-165.**

No.	**Compound**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**Mass m/z(%)**
160		8.84(d,1H), 8.52(d,1H), 8.15(t,1H), 7.94-7.92(m,1H), 7.89-7.87(m,1H), 7.69(t,1H), 7.57-7.55(m,2H), 6.10-6.01(m,2H), 5.54(d,4H), 5.20-5.15(dd,4H)	150.9, 149.9, 148.8, 142.958, 137.4, 137.0, 133.9, 124.7, 123.9, 123.4, 122.6, 120.1, 116.6, 110.7, 48.1	235 M$^{\circ+}$ (100)
161		8.26(d,2H), 7.91(t,1H), 7.72(d,2H), 7.35(d,2H), 7.24(t,4H), 5.87-5.80(m,2H,2CH), 5.01(d,4H), 4.81(d ,4H)	150.1, 150.0, 143.0, 138.21, 136.7, 133.2, 125.7, 123.71, 122.9, 120.2, 116.8, 111.1, 47.6	391 M$^{\circ+}$ (100)
162		7.84(d,2H), 7.73-7.65(m,4H), 7.59-7.47(m,4H), 7.19(t,2H), 5.71-5.70(m,2H), 5.13-4.99(dd,4H), 4.60(d,4H)	151.2, 132.9, 132.8, 131.8, 130.7, 130.3, 130.2, 129.7, 118.6, 66.2	390 M$^{\circ+}$ (100)
163		7.67(s,2H), 7.18-7.17(m,6H), 5.86-5.83(m,2H,2CH), 4.98(d,4H), 4.76(s,4H), 3.48(s,4H,2CH$_2$)	154.0, 142.7, 135.4, 132.0, 122.6, 122.2, 119.3, 117.4, 109.7, 45.7, 24.9	342 M$^{\circ+}$ (100)
164		7.58(d,2H), 7.50(d,2H), 7.20(t,4H), 5.99-5.92(m,2H,2CH), 5.14(d,4,H), 5.00(d,4H), 4.61(s,2H,CH)	150.8, 142.9, 135.9, 133.8, 122.8, 122.3, 119.5, 117.6, 111.1, 46.3, 25.6	328 M$^{\circ+}$ (100)
165		7.19(s,8H), 5.90-5.84(m,2H,CH), 5.25-5.18(m,4H), 4.82(s,4H)	154.2, 130.6, 126.8, 124.4, 118.5, 115.9, 45.7	314 M$^{\circ+}$ (100)

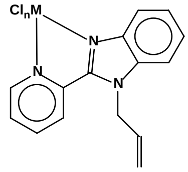
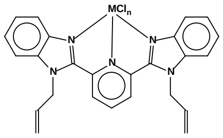
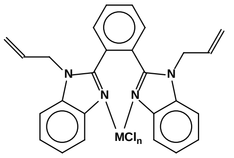
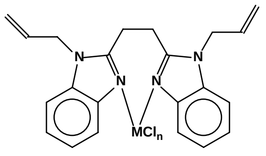
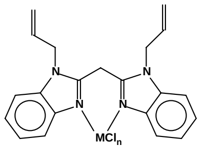
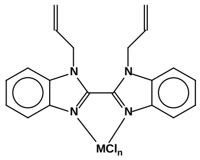
5.4. Synthesis of complexes 166-181

The complexes **166-169** were synthesized according to Scheme 63 by mixing the THF adducts of titanium or zirconium tetrachloride in dichloromethane with the ligand precursors under constant stirring for 24h. The vanadium complexes were prepared similarly using diethyl ether as solvent. The complexes **170-181** were prepared in an analogous manner. They were precipitated quantitatively.



Scheme 63. Synthesis of the complexes **166-169.**

Table 14. The synthesized complexes of N-allyl substituted benzimidazole based ligands.

Structure	Complex No.	M
	**166**	Ti
	167	Zr
	168	V
	**169**	V
	**170**	Ti
	171	Zr
	172	V
	**173**	Ti
	174	Zr
	175	V
	**176**	Ti
	177	Zr
	178	V
	**179**	Ti
	180	Zr
	181	V

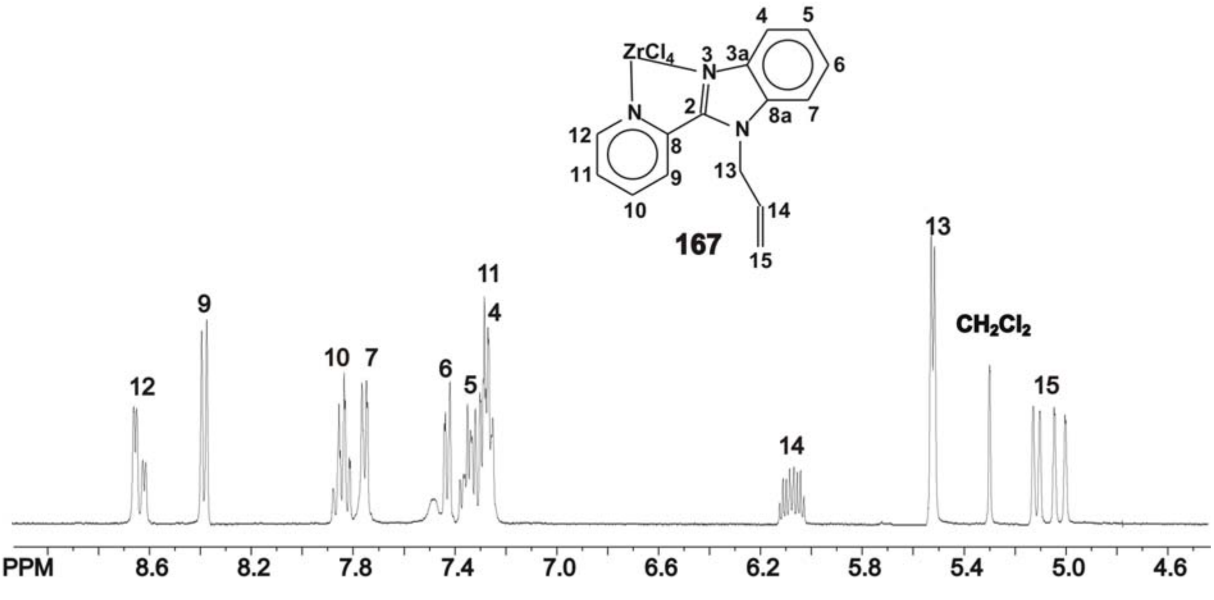
5.5. Characterization of the N-allyl substituted benzimidazole transition metal complexes166-181

5.5.1. NMR spectroscopy

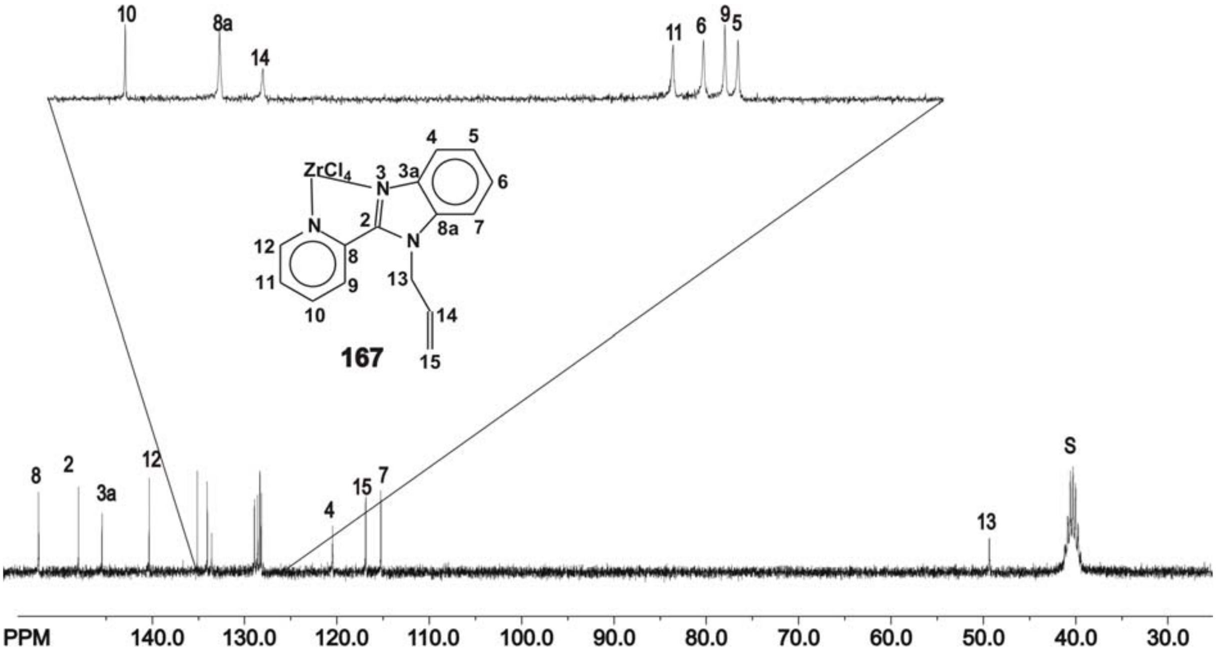
The complexes **166-181** were characterized by their ^{1}H NMR and ^{13}C NMR spectra. The spectra of complexes slightly differ from those of the free ligands. The ^{1}H NMR spectrum of complex **167** (Scheme 64) shows 11 set of resonance signals. The doublet at δ = 8.69 ppm [$J_{H,H}$ = 5.0 Hz] is assigned to H12. The doublet at δ = 8.41 ppm [$J_{H,H}$ = 8.0 Hz] can be assigned to H9. The triplet at δ = 7.75 ppm [$J_{H,H}$ = 8.0 Hz] is assigned to H10. H7 and H6 appear as doublet at δ = 7.69 and 7.46 ppm [$J_{H,H}$ = 7.5 Hz]. The triplet appears at δ = 7.35

ppm [$J_{H,H}$ = 5.0 Hz] can be assigned to H5. The multiplet at δ = 7.28-7.22 ppm is assigned to H4, H11. The multiplet at δ = 6.18-6.01 ppm corresponds to the CH protons of the allyl group. The doublet at δ = 5.50 ppm [$J_{H,H}$ = 5.2 Hz] corresponds to the methylene protons H13. The terminal methylene protons H15 appears as two doublets at δ = 5.12 ppm [$J_{H,H}$ = 12.0 Hz] and 5.02 ppm [$J_{H,H}$ = 16.0 Hz].

The ^{13}C NMR spectrum of complex **167** (see Scheme 65) shows 15 resonance signals each corresponding to one carbon atom. The signal at δ = 151.1 ppm corresponds to C8 which is slightly shifted downfield compared to that of the free ligand. The signal at δ = 146.8 ppm is assigned to C2, at δ = 144.1 ppm C3a appears. The signals at δ = 139.1 and 134.0 ppm are assigned to C12 and C10. The signal at δ = 132.9 ppm corresponds to C8a. At δ = 132.4 ppm a signal is assigned to C14. The signal at δ = 127.7 ppm is assigned to C11, the signals at δ = 127.4 and 127.1 ppm to C6 and C9, the signals at δ = 127.0, 119.5, 116.0, 114.6 and 49.1 ppm to C5, C4, C15, C7 and C13.



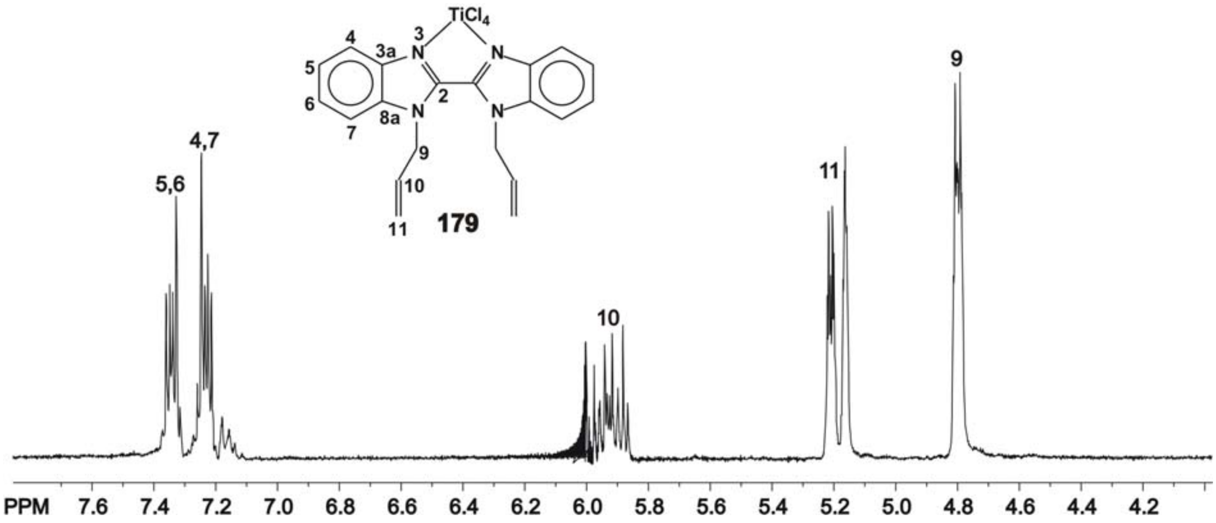
Scheme 64. ^{1}H NMR spectrum of complex **167.**



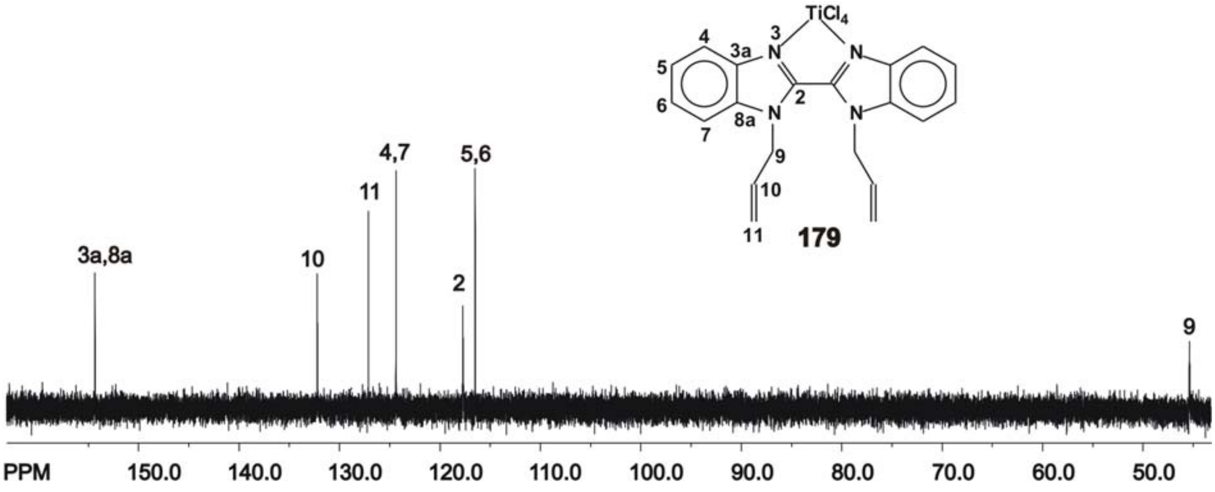
Scheme 65. ^{13}C NMR spectrum of complex **167.**

The ^{1}H NMR spectrum of complex **179** (Scheme 66) shows five sets of resonance signals. The multiplet at δ = 7.36-7.33 ppm is assigned to the protons H5 and H6. The multiplet at δ = 7.25-7.21 ppm can be assigned to the protons H4 and H7. The multiplet at δ = 5.98-5.88 ppm is assigned to the CH protons of the allyl group, the multiplet at δ = 5.22-5.16 ppm to the terminal methylene protons H11. At δ = 4.81-4.79 ppm the methylene protons (H9) appear.

The ^{13}C NMR spectrum of complex **179** (Scheme 67) shows seven resonance signals. The signal at δ = 154.3 ppm is assigned to the carbon atoms C3a and C8a. At δ = 132.2 ppm a signal corresponding to C10 can be found. The signal at δ = 127.1 ppm is assigned to C11. The signal at δ = 124.4 ppm corresponds to C4 and C7, and at δ = 117.7 ppm a signal appears which can be assigned to the carbon atom C2. The signal at δ = 116.5 ppm belongs to C5 and C6, and that at δ = 45.4 ppm to C9.



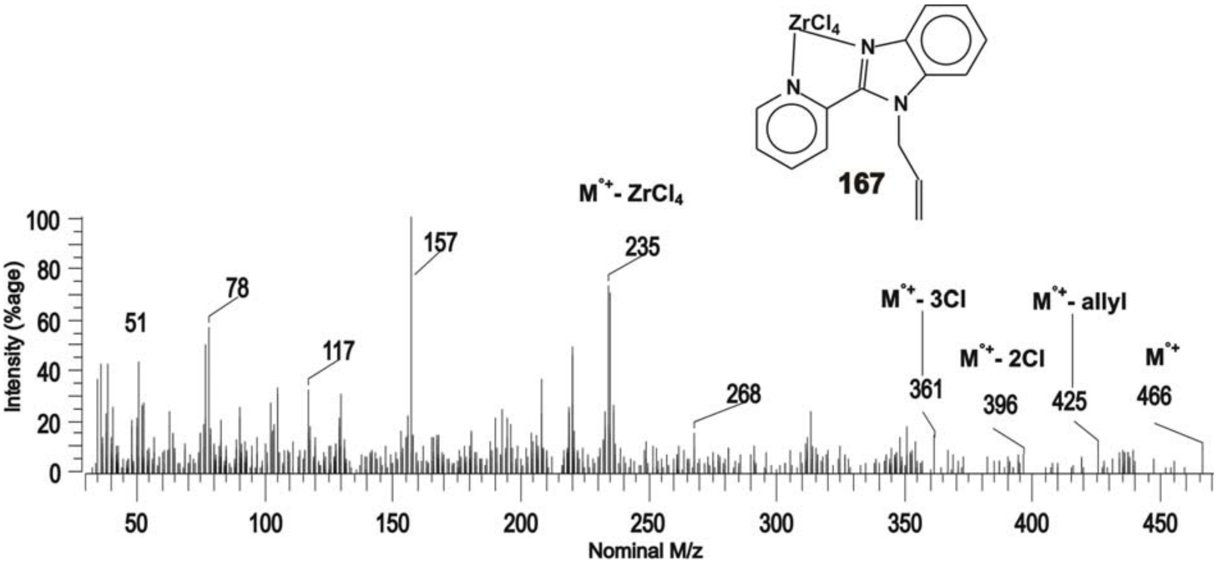
Scheme 66. ^{1}H NMR spectrum of complex **179.**



Scheme 67. ^{13}C NMR spectrum of complex **179.**

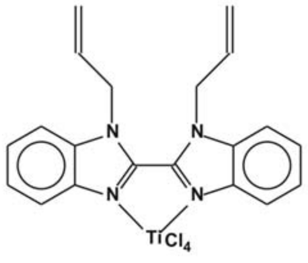
5.5.2. Mass spectroscopy

The mass spectrum of complex **167 (**see Scheme 68) shows an the molecular ion peak at m/z = 466 ($M^{\circ+}$). The loss of one allyl group results in a fragment with m/z = 425. The peak with m/z = 396 represents a fragment with the loss of two chlorides from the molecular ion. At m/z = 361 ($M^{\circ+}$-3Cl) and m/z = 235 (the mass of the free ligand), further characteristic ions are detected.

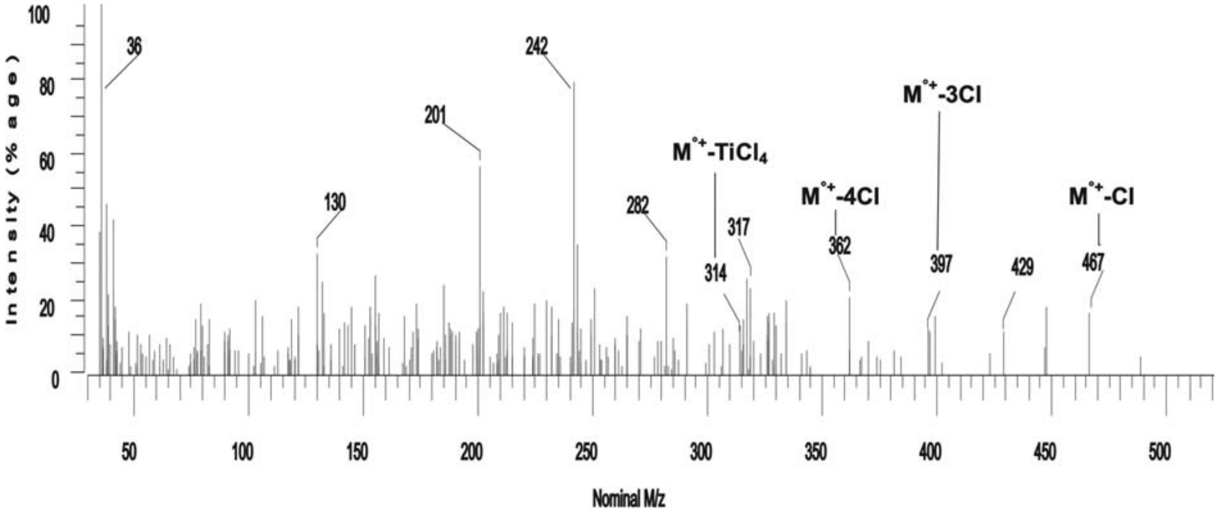


Scheme 68. Mass spectrum of complex **167.**

The mass spectrum of complex **179** (Scheme 69) shows the ion resulting from the loss of one chloride at m/z = 467. The ion with m/z = 426 represents the loss of one chloride and one allyl group. The loss of three chlorides results in an ion with m/z = 397. At m/z = 362, the ion resulting from the loss of four chlorides can be found. Finally, at m/z = 314, an ion representing the free ligand mass appears.

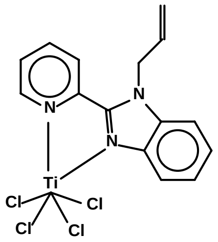
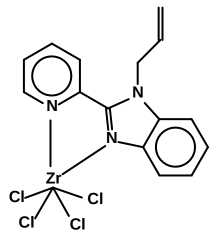


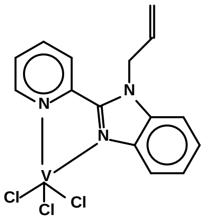
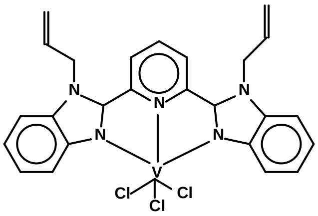
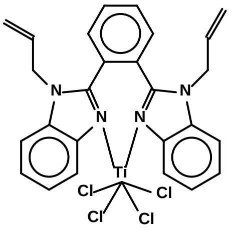
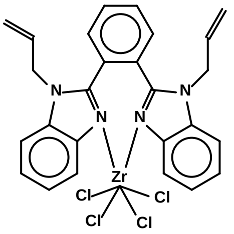
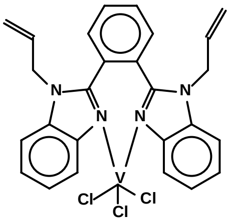
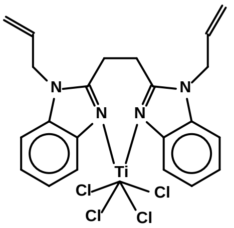
179

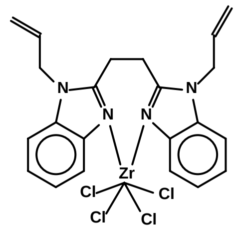
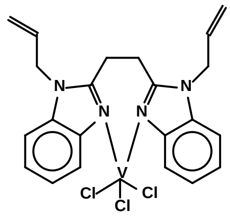
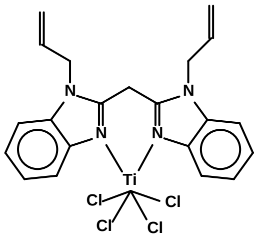
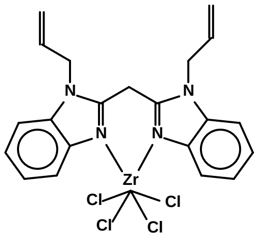
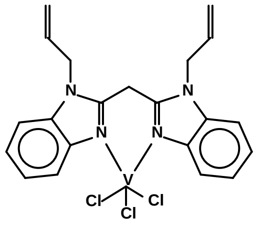
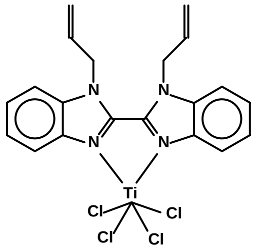


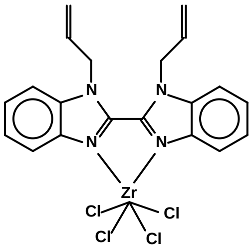
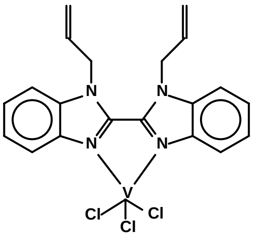
Scheme 69. Mass spectrum of complex **179.**

Table 15. NMR and mass spectroscopic data of complexes **166-181.**

No.	**Complex**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**Mass m/z(%)**
166		8.84(d,1H), 8.52(d,1H), 8.15(t,1H), 7.94-7.92(m,1H), 7.89-7.87(m,1H), 7.70-7.67(m,1H), 7.58-7.54(m,2H), 6.09-6.02(m,2H,2CH), 5.55(s,4H, 2CH$_2$), 5.20-5.16(dd,4H,2CH$_2$)	150.8, 146.5, 144.0, 139.0, 133.8, 132.8, 132.3, 127.7, 127.4, 127.1, 127.0, 119.3, 115.8 114.2, 49.1	347 $M^{\circ+}$ -Cl-allyl (7), 312 $M^{\circ+}$-2Cl-allyl (5), 235 $M^{\circ+}$-TiCl$_4$, (100)
167		8.69(d,1H), 8.41(d,1H), 7.75(t,1H), 7.69(d,1H), 7.46(d,1H), 7.35(t,1H), 7.28-7.22(m,2H), 6.02-6.18-6.01(m,2H,2CH), 5.50(d,4H, 2CH$_2$), 5.12-5.02 (dd,4H,2CH$_2$)	151.1, 146.8, 144.1, 139.1, 134.0, 132.9, 132.4, 127.7 127.4, 127.1, 127.0, 119.5, 116.0, 114.6, 49.1	431 $M^{\circ+}$-Cl (5), 425 $M^{\circ+}$-allyl (3), 396 $M^{\circ+}$ -2Cl (5), 361 $M^{\circ+}$-3Cl (5), 235 $M^{\circ+}$-ZrCl$_4$, (70)

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
168		n.d.	n.d.	392 $M^{\circ+}$(1), 356 $M^{\circ+}$-Cl (5), 321 $M^{\circ+}$ -2Cl (5), 315 $M^{\circ+}$-Cl-allyl (5), 235 $M^{\circ+}$-VCl$_3$, (100)
169		n.d.	n.d.	548 $M^{\circ+}$(2), 512 $M^{\circ+}$-Cl (5), 477 $M^{\circ+}$-2Cl (5), 441 $M^{\circ+}$ -3Cl (2), 430 $M^{\circ+}$ -Cl-2allyl (3), 391 $M^{\circ+}$-VCl$_3$ (100)
170		8.13(d,2H), 7.91(t,2H), 7.82-7.81 (m,4H), 7.59-7.56(m,4H), 5.92-5.85(m,2H), 5.22-5.09(dd,4H), 4.69(d,4H)	149.7, 133.5, 132.8, 132.2, 131.5, 130.9, 125.7, 118.9, 115.1, 66.3	580 $M^{\circ+}$(1), 544 $M^{\circ+}$-Cl (5), 507 $M^{\circ+}$-2Cl (2), 472 $M^{\circ+}$ -3Cl (2), 462 $M^{\circ+}$ -Cl-2allyl (3), 390 $M^{\circ+}$-TiCl$_4$ (100)
171		8.15(d,2H), 7.90(t,2H), 7.85-7.82(m,4H), 7.58-7.53(m,4H), 5.85-5.72(m,2H), 5.24-5.07(dd,4H), 4.67(d,4H)	149.9, 133.4, 133.0, 132.5, 131.4, 131.3, 125.9, 119.2, 115.0, 66.6	623 $M^{\circ+}$(2), 587 $M^{\circ+}$-Cl (3), 550 $M^{\circ+}$-2Cl (3), 514 $M^{\circ+}$ -3Cl (1), 505 $M^{\circ+}$ -Cl-2allyl (5), 390 $M^{\circ+}$-ZrCl$_4$ (100)
172		n.d.	n.d.	550 $M^{\circ+}$(2), 511 $M^{\circ+}$-Cl (3), 475 $M^{\circ+}$-2Cl (1), 440 $M^{\circ+}$ -3Cl (2), 396 $M^{\circ+}$ -2Cl-2allyl (3), 390 $M^{\circ+}$-VCl$_3$ (100)
173		7.80(d,2H), 7.71(d,2H), 7.43(t,4H), 6.15-6.03(m,2H,2CH), 5.78(d,4H,2CH$_2$), 5.24(d,4H,2CH$_2$), 3.86(s,4H,2CH$_2$)	153.2, 133.6, 132.6, 125.1, 125.0, 118.9, 116.3, 115.3, 112.8, 47.0, 23.6	532 $M^{\circ+}$(1), 495 $M^{\circ+}$-Cl (5), 461 $M^{\circ+}$-2Cl (5), 424 $M^{\circ+}$ -3Cl (1), 414 $M^{\circ+}$ -Cl-2allyl (2), 342 $M^{\circ+}$-TiCl$_4$ (100).

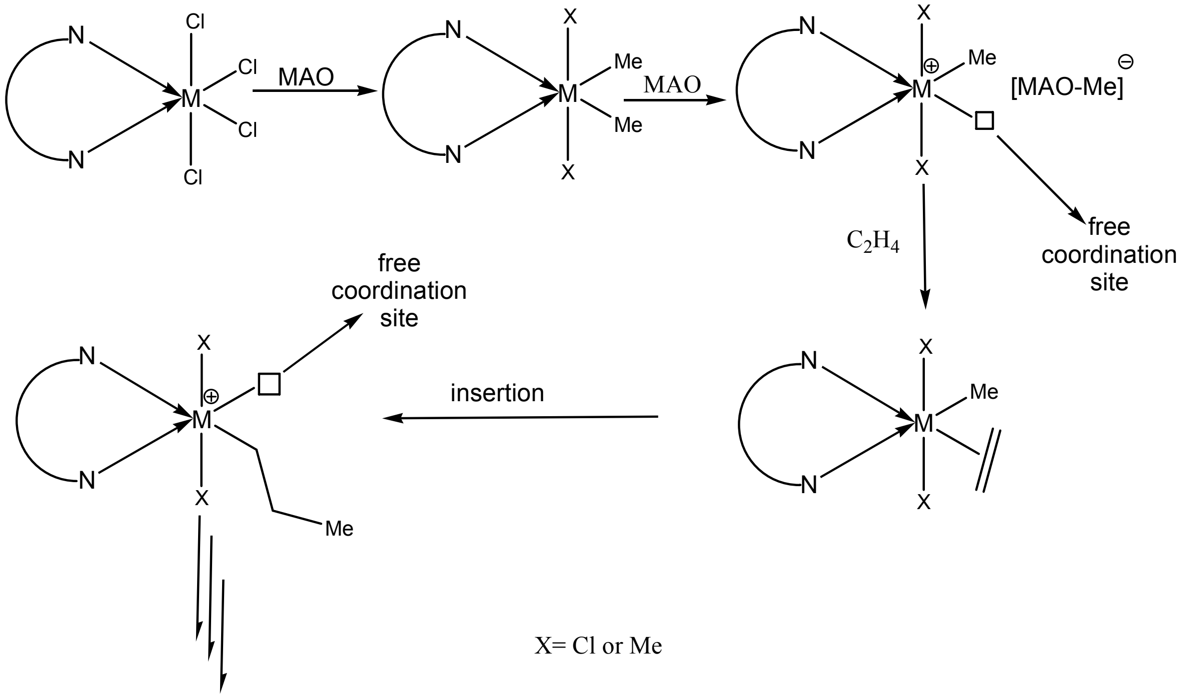
No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
174		7.92(d,2H), 7.81(d,2H), 7.56(t,4H), 6.11-6.08(m,2H,2CH), 5.36(d,4H,2CH$_2$), 5.27(d,4H,2CH$_2$), 4.03(s,4H,2CH$_2$)	152.5, 132.7, 132.2, 126.1, 125.8, 119.4, 115.3, 114.4, 113.4, 47.4, 23.4	575 $M^{\circ+}$(2), 505 $M^{\circ+}$-2Cl (3), , 468 $M^{\circ+}$ -3Cl (1), 423 $M^{\circ+}$ -2Cl-2allyl (5), 342 $M^{\circ+}$-ZrCl$_4$ (100).
175		n.d.	n.d.	500 $M^{\circ+}$(3), 463 $M^{\circ+}$-Cl (5), 429 $M^{\circ+}$-2Cl(2), 418 $M^{\circ+}$ - 2allyl (3), 342 $M^{\circ+}$-VCl$_3$ (100)
176		7.85(d,2H), 7.81-7.72(dd,2H), 7.48(t,4H), 6.07-5.92(m,2H,2CH), 5.38-5.27(dd,4H,2CH$_2$), 5.21(d,4H,2CH$_2$), 5.08(s,2H,CH$_2$)	150.6, 148.1, 135.0, 134.2, 134.0, 133.7, 132.6, 132.4, 125.6, 125.5, 125.3, 125.2, 119.3, 118.5, 117.5, 116.7, 113.2, 113.0, 47.5, 47.2, 24.9	518 $M^{\circ+}$(3), 482 $M^{\circ+}$-Cl (5), 447 $M^{\circ+}$-2Cl (2), 410 $M^{\circ+}$ -3Cl (5), 401 $M^{\circ+}$ -Cl-2allyl (5), 328 $M^{\circ+}$-TiCl$_4$ (100).
177		7.85(d,2H), 7.75-7.72(dd,2H), 7.49(t,4H), 6.03-5.98(m,2H,2CH), 5.34-5.27(dd,4H,2CH$_2$), 5.22- (s,4H,2CH$_2$), 5.19(s,2H,CH$_2$)	150.6, 148.2, 135.2, 134.2, 134.0, 133.8, 132.6, 132.4, 125.5, 125.3, 125.3, 125.0, 119.3, 118.5, 117.5, 116.8, 113.1, 113.1, 47.4, 47.2, 24.9	561 $M^{\circ+}$(3), 525 $M^{\circ+}$-Cl (5), 454 $M^{\circ+}$ -3Cl (2), 407 $M^{\circ+}$ -2Cl-2allyl (5), 328 $M^{\circ+}$-ZrCl$_4$ (100).
178		n.d.	n.d.	485 $M^{\circ+}$(2), 449 $M^{\circ+}$-Cl (3), 415 $M^{\circ+}$-2Cl (2), 367 $M^{\circ+}$ -2Cl-2allyl (5), 328 $M^{\circ+}$-VCl$_3$ (100)
179		7.36-7.33(m,4H), 7.25-7.21(m,4H), 5.98-5.88(m,2H,2CH), 5.22-5.16(m,4H,2CH$_2$), 4.81-4.79(m,4H,2CH$_2$)	154.3, 132.2, 127.1, 124.4, 117.7, 116.5, 45.4,	467 $M^{\circ+}$-Cl (10), 425$M^{\circ+}$ -Cl –allyl (10), 397 $M^{\circ+}$-3Cl (10), 362$M^{\circ+}$-4Cl (15), 314 $M^{\circ+}$-TiCl$_4$ (20),

No.	Complex	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	Mass m/z(%)
180		7.30-7.29(m,4H), 7.24-7.21(m,4H), 5.99-5.90(m,2H,2CH), 5.23-5.19(m,4H,$2CH_2$), 4.85-4.79 (m,4H,$2CH_2$)	154.0, 132.5, 126.6, 124.8, 118.1, 116.2, 45.7,	547 $M^{\circ+}$(2), 511 $M^{\circ+}$-Cl (5), 476 $M^{\circ+}$ -2Cl (5), 440 $M^{\circ+}$-3Cl (3), 314 $M^{\circ+}$-$ZrCl_4$ (20),
181		n.d.	n.d.	472 $M^{\circ+}$(6), 400 $M^{\circ+}$ -2Cl (5), 363 $M^{\circ+}$-3Cl (3), 314 $M^{\circ+}$-VCl_3 (15), 278 $M^{\circ+}$-3Cl-2allyl (20)

6. Polymerization experiments and polymer analysis

6.1 General aspects and mechanism

All coordination compounds were activated with MAO according to Scheme 70 which is in agreement to the mechanism proposed for the activation of metallocene[102,103] and 2,6-bis(imino)pyridine iron (II)[104] catalyst precursors. The high molecular weight resins and the decrease of molecular weight with increasing polymerization temperature suggest that, the rate of propagation reactions (the activation barrier for propagation is usually low if existent at all)[105,106] are much faster than the rate of termination (the termination reactions are subjected to activation barriers). This finding is in agreement with GPC analysis of the polyethylene produced with the system **40/MAO** (Schemes 96, 97, 98) at different temperatures.



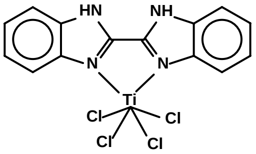
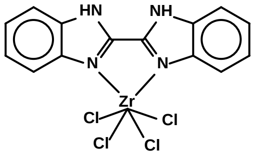
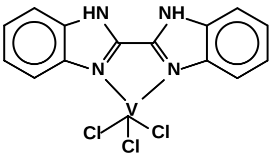
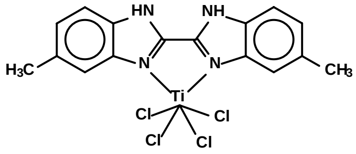
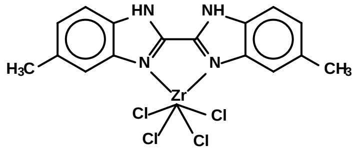
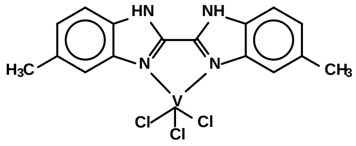
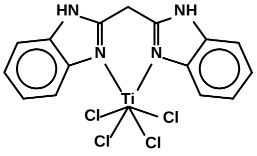
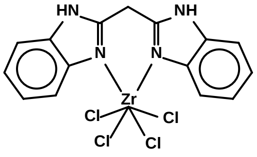
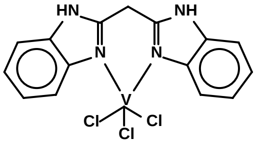
Scheme 70. Proposed mechanism for the activation of the catalyst precursors.

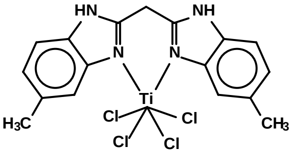
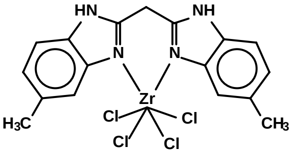
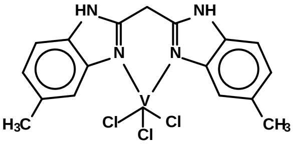
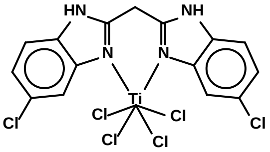
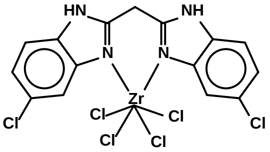
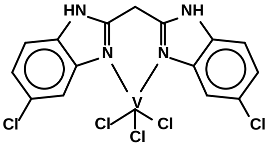
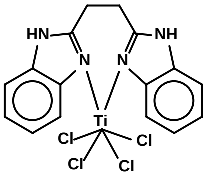
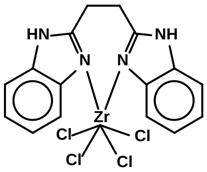
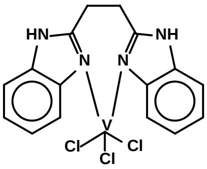
6.2 Ethylene polymerization activities of bis-(benzimidazole) complexes 15-56

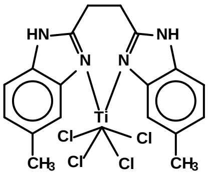
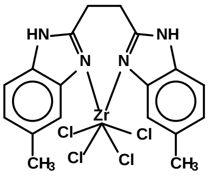
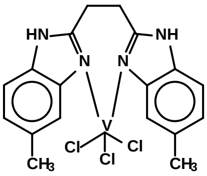
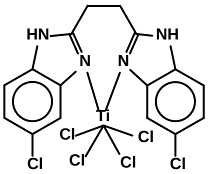
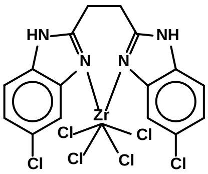
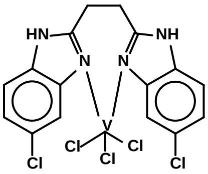
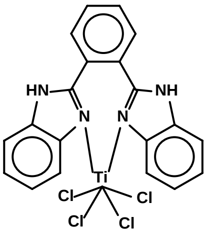
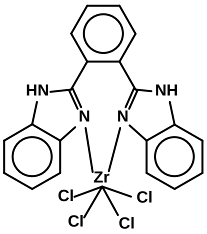
The complexes **15-56** were tested for ethylene polymerization after activation with methylaluminoxane (MAO). All catalysts systems showed activities towards the polymerization of ethylene (Table 16). Vanadium and titanium complexes generally showed the highest activities in comparison to zirconium complexes with the same ligand systems.

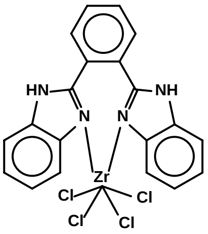
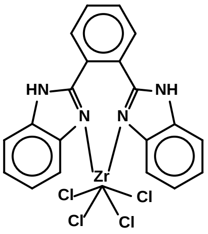
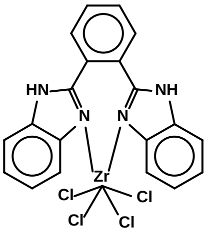
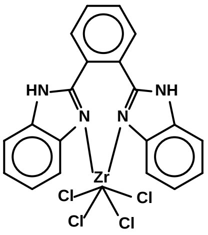
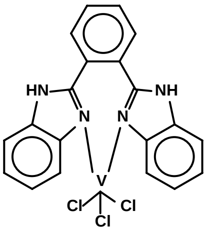
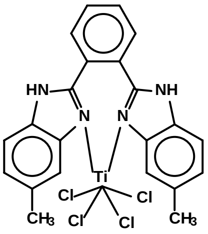
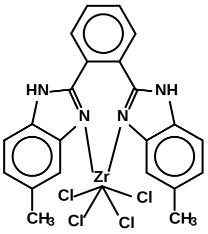
Table 16. Polymerization activities of complexes **15-56**.

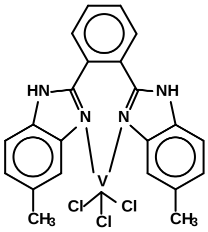
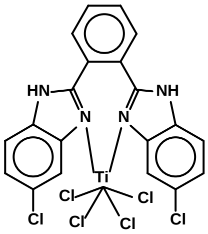
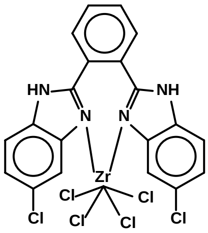
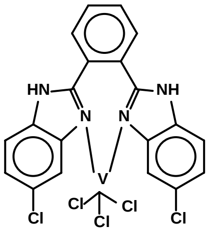
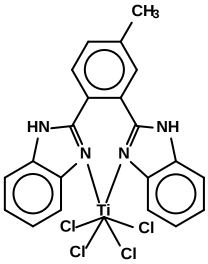
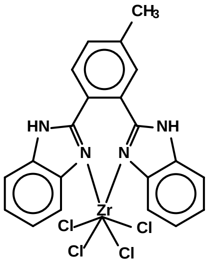
All polymerization reactions were carried out in 250 ml pentane with MAO as cocatalyst (Al: M, 2500:1) at 50°C and 10 bar ethylene pressure).

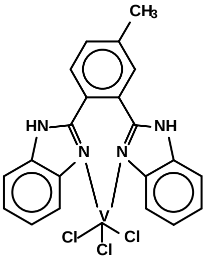
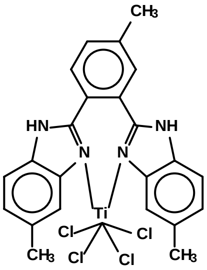
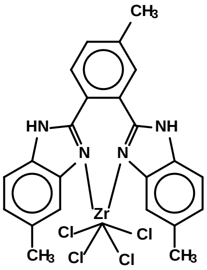
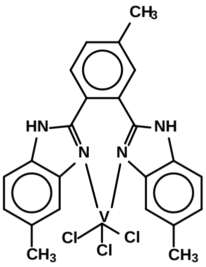
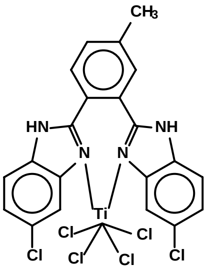
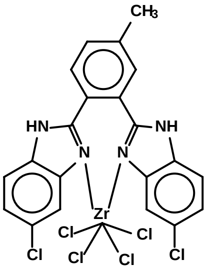
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**15**	208.6	82009	1333411	16.3
	**16**	52.60	169762	1840146	10.8
	**17**	231.10	275392	1662030	6.0
	**18**	525.55	336423	1770459	5.3
	**19**	48.54	n.d.	n.d.	n.d.
	**20**	93.50	n.d.	n.d.	n.d.
	**21**	315.70	136621	1149594	8.4
	**22**	172.41	352532	1906473	5.4
	**23**	173.33	133215	424279	3.2

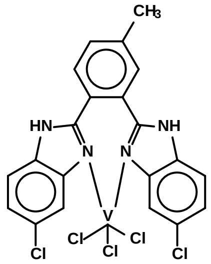
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**24**	244.70	83422	466376	5.6
	**25**	43.20	55267	268276	4.9
	**26**	178.60	79720	246996	3.1
	**27**	148.15	n.d.	n.d.	n.d.
	**28**	21.74	n.d.	n.d.	n.d.
	**29**	337.50	514683	920237	1.8
	**30**	207.80	n.d.	n.d.	n.d.
	**31**	129.50	n.d.	n.d.	n.d.
	**32**	285.10	n.d.	n.d.	n.d.

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**33**	340.70	49097	444669	9.1
	**34**	37.23	n.d.	n.d.	n.d.
	**35**	158.70	n.d.	n.d.	n.d.
	**36**	250.00	n.d.	n.d.	n.d.
	**37**	39.90	n.d.	n.d.	n.d.
	**38**	133.33	n.d.	n.d.	n.d.
	**39**	252.42	66247	1273127	19.2
	**40** (20°C) 1: 2500 M : Al	116.2	1832	1271018	693

Complex	**No.**	**Activity** [kg/ mol cat. h]	**M_n** [g / mol]	**M_w** [g / mol]	**PD**
	**40** (40°C) 1: 2500 M : Al	225.5	4734	1177503	248
	**40**	285.50	98435	1638338	16.4
	**40** (60°C) 1: 2500 M : Al	227.9	4356	972211	223
	**40** (80°C) 1: 2500 M : Al	191	n.d.	n.d.	n.d.
	**41**	404.80	n.d.	n.d.	n.d.
	**42**	202.40	74432	439497	5.9
	**43**	66.50	40979	196803	4.8

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**44**	307.70	184982	674295	3.6
	**45**	35.70	n.d.	n.d.	n.d.
	**46**	122.50	233841	1510535	6.5
	**47**	165.00	141554	1311190	9.3
	**48**	88.30	n.d.	n.d.	n.d.
	**49**	131.60	n.d.	n.d.	n.d.

Complex	**No.**	**Activity [kg/ mol cat. h]**	**M_n [g / mol]**	**M_w [g / mol]**	**PD**
	**50**	105.75	n.d.	n.d.	n.d.
	**51**	314.80	62649	434343	6.9
	**52**	120.48	n.d.	n.d.	n.d.
	**53**	103.75	86722	311274	3.6
	**54**	203.50	n.d.	n.d.	n.d.
	**55**	132.40	n.d.	n.d.	n.d.

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**56**	69.60	n.d.	n.d.	n.d.

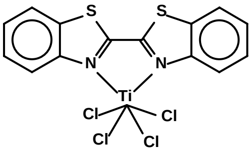
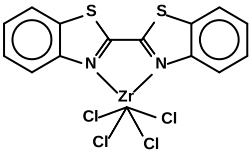
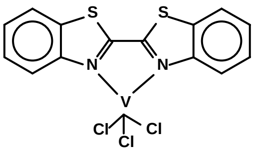
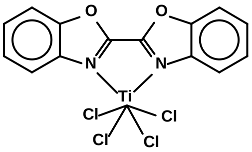
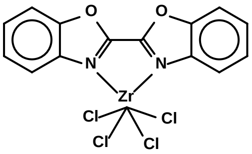
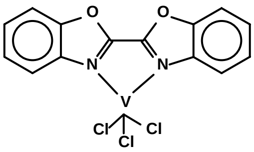
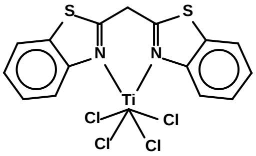
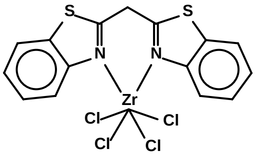
6.3. Ethylene polymerization results of 1,2-bis(benzothiazole), 1,2-bis(benzoxazole) complexes 76-123 and 2,6-bis(benzothiazolyl, benzoxazolyl)pyridine vanadium complexes 124-126

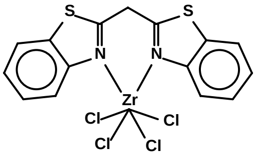
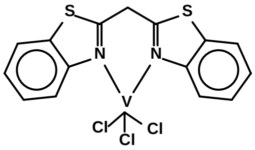
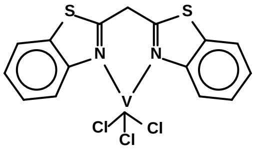
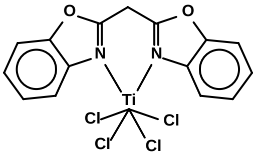
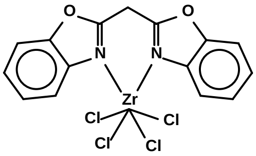
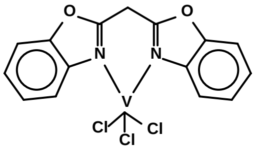
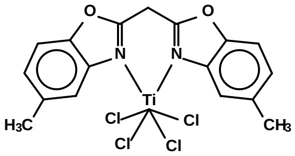
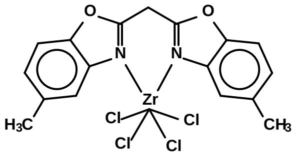
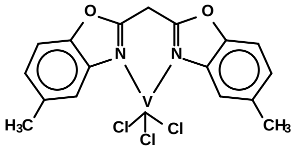
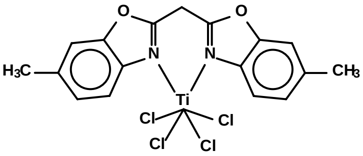
1,2-bis(benzothiazole), 1,2-bis(benzoxazole) titanium, zirconium and vanadium complexes and 2,6-bis(benzothiazolyl, benzoxazolyl)pyridine vanadium complexes were used as catalysts for ethylene polymerization reactions after activation with methylaluminoxane (MAO) as co-catalyst. The complexes showed different catalytic behaviours towards ethylene polymerization. Table 17 summarizes the polymerization results.

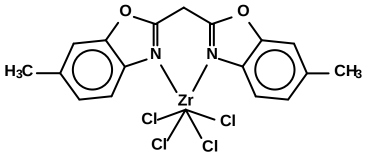
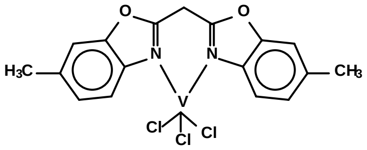
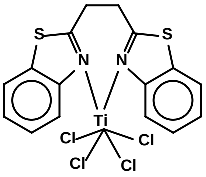
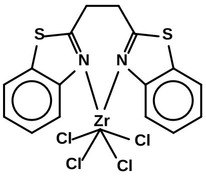
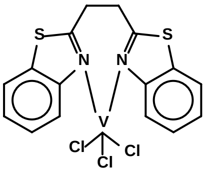
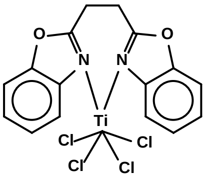
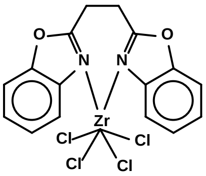
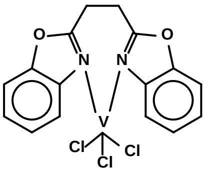
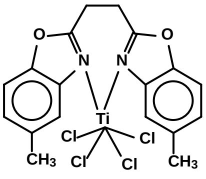
All polymerization reactions were carried out in 250 ml pentane, with MAO as cocatalyst (Al:M, 2500:1) at 50°C and 10 bar ethylene pressure.

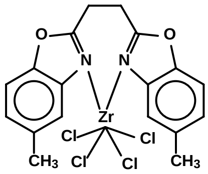
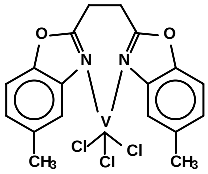
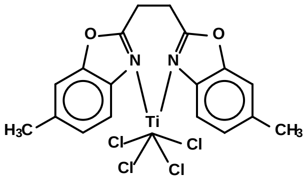
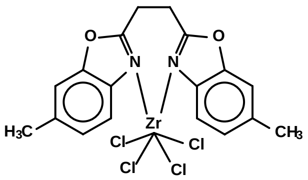
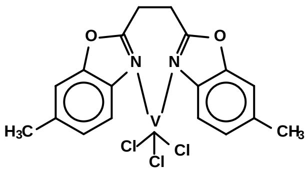
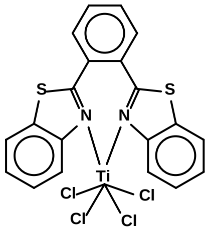
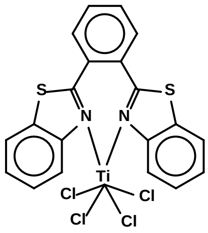
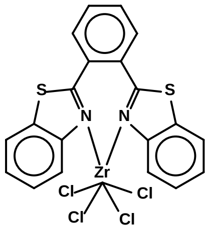
Table 17. Polymerization results of the complexes **76-126.**

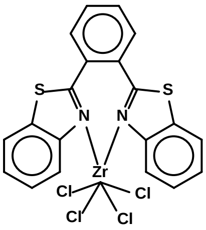
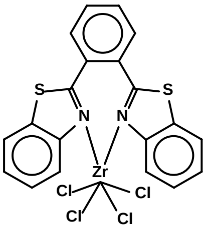
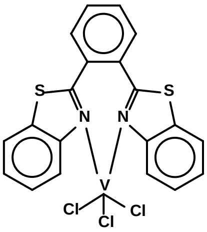
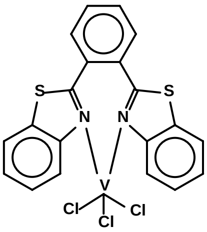
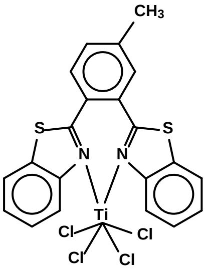
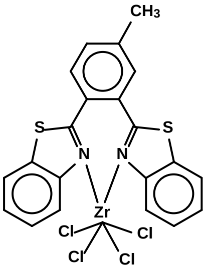
All polymerization reactions were carried out in 250 ml pentane with MAO as cocatalyst (Al: M, 2500:1) at 50°C and 10 bar ethylene pressure).

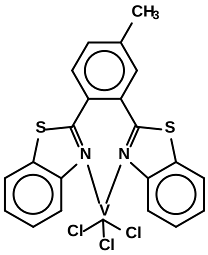
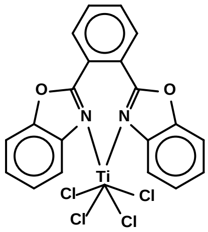
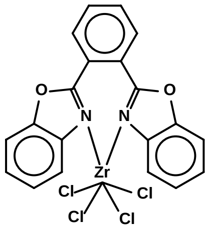
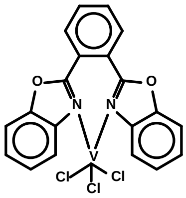
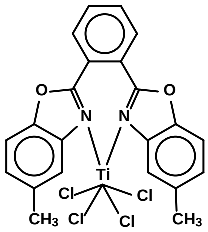
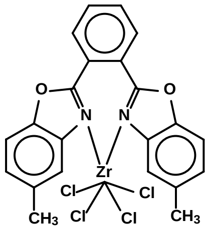
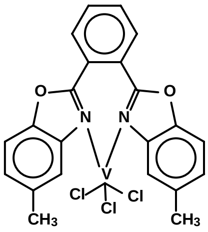
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**76**	140.15	62467	328060	5.3
	**77**	268.20	n.d.	n.d.	n.d.
	**78**	147.54	106495	422106	4.0
	**79**	185.3	n.d.	n.d.	n.d.
	**80**	60.24	n.d.	n.d.	n.d.
	**81**	192.20	90187	284484	3.2
	**82** (Al:Ti) (1000:1)	279.20	80011	527916	6.6
	**83** (Al:Zr) (1000:1)	40.45	83528	362916	4.3

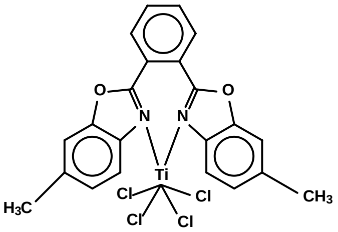
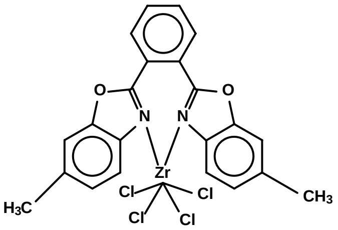
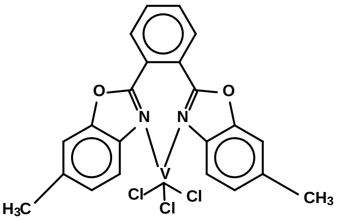
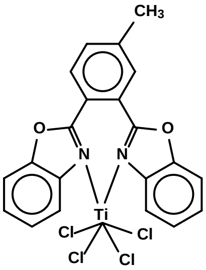
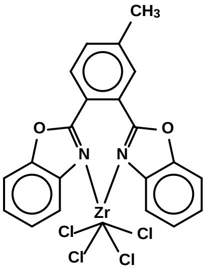
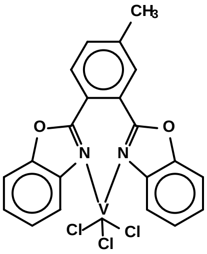
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**83** (Al:Zr) (1000:1) 40°C	22.40	n.d.	n.d.	n.d.
	**84**	379.75	250092	2883589	11.5
	**84** (Al:V) (1000:1)	493.30	14200	42013	3.0
	**85**	472.00	108445	356538	3.3
	**86**	424.20	41804	964097	23.1
	**87**	403.32	207211	417412	2.0
	**88**	573.03	92483	514037	5.6
	**89**	144.90	n.d.	n.d.	n.d.
	**90**	207.90	n.d.	n.d.	n.d.
	**91**	374.15	6602	425865	64.5

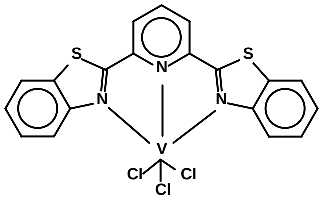
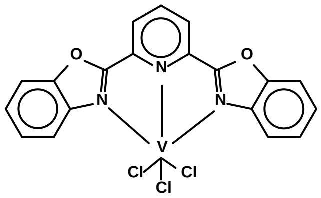
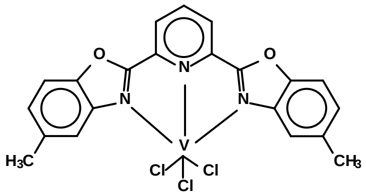
Complex	**No.**	**Activity** **[kg/ mol cat. h]**	**M_n** **[g / mol]**	**M_w** **[g / mol]**	**PD**
	**92**	137.60	n.d.	n.d.	n.d.
	**93**	158.40	n.d.	n.d.	n.d.
	**94**	154.70	70356	373250	5.3
	**95**	102.04	398875	1762725	4.42
	**96**	208.10	140016	460106	3.3
	**97**	239.00	83980	633535	7.5
	**98**	122.81	68298	408560	6.0
	**99**	310.34	147272	478514	3.3
	**100**	385.82	86999	814040	9.4

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**101**	144.10	n.d.	n.d.	n.d.
	**102**	333.33	648069	1559675	2.4
	**103**	205.13	n.d.	n.d.	n.d.
	**104**	167.72	n.d.	n.d.	n.d.
	**105**	300.90	1921813	2847628	1.5
	**106** (20°C) 1: 2500 M : Al	861.6	3468	1512260	436
	**106**	219.50	237250.	1349417.	5.6.
	**107** (40°C) 1: 1000 M : Al	1311	149349	1371582	9.18

Complex	**No.**	**Activity** **[kg/ mol cat. h]**	**M_n** **[g / mol]**	**M_w** **[g / mol]**	**PD**
	**107** (40°C) 1:2500 M : Al	450	n.d.	n.d.	n.d.
	**107**	131.57	70555	462381	6.6
	**108** (20°C) 1:1000 M : Al	54.3	458223	1389040	3.03
	**108**	442.11	456380	2134694	4.5
	**109**	260.42	327213	3344215	10.2
	**110**	127.74	143782	1580130	11.0

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**111**	241.40	n.d.	n.d.	n.d.
	**112**	354.90	16364	166086	10.2
	**113**	113.82	n.d.	n.d.	n.d.
	**114**	260.70	n.d.	n.d.	n.d.
	**115**	401.52	201827	1545925	7.7
	**116**	87.92	n.d.	n.d.	n.d.
	**117**	391.30	n.d.	n.d.	n.d.

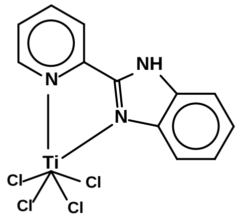
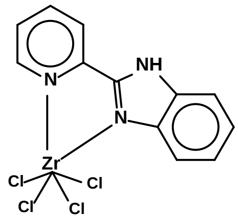
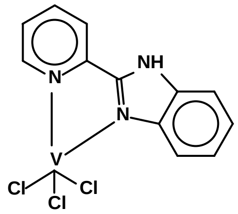
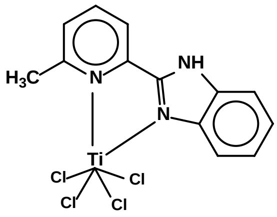
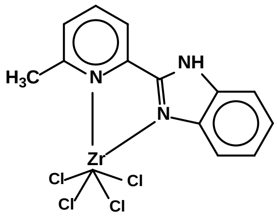
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**118**	110.10	n.d.	n.d.	n.d.
	**119**	73.60	n.d.	n.d.	n.d.
	**120**	166.67	n.d.	n.d.	n.d.
	**121**	175.82	n.d.	n.d.	n.d.
	**122**	147.90	n.d.	n.d.	n.d.
	**123**	26.55	n.d.	n.d.	n.d.

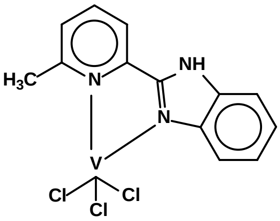
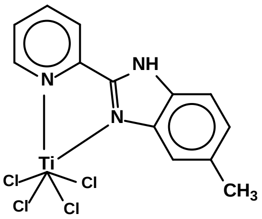
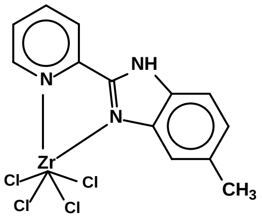
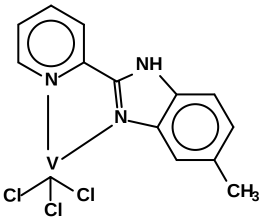
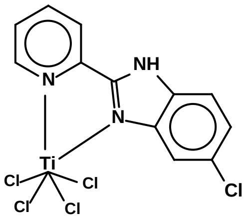
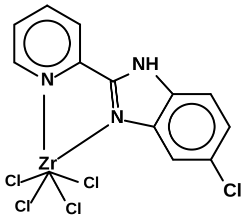
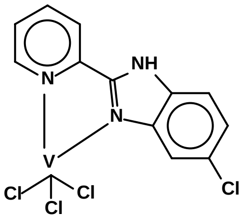
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**124**	284.43	275309	1652779	6.0
	**125**	137.50	n.d.	n.d.	n.d.
	**126**	314.94	1709531	2730117	1.6

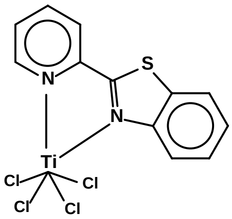
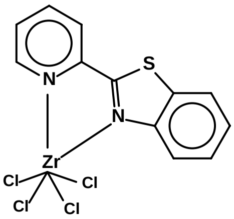
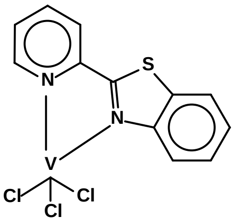
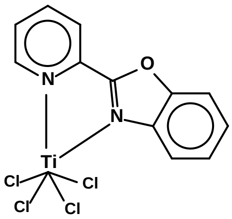
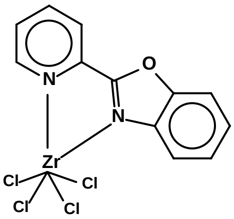
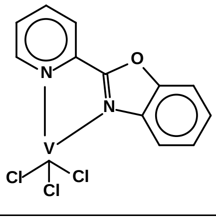
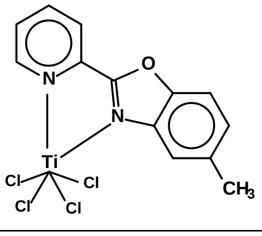
6.4. Polymerization results of 2-(benzimidazolyl, benzothiazolyl and benzoxazolyl)-pyridine complexes 136-159

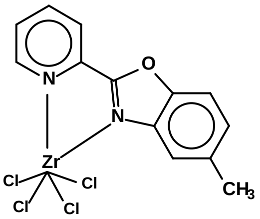
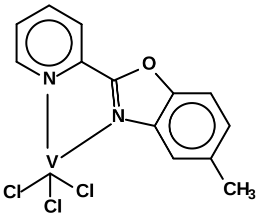
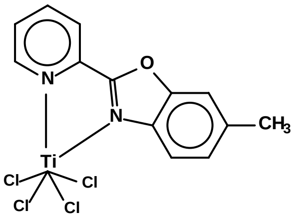
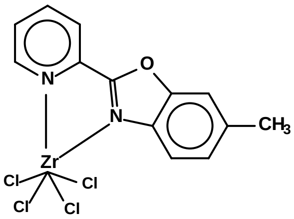
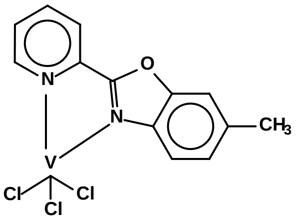
All polymerization reactions were carried out in 250 ml pentane with MAO as cocatalyst (Al: M, 2500:1) at 50°C and 10 bar ethylene pressure).

Table 18. Ethylene polymerization activities of complexes **136-159.**

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**136**	306.93	406225	1765524	4.4
	**137**	126.32	n.d.	n.d.	n.d.
	**138**	164.25	79394	1083276	13.6
	**139**	221.50	n.d.	n.d.	n.d.
	**140**	191.73	n.d.	n.d.	n.d.

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**141**	295.40	n.d.	n.d.	n.d.
	**142**	37.50	n.d.	n.d.	n.d.
	**143**	47.10	n.d.	n.d.	n.d.
	**144**	278.20	323756	1460196	4.5
	**145**	289.77	n.d.	n.d.	n.d.
	**146**	160.70	n.d.	n.d.	n.d.
	**147**	109.30	n.d.	n.d.	n.d.

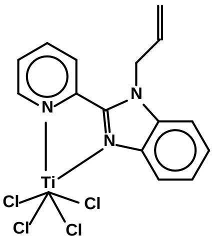
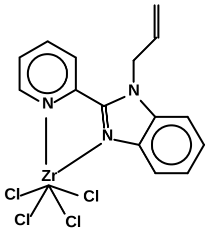
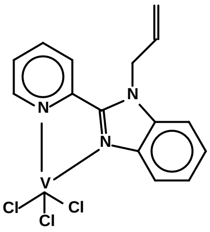
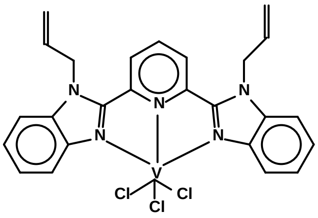
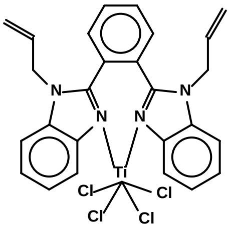
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**148**	548.10	296045	1685769	5.7
	**149**	56.10	n.d.	n.d.	n.d.
	**150**	286.31	n.d.	n.d.	n.d.
	**151**	336.02	205994	447010	2.2
	**152**	127.10	n.d.	n.d.	n.d.
	**153**	634.50	n.d.	n.d.	n.d.
	**154**	297.03	n.d.	n.d.	n.d.

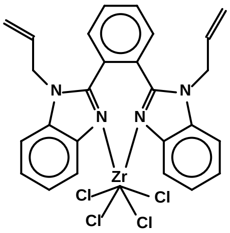
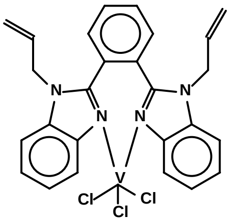
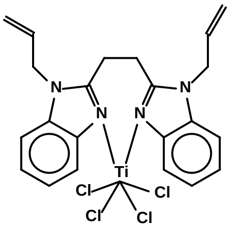
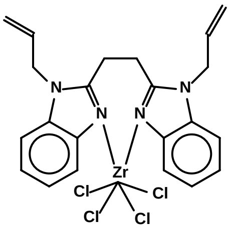
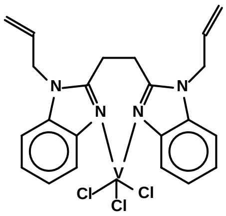
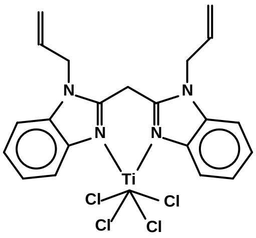
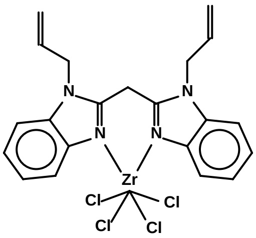
Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**155**	54.90	n.d.	n.d.	n.d.
	**156**	1154.84	1765348	2876365	1.6
	**157**	275.90	n.d.	n.d.	n.d.
	**158**	47.70	n.d.	n.d.	n.d.
	**159**	148.60	n.d.	n.d.	n.d.

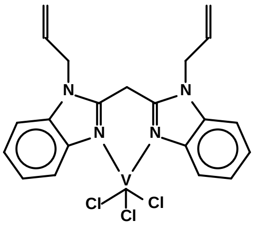
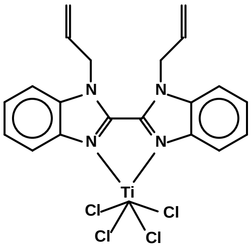
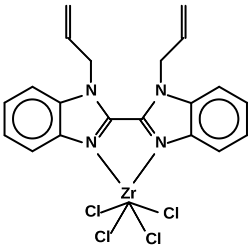
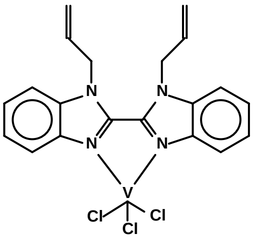
6.5. Polymerization results of N-allyl-substituted complexes 166-181

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).

Table 19. Polymerization activities of complexes **166-181**.

Complex	**No.**	**Activity [kg/ mol cat. h]**	**M_n [g / mol]**	**M_w [g / mol]**	**PD**
	**166**	432.61	460981	1915174	4.2
	**167**	166.70	n.d.	n.d.	n.d.
	**168**	3278.7	n.d.	n.d.	n.d.
	**169**	117.65	n.d.	n.d.	n.d.
	**170**	98.20	n.d.	n.d.	n.d.

Complex	No.	Activity [kg/ mol cat. h]	M_n [g / mol]	M_w [g / mol]	PD
	**171**	209.00	n.d.	n.d.	n.d.
	**172**	663.90	196156	407595	2.1
	**173**	175.73	n.d.	n.d.	n.d.
	**174**	95.00	n.d.	n.d.	n.d.
	**175**	93.75	n.d.	n.d.	n.d.
	**176**	246.80	n.d.	n.d.	n.d.
	**177**	78.43	n.d.	n.d.	n.d.

Complex	**No.**	**Activity** **[kg/ mol cat. h]**	**M_n** **[g / mol]**	**M_w** **[g / mol]**	**PD**
	**178**	114.58	n.d.	n.d.	n.d.
	**179**	541.10	36205	447121	12.4
	**180**	125.70	n.d.	n.d.	n.d.
	**181**	134.25	n.d.	n.d.	n.d.

7. Discussion of the polymerization results and the polymer properties

7.1. Polymerization activities of 1,2-bis(benzimidazole) transition metal complexes

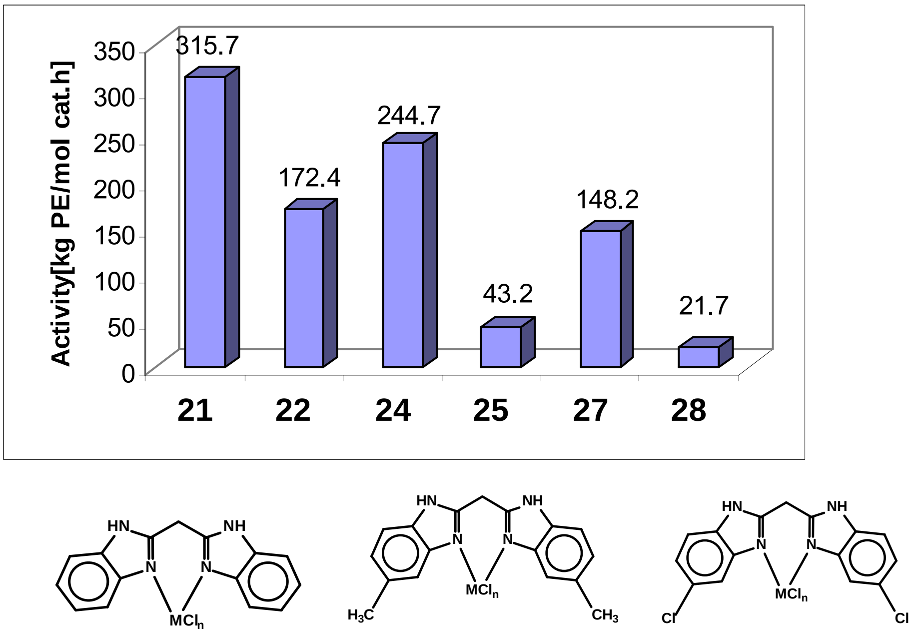
7.1.1. Activities of titanium and zirconium complexes

1,1-Bis(benzimidazolyl)methane, 1,2-bis(benzimidazolyl)ethane and 1,2-bis(benzimidazolyl) benzene titanium and zirconium complexes act as catalysts for ethylene polymerization, after activation with methylaluminoxane (MAO). They showed variable activities under different polymerization conditions. The titanium complexes generally show higher activities compared to zirconium complexes derived from the same ligand system. Among the titanium complexes with 1,2-bis(benzimidazolyl)methane derived ligands, the activities of the systems decrease in the order **21/MAO** > **24/MAO** > **27/MAO** (see Scheme 70)**.** This result is in contrast to the fact that complexes with both large steric bulk and high electron withdrawing effect will have the highest activities. Complex **27** with a chloro-substituent in *meta* position to the imino nitrogen atoms shows a reduced activity, while complex **24** with a methyl group in the same position shows a somewhat higher activity. One explanation could be the fact that chlorine as a Lewis base can block the active sites of a neighbouring catalyst molecule.

The unsubstituted complex **21** shows the highest activity. The same trend is observed for the titanium complexes of 1,2-bis(benzimidazolyl)benzene: **39/MAO > 42/MAO** > **45/MAO.**

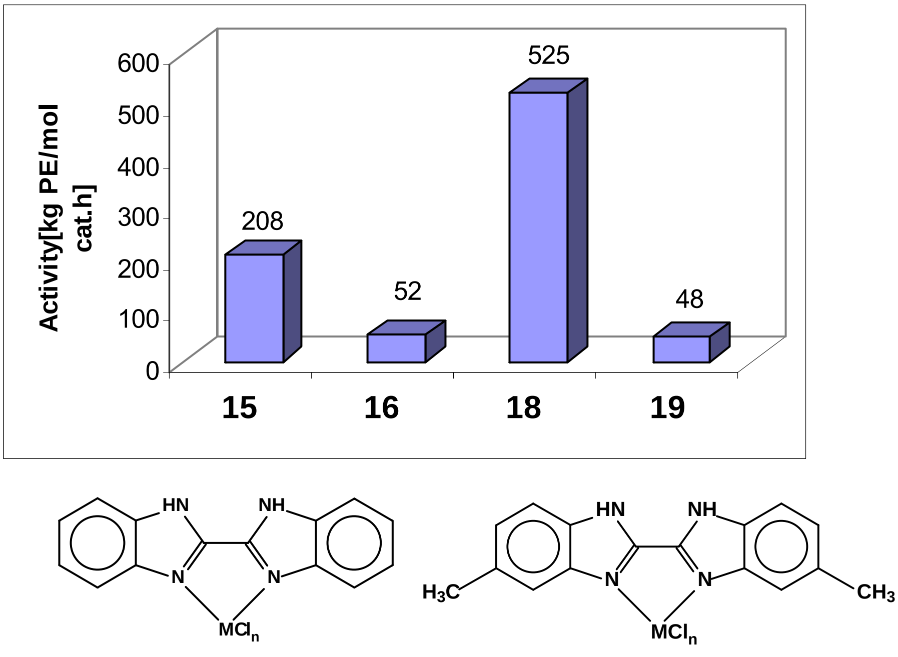
For the titanium complexes derived from 1,2-bis(benzimidazolyl)ethane, the activities decrease in the following order: **33/MAO > 36/MAO** > **30/MAO** (Scheme 76) and for bis(benzimidazole) **18/MAO > 15/MAO** (Scheme 75), i.e the substituted complexes show higher activities compared to the unsubstituted complexes. The different behaviours most probably occur due to the structure of the ligands in which the steric bulk and the electronic state greatly influence the activities of the complexes.

Zirconium complexes of the ligand bis(benzimidazole) (Scheme 71), 1,1-bis(benzimidazolyl)methane (Scheme 70), and 1,2-bis(benzimidazolyl)ethane (Scheme 72) show the same trend like the titanium complexes. The 1,2-bis(benzimidazolyl)benzene zirconium complexes behave differently, however. The unsubstituted complex **40** still shows the highest activity.



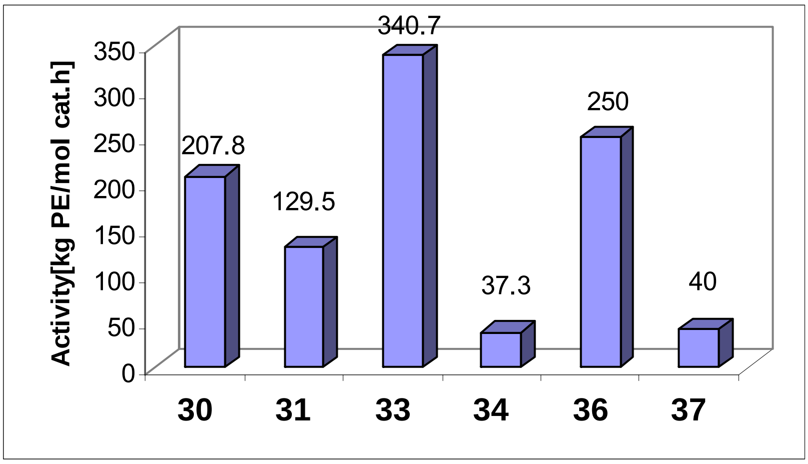
21, 22 **24, 25** **27, 28**

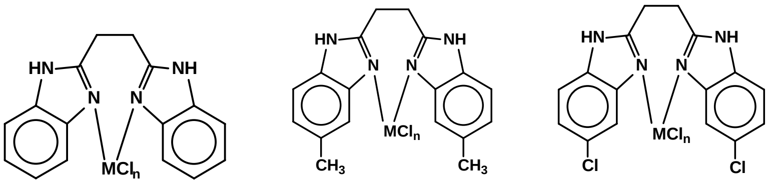
Scheme 70. Polymerization activities of 1,1-bis(benzimidazolyl)methane titanium (**21,24,27**) and zirconium (**22,25,28**) complexes.



15,16 **18,19**

Scheme 71. Polymerization activities of bis(benzimidazolyl) titanium (**15, 18**) and zirconium complexes (**16, 19**)



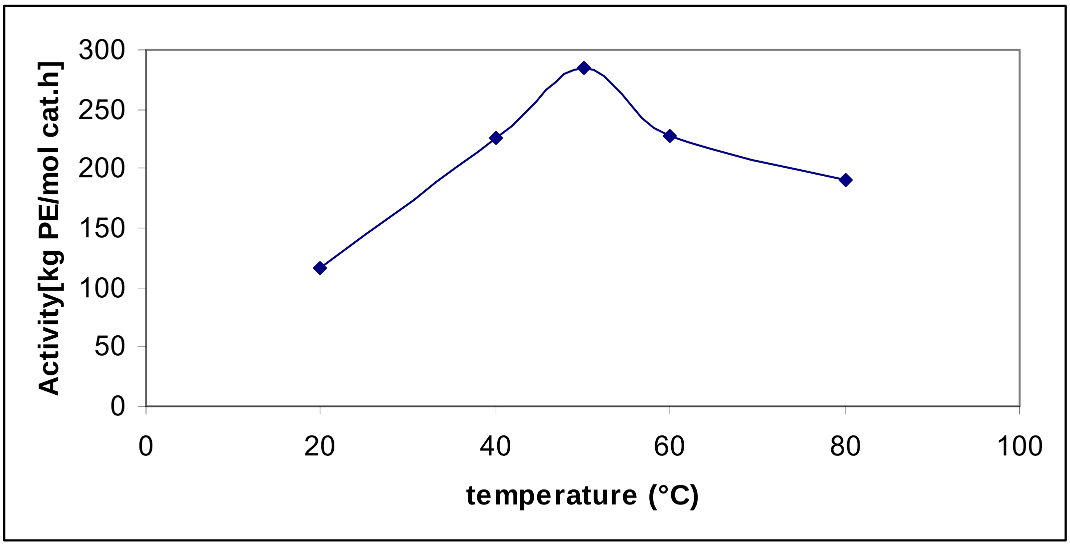


30, 31 **33, 34** **36, 37**

Scheme 72. Polymerization activities of 1,2-bis(benzimidazolyl)ethane titanium **(30,33,36)** and zirconium **(31,34,37)** complexes.

7.1.2. Effect of the reaction temperature on the polymerization activities of 1,2-bis(benzimidazolyl)benzene zirconium complexes

The activity of the catalyst system **40**/**MAO** was tested at different temperatures. At 20°C, the catalyst shows an activity of 116 [kg PE/mol cat.h]. Increasing the temperature to 50°C, results in an activity increase to 285 [kg PE/mol cat.h]. A further increase of the temperature results in an activity decrease to 191 [kg PE/mol cat.h]. The decrease of activity with rising temperature may be explained by the deactivation of active centres[107] as a consequence of thermal decomposition of the original catalyst[108,109] (Scheme 73).

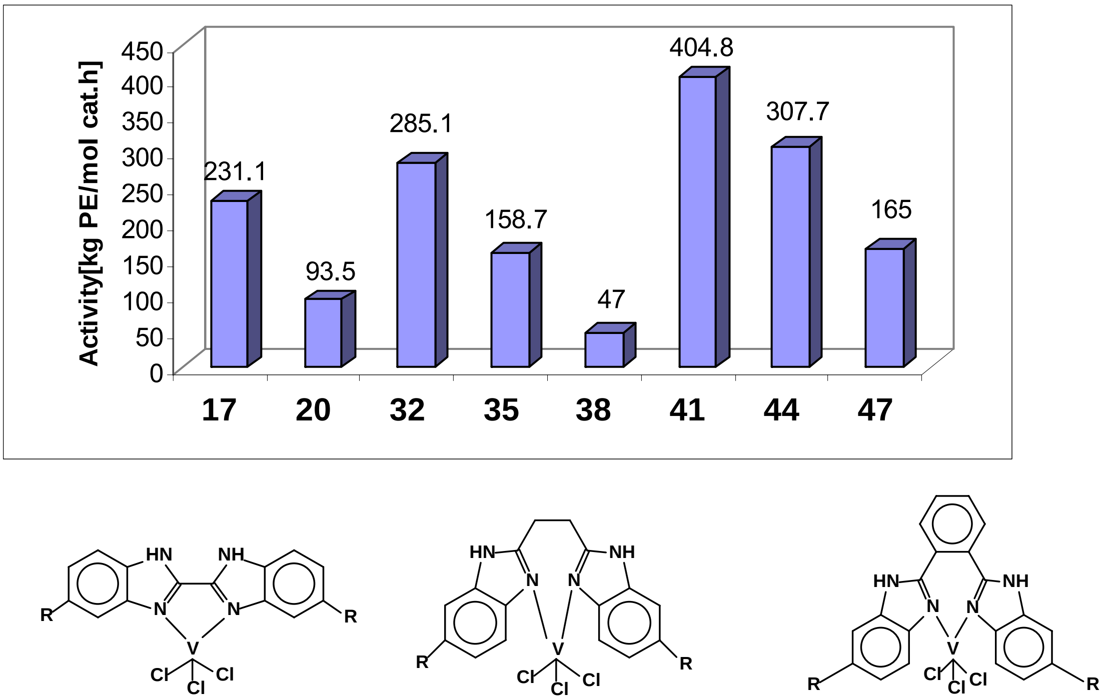


Scheme 73. Effect of temperature on the activity of **40/MAO.**

7.1.3. Polymerization activities of bis(benzimidazole)vanadium complexes

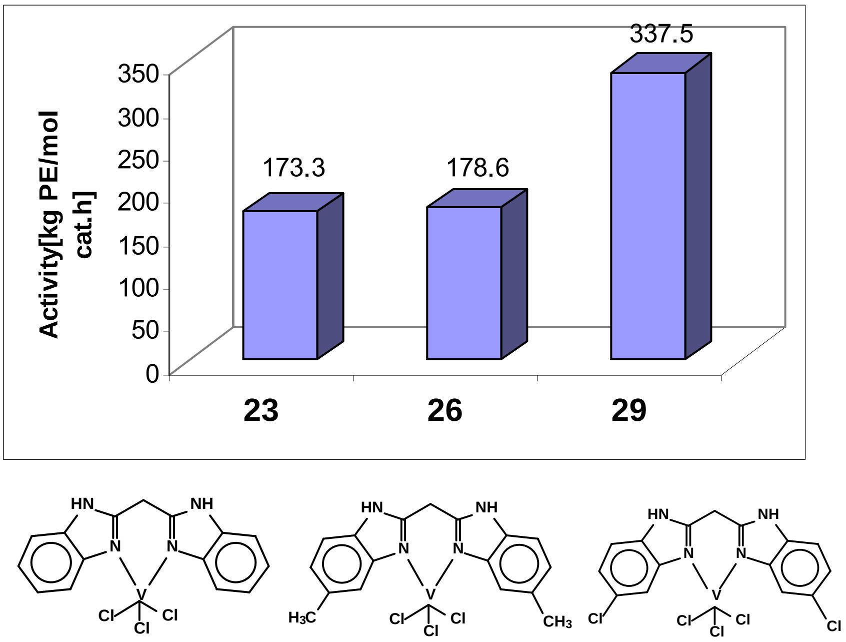
The activities of the vanadium complexes at higher temperatures (50°C) are in contrast to the typical behaviour of vanadium catalysts which invariably require temperatures below room temperatures to maintain their productivity[110].

The vanadium complexes of 1,2-bis(benzimidazolyl), 1,2-bis(benzimidazolyl)ethane, and 1,2-bis(benzimidazolyl)benzene generally show higher activities compared with zirconium and titanium complexes derived from the same ligand system. They follow the same order of activity observed for the zirconium and titanium complexes, where the unsubstituted complexes **17, 32 and 41** (Scheme 73) are more active than the substituted ones. The methyl substituted catalysts **20, 35 and 38** (Scheme 73) are more active than the chloro-substituted compounds **29, 38 and 47** (Scheme 73). The complexes derived from the ligand 1,1-bis(benzimidazolyl)methane show a different behaviour (Scheme 74). The *meta*–chloro substituted complex **29** shows the highest activity compared to the unsubstituted complex **23** and the *meta*-methyl substituted complex **26.** this is mostly due to the steric effect imposed by the larger chloro substituent compared to the methyl and hydrogen substituents occupying the same positions. The ligand structure may also account for this different behaviour. From Schemes 78, 79 and 80 it is obvious that the activities of the complexes are controlled by the ligand structures.



R=H	**17**	**32**	**41**
R=CH_3	**20**	**35**	**44**
R=Cl		**38**	**47**

Scheme 74. Polymerization activities of bis(benzimidazole) (**17**, **20**) 1,2-bis(benzimidazolyl) ethane (**32**, **35**, **38**) and 1,2-bis(benzimidazolyl)benzene (**41**, **44**, **47)** vanadium complexes.



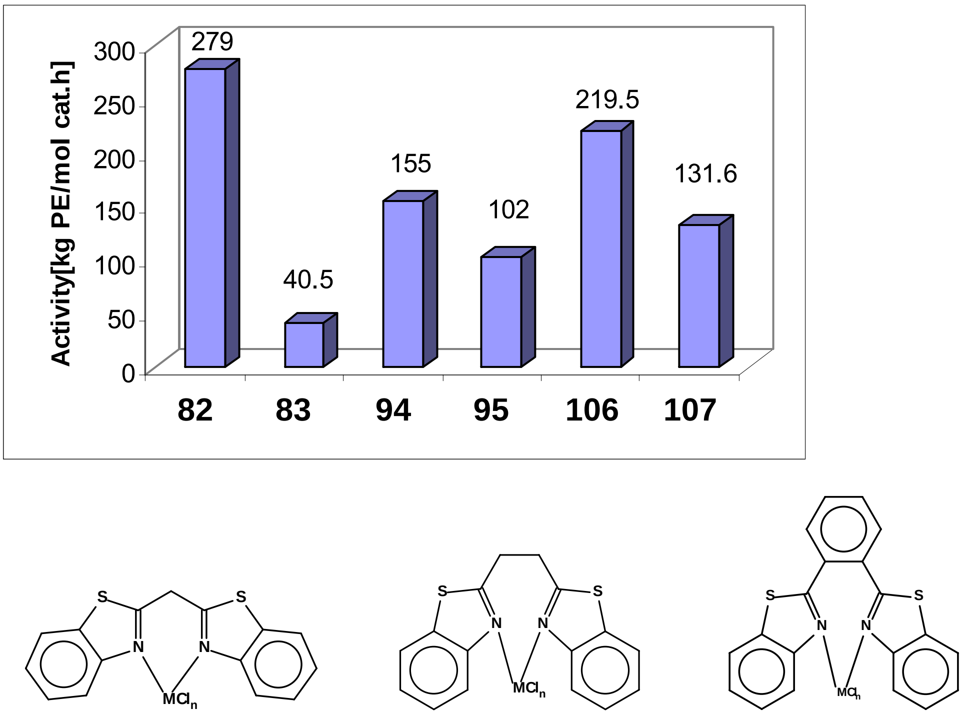
Scheme 74. Substituent effect on the polymerization activities of the vanadium complexes **23**, **26**, and **29.**

7.2. Polymerization activities of bis(benzothiazolyl) and bis(benzoxazolyl) complexes

7.2.1. Activities of titanium and zirconium complexes

The complexes of titanium, zirconium and vanadium with ligands derived from bis(benzoxazolyl) and bis(benzothiazolyl) compounds showed variable activities for ethylene polymerization. The activities are greatly influenced by the hetero atoms in addition to the ligand environment and the nature of the coordinated central metal atom.

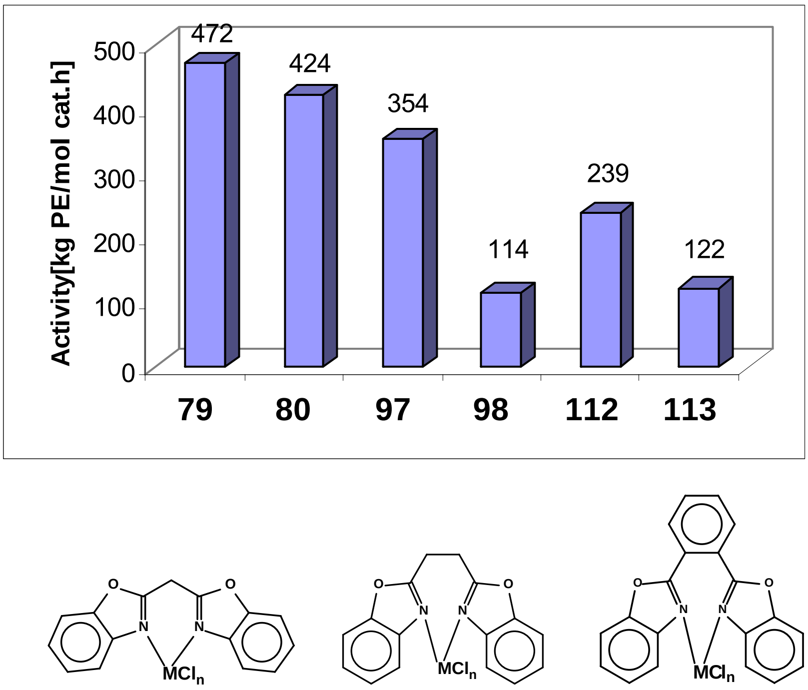
Ethylene polymerization reactions with complexes of titanium and zirconium with the ligand systems 1,1-bis(benzothiazolyl)methane, 1,2-bis(benzothiazolyl)ethane, and 1,2-bis(benzothiazolyl)benzene revealed that the titanium complexes are more active than the zirconium complexes. The activities of titanium complexes decrease in the order of 1,1-bis(benzothiazolyl)methane (**82**) > 1,2-bis(benzothiazolyl)benzene (**106**) > 1,2-bis(benzothiazolyl) ethane (**94**) (Scheme 75). Zirconium complexes with the same ligand systems behave differently following the order 1,2-bis(benzothiazolyl)ethane (**95**) > 1,2-bis(benzothiazolyl)benzene (**107**) > 1,1-bis(benzothiazolyl)methane (**83**) (Scheme 75). This order of activity can be accounted for by structural variations of the ligand systems.



M=Ti	**82**	**94**	**106**
M=Zr	**83**	**95**	**107**

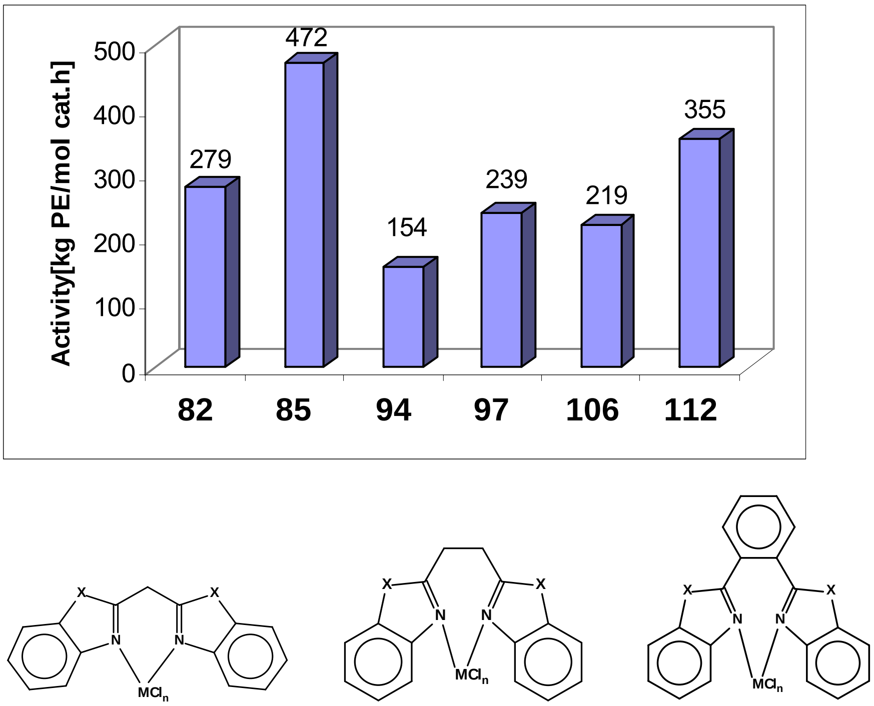
Scheme 75. Variations of activities with the structure of the ligand.

The activities of titanium complexes obtained from 1,1-bis(benzoxazolyl)methane, 1,2-bis(benzoxazolyl)ethane, and 1,2-bis(benzoxazolyl)benzene follow the same order of activity like the titanium benzothiazolyl complexes. The 1,1-bis(benzoxazolyl)methane complex **79** shows a higher activity than the 1,2-bis(benzoxazolyl)benzene complex **112** and the 1,2-bis(benzoxazolyl)ethane complex **97** (Scheme 76). They show higher activities than those obtained from the benzothiazole ligand of the same type (Scheme 77). This is most probably due to extra stabilization of the active species caused by the strong electronegative oxygen atom leading to an increase in electrophilicity of the metal center.



M=Ti	**79**	**97**	**112**
M=Zr	**80**	**98**	**113**

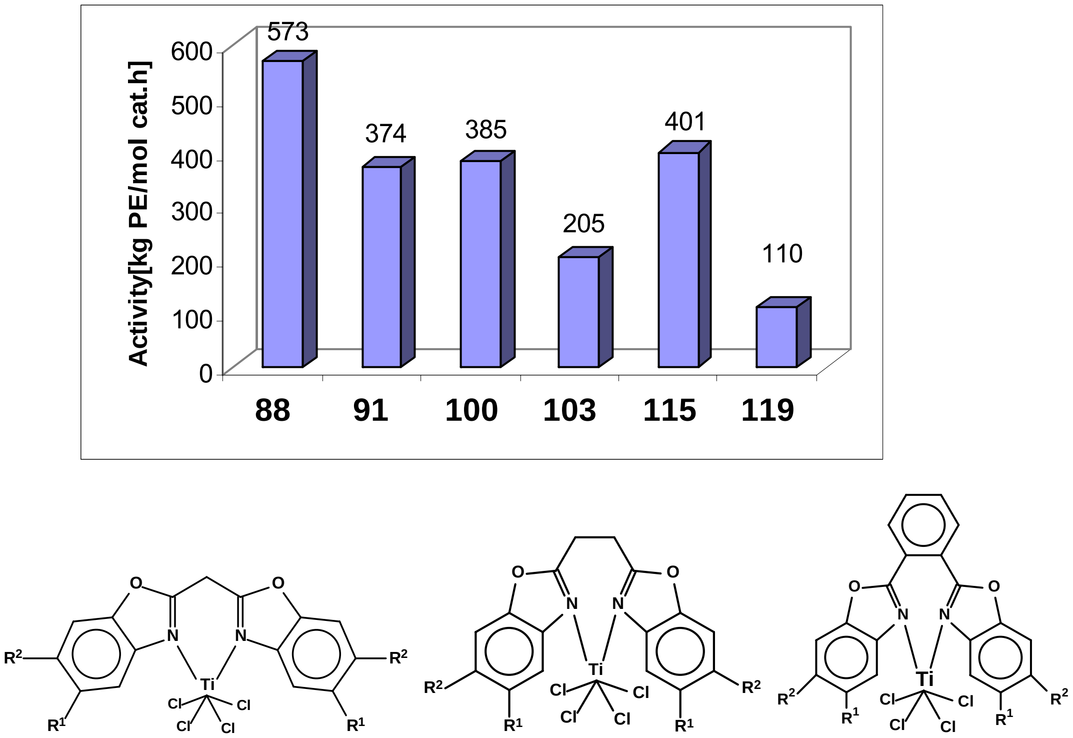
Scheme 76. The effect of the ligand structure on catalyst activities.



X = S	**82**	**94**	**106**
X = O	**85**	**97**	**112**

Scheme 77. Effect of the hetero atom (X=S,O) on the activity of bis(benzothiazole) and bis-(benzoxazole) titanium complexes

The methyl substituted bis-benzoxazole titanium complexes (Scheme 78) behave differently depending on the position of the methyl group at the phenyl ring of the benzimidazolyl moiety. When the methyl group is introduced in the *meta*-position to the imino-nitrogen atom (**88, 100, 115**) it leads to an increase of the activity due to both electronic and steric effects. On the other hand, when the methyl group is introduced in the *para* position (**91, 103, 119)** with respect to the imino nitrogen atom, the activities drop because the electron density on the nitrogen atom increases and consequently the nucleophilicity of the central metal atom increases which weakens the interaction between the metal atom and the π-electrons of the ethylene monomer and hence this decreases the rate of ethylene insertion in the chain-growth steps[74,111].



$R^1=CH_3$, $R^2=H$	**88**	**100**	**115**
$R^1=H$, $R^2=CH_3$	**91**	**103**	**119**

Scheme 78. Effect of the substituent position on the activity of bis(benzoxazole)titanium complexes.

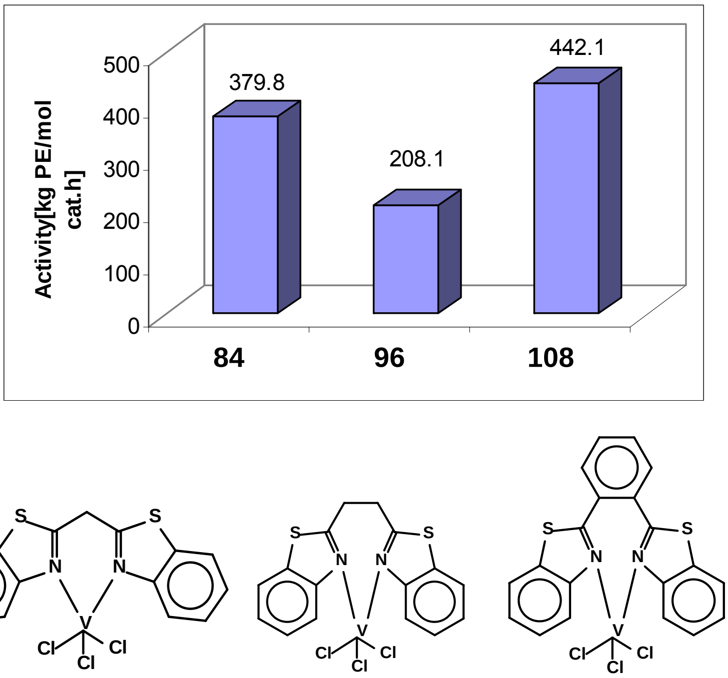
7.2.2. Activities of the vanadium complexes

The vanadium complexes of 1,2-bis(benzothiazolyl) and 1,2-bis(benzoxazolyl) compounds show moderate activities towards ethylene polymerization reactions after activation with MAO.

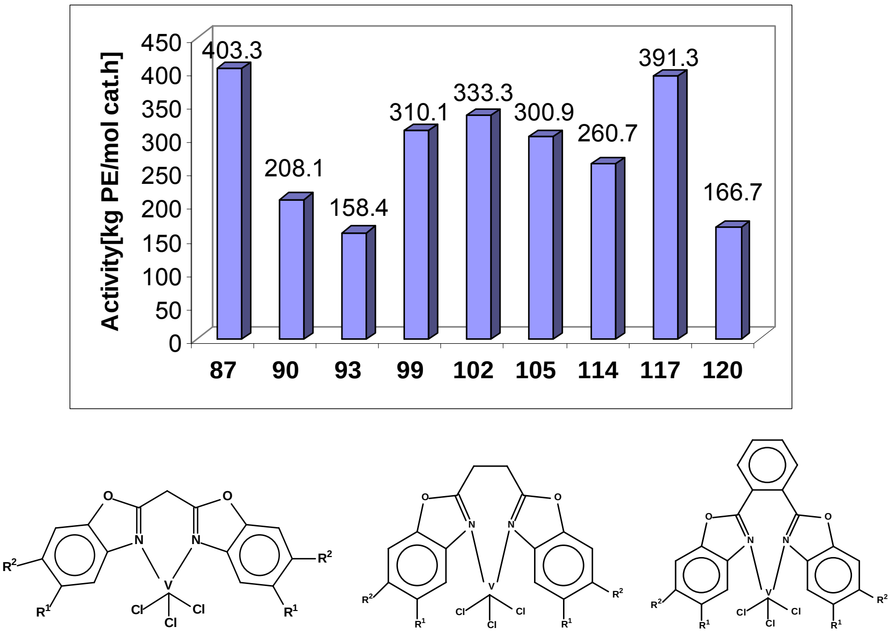
From the ligand structure point of view, the activities of the vanadium complexes follow the order: 1,2-bis(benzothiazolyl)benzene > 1,1-bis(benzothiazolyl)methane > 1,2-bis(benzothiazolyl) ethane (Scheme 79).

The benzoxazolyl vanadium complexes show a similar behaviour to that observed for the titanium complexes and their activities follow the order: 1,1-bis(benzothiazolyl)methane > 1,2-bis(benzothiazolyl) ethane > 1,2-bis(benzothiazolyl)benzene (Scheme 80).

The position of the methyl group relative to the imino nitrogen influences the catalytic activity of the 1,2-bis(benzoxazolyl) vanadium complexes. The methyl group in *para* position to the imino nitrogen 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[111] (Scheme 81). On the other hand, a methyl group *meta* to the imino nitrogen increases the activities of the complexes (Scheme 82) which can be explained withelectronic effectss[74].



Scheme 79. Activity variation of 1,2-bis(benzothiazole) vanadium complexes by changing the ligand structure.

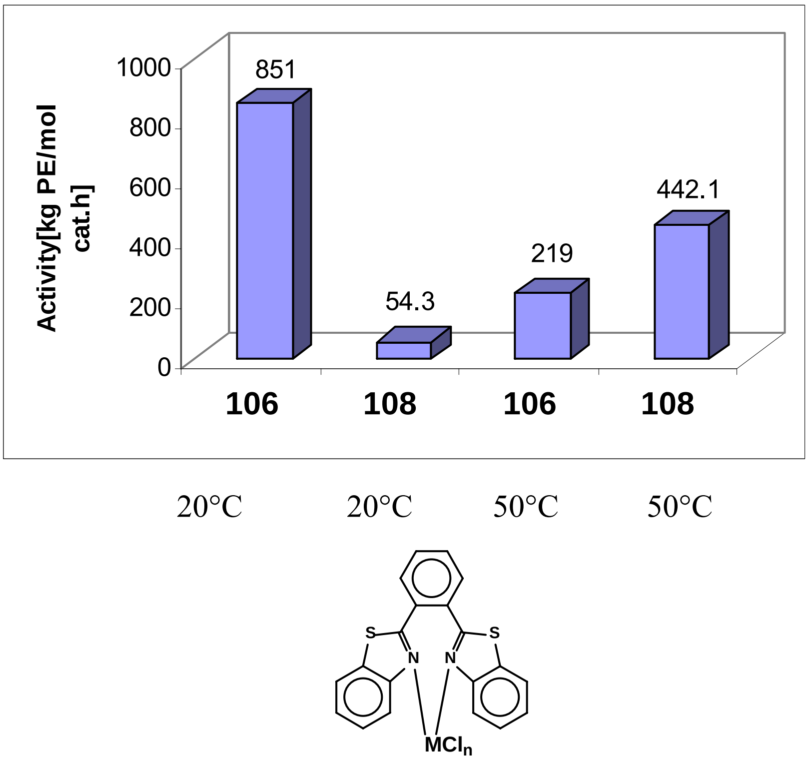


R^1, R^2 = H	**87**	**99**	**114**
R^1 = CH_3, R^2= H	**90**	**102**	**117**
R^1 = H, R^2= CH_3	**93**	**105**	**120**

Scheme 80. Activity variation of 1,2-bis(benzoxazole) vanadium complexes by changing the ligand structure.

Applying complexes **106** and **108**, the temperature dependence of polymerization activities was investigated.

Under identical polymerization conditions (cocatalyst concentration and reaction temperature), the titanium complex showed higher activity at low temperature, while the vanadium complex showed higher activity at elevated temperature (Scheme 81).

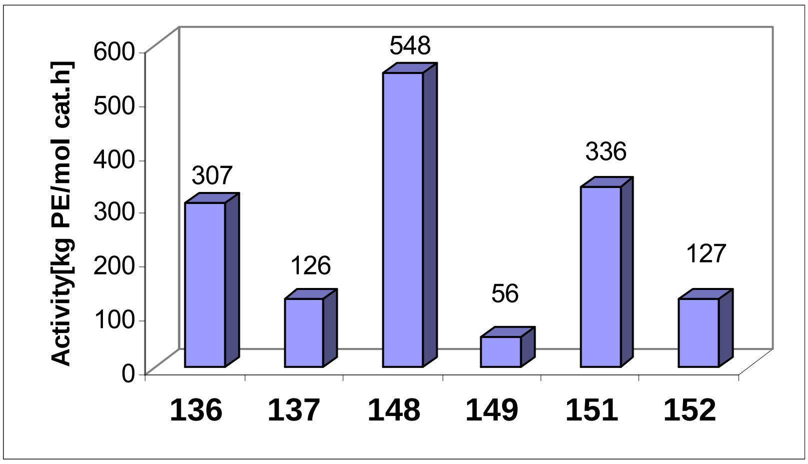


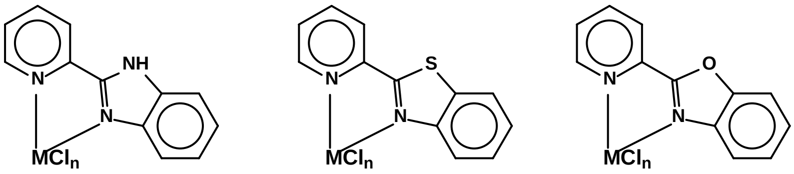
Scheme 81. Effect of the temperature on the activities of 1, 2-bis(benzothiazolyl)benzene titanium (**106**) and vanadium (**108**) complexes.

7.3. Polymerization activities of 2-(benzimidazolyl)pyridine, 2-(benzothiazolyl)pyridine and 2-(benzoxazolyl)pyridine complexes

7.3.1. Activities of titanium and zirconium complexes

The titanium and zirconium complexes of 2-(benzimidazolyl)pyridine, 2-(benzothiazolyl)pyridine and 2-(benzoxazolyl)pyridine, after activation with MAO, all showed catalytic activities for ethylene polymerization reactions. In all cases, the titanium complexes are more active than the zirconium complexes with the same ligand system (Scheme 82). The 2-(benzothiazolyl)pyridine titanium complex **148** showed an activity of 548 kg PE/mol cat.h which can be attributed to extra stabilization of the active centre via a secondary interaction with the large sulphur atom. Titanium complexes of 2-(benzimidazolyl)pyridine (**136**), and 2-(benzoxazolyl)pyridine (**151**) show the same activities most probably due to the comparable sizes and electronegativities of the hetero atoms (N, O). The same behaviour was observed for the zirconium complexes of the same ligand systems (Scheme 82).

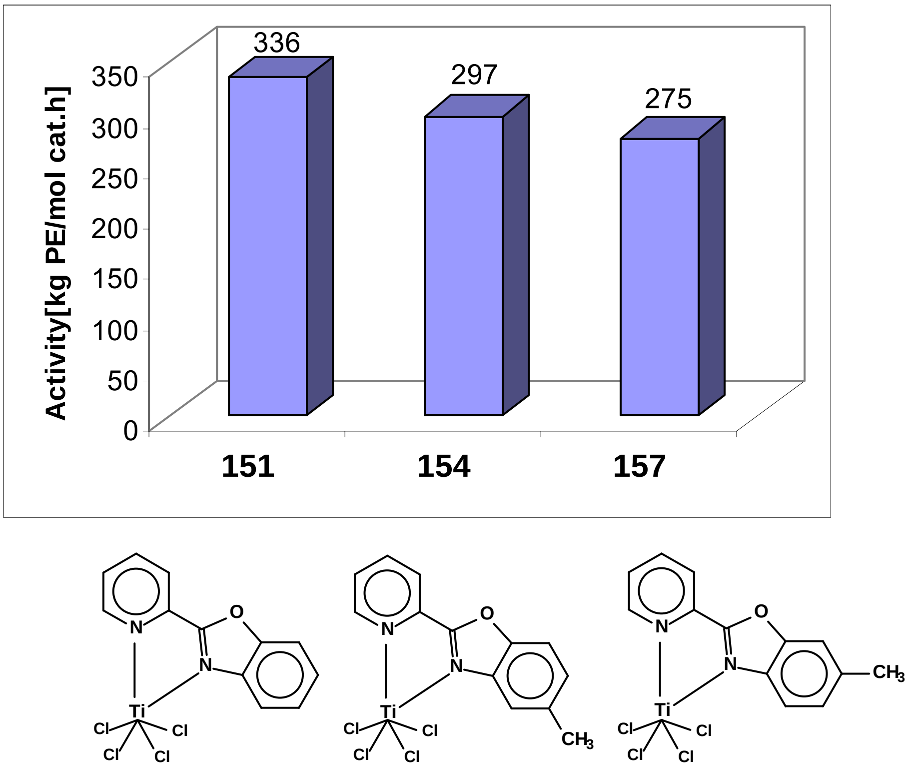




136, 137 **148, 149** **151, 152**

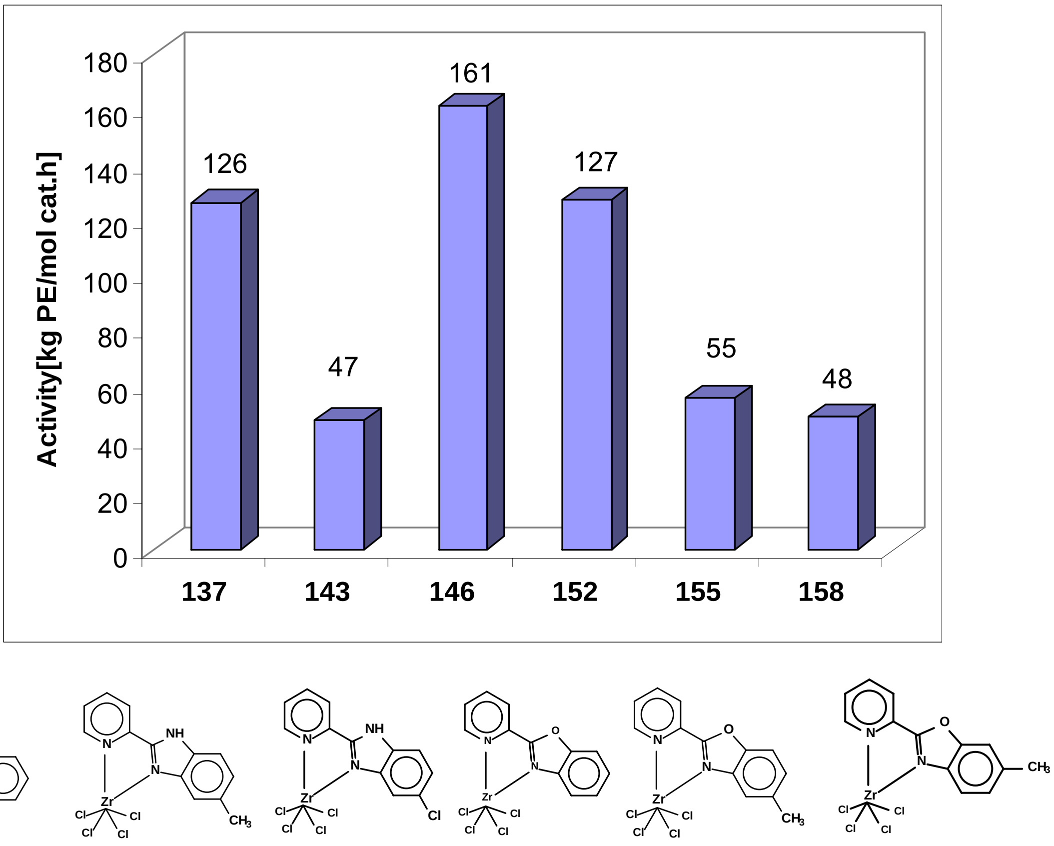
Scheme 82. Polymerization activities of 2-(benzimidazolyl)pyridine, 2-(benzothiazolyl)pyridine and 2-(benzoxazolyl) pyridine titanium (**136**, **148**, **151**) and zirconium(**137**, **149**, **152**) complexes.

Methyl substituted 2-(benzoxazolyl)pyridine titanium complexes in all cases showed lower activities compared to the unsubstituted complexes (Scheme 83). The position of the methyl group influences the activity via electronic and/or steric effects. The catalyst system **154**/**MAO** with a methyl substituent *meta* to the imino nitrogen atom showed an activity of 297 [kg PE/mol cat.h]. The catalyst system **158**/**MAO** with a methyl substituent *para* to the imino nitrogen atom gave an activity of 275 [kg PE/mol cat.h] while the unsubstituted complex **136**/**MAO** showed an activity of 307 [kg PE/mol cat.h].



Scheme 83. Effect of substituents on the activities of the 2-(benzoxazolyl)pyridine titanium complexes **151, 154, and 157.**

The investigation of the ethylene polymerization activities of 2-(benzimidazolyl)pyridine and 2-(benzoxazolyl)pyridine zirconium complexes revealed that the unsubstituted complexes showed higher activities than those with methyl substituents on the phenyl ring, which gave the same activities regardless to the position of the substituent. The 2-(benzimidazolyl)pyridine zirconium complex with a chloro substituent *meta* to the imino nitrogen showed higher activities compared with the unsubstituted complex most probably for electronic reasons (Scheme 84).



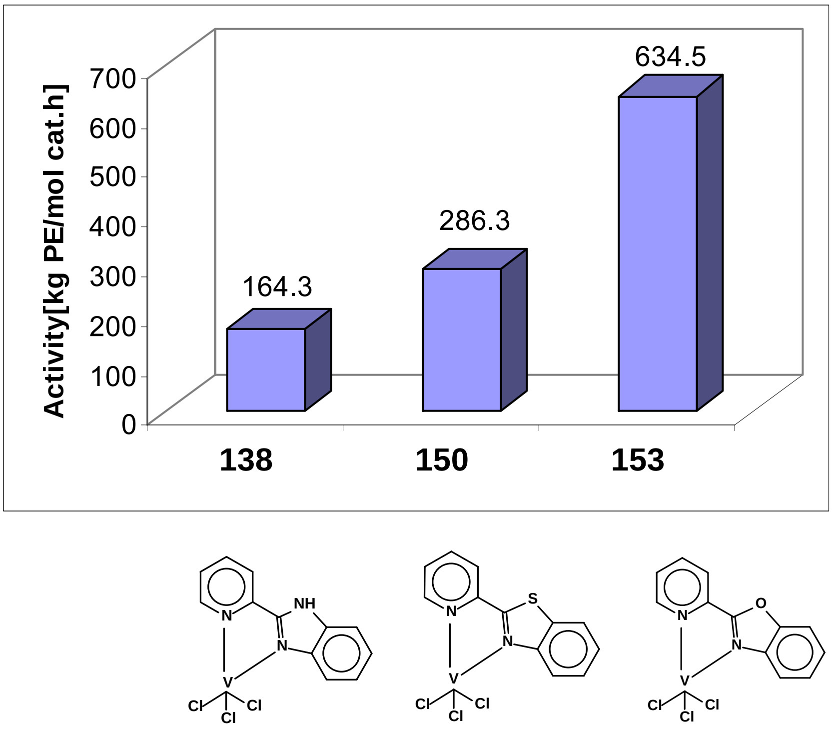
137 **143** **146** **152** **155** **158**

Scheme 84. Effect of the substituent position and type on the activities of 2-(benzimidazolyl, benzoxazolyl)pyridine zirconium complexes.

7.3.2. Polymerization activities of vanadium complexes

Vanadium complexes of 2-(benzimidazolyl)pyridine, 2-(benzothiazolyl)pyridine and 2-(benzoxazolyl)pyridine, after activation with MAO, showed catalytic activities in ethylene polymerization reactions.

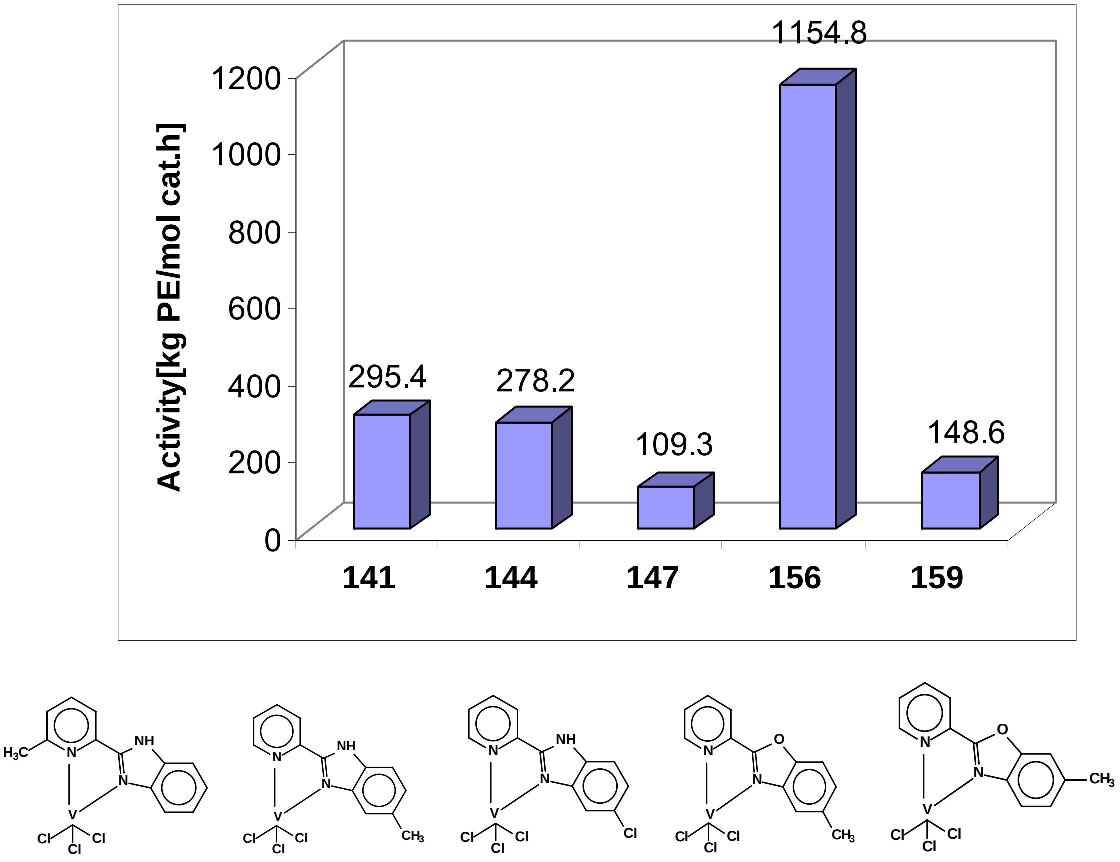
The activities show the following trend: 2-(benzoxazolyl)pyridine vanadium complexes are more active than 2-(benzothiazolyl)pyridine complexes and 2-(benzimidazolyl)pyridine complexes; i. e. the activities of these vanadium complexes with such ligands are greatly influenced by different hetero atoms (Scheme 85).



Scheme 85. Effect of the hetero atoms on the activities of the vanadium complexes **138**, **150** and **153.**

The position and the type of the substituent influences the activities of 2-(benzimidazolyl)pyridine and 2-(benzoxazolyl)pyridine vanadium complexes. The methyl substituted (*meta* to the imino nitrogen) 2-(benzimidazolyl)pyridine vanadium complex **141** shows an activity of 278 [kg PE/mol cat.h]. Complex **144** with a methyl substituent on position **six** of the pyridine ring shows an activity of 295 [kg PE/mol cat.h] while the chloro (*meta* to the imino nitrogen) substituted complex **147** shows an activity of 109 [kg PE/mol cat.h] (Scheme 86). It is obvious that electron donating groups on those positions increase the activities of the catalysts while electron withdrawing group reduce their activities.

In an analogous manner the activities of the vanadium 2-(benzoxazolyl)pyridine complexes **156** and **159** with a methyl substituent at the *meta* or *para* to the imino nitrogen show activities of 1155 [kg PE/mol cat.h] and 149 [kg PE/mol cat.h] respectively (Scheme 86).



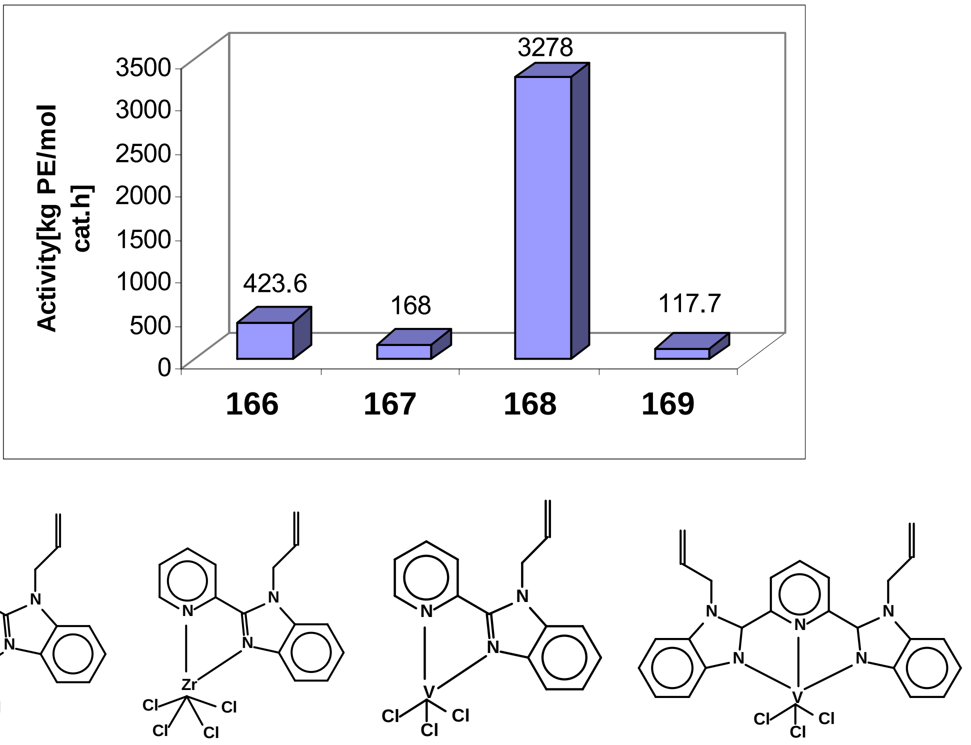
141 144 147 156 159

Scheme 86. Effect of substituent position and type on the activities of 2-(benzimidazolyl, benzoxazolyl)pyridine vanadium complexes.

7.4. Polymerization activities of N-allyl substituted 2-(benzimidazolyl)pyridine, 2,6- bis-(benzimidazolyl)pyridine, and 1,2-bis (benzimidazolyl)benzene, –ethane, and -methane complexes

7.4.1. Activities of N-allyl substituted 2-(benzimidazolyl)pyridine and 2,6-bis(benzimidazolyl)pyridine complexes 166-169

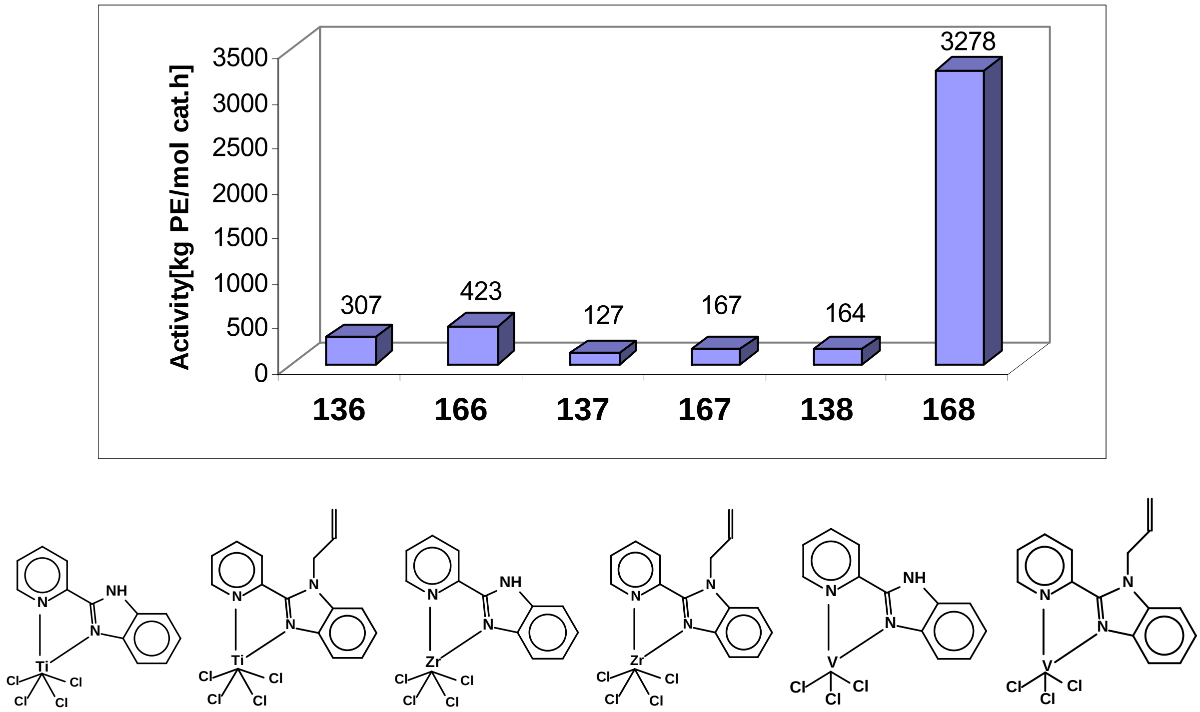
The polymerization activities of N-allyl-2-benzimidazolyl pyridine titanium, zirconium, and vanadium complexes were investigated. The vanadium catalyst **168/MAO** showed the highest activity (3278 [kg PE/mol cat.h]) compared to the titanium catalyst **166/**MAO (423.6 [kg PE/mol cat.h]) and the zirconium catalyst **167/MAO** (166.7 [kg PE/mol cat.h]). The 2,6-bis(benzimidazolyl)pyridine vanadium catalyst **169/MAO** showed an activity of 117.7 [kg PE/ mol cat.h].(Scheme 87).



166 **167** **168** **169**

Scheme 87. Polymerization activities of the 2-(N-allyl-benzimidazolyl)pyridine complexes **166**-**168** and the 2,6-bis(N-allyl-benzimidazolyl)pyridine complex **169.**

In comparison to the systems without an allyl substituent (**136**-**138/MAO),** the activities were greatly enhanced by the introduction of the allyl substituent which can be explained by the effect of the allyl group on the active centre by increasing its electrophilicity and hence increase the activity. The allyl group may also block the free electron pair of the nitrogen atom, so the coordination to the cationic metal centers is less probable (Scheme 88).



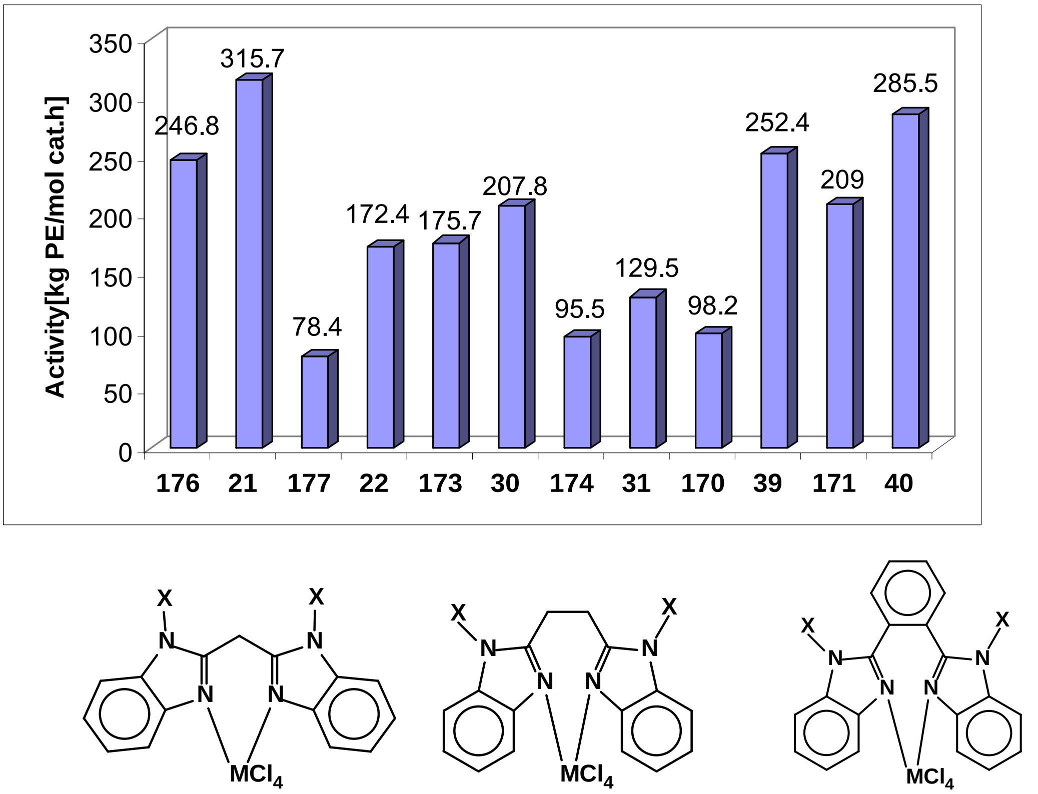
136 **166** **137** **167** **138** **168**

Scheme 88. Effect of the allyl substituent on the polymerization activities of complexes **166-168** compared to unsubstituted **136-138.**

7.4.2. Polymerization activities of 1,2-bis(N-allyl-benzimidazolyl)(benzene and ethane and 1,1-bis(N-allyl-benzimidazolyl)methane titanium zirconium and vanadium complexes

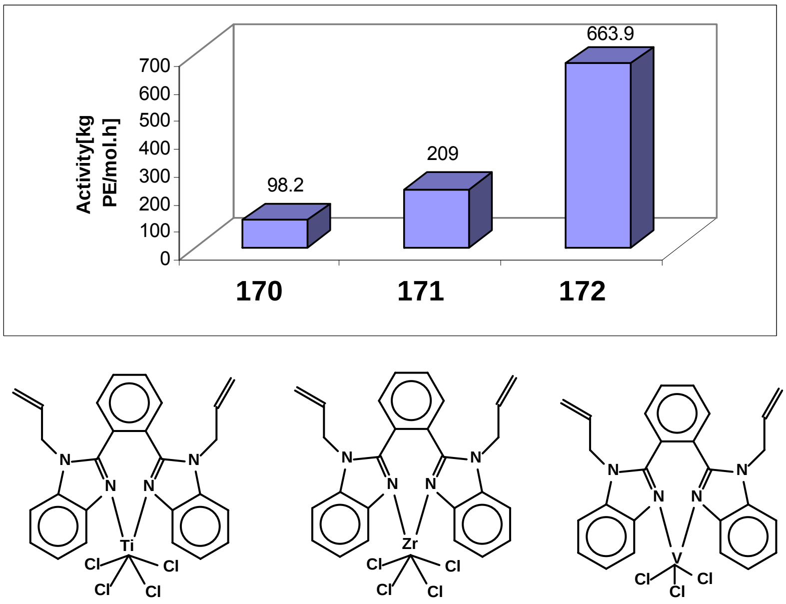
The complexes containing N-H groups showed relatively high catalytic activities compared to the N-allyl substituted analogues (Scheme 89). This could be possibly caused by their deprotonation to give anionic amide ligands when activated with MAO (or residual $AlMe_3$). The anionic amide ligands form N-Al species to increase their catalytic activities[74,112].

Titanium, zirconium and vanadium complexes with the titled ligand systems behave differently depending on the ligand structure. The zirconium complex **171** obtained from the ligand 1,2-bis(N-allyl-benzimidazolyl)benzene showed a higher activity than the titanium complex **170**. The vanadium complex **172** is again the most active catalyst in this series (663.9 [kg PE/mol cat.h]) (Scheme 90). The titanium complexes **173, 176,** and **179** showed activities of 175.7 [kg PE/mol cat.h], 246.8 [kg PE/mol cat.h] and 541 [kg PE/mol cat.h] respectively. The same order of activity is observed for the zirconium complexes obtained from the same ligand systems (**174**, **177**, **180**) (Scheme 91). This activity order seems to depend on the length of the bridging unit.

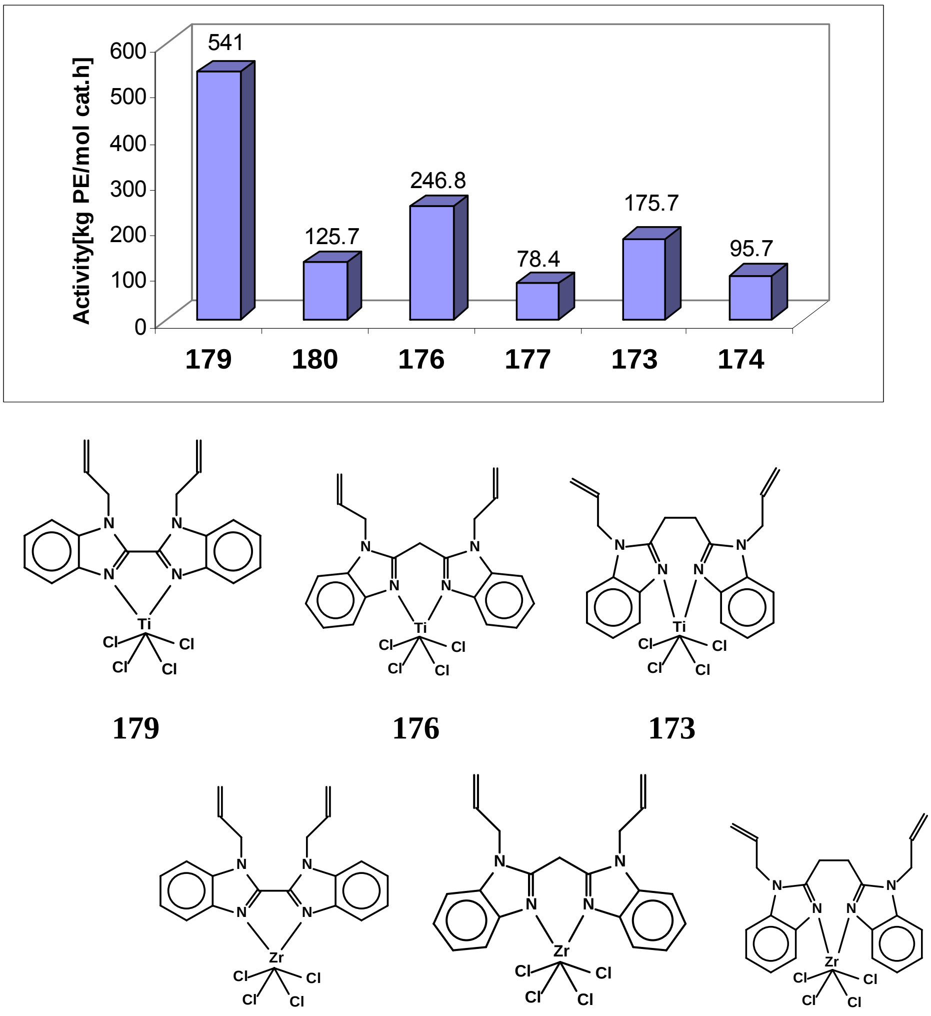


X	M = Ti	M = Zr	M = Ti	M = Zr	M = Ti	M = Zr
H	**21**	**22**	**30**	**31**	**39**	**40**
allyl	**176**	**177**	**173**	**174**	**170**	**171**

Scheme 89. Effect of the allyl substituent on polymerization activities of bis(benzimidazolyl) titanium and zirconium complexes.



Scheme 90. Activities of 1,2-bis(N-allyl benzimidazolyl)benzene complexes**.**



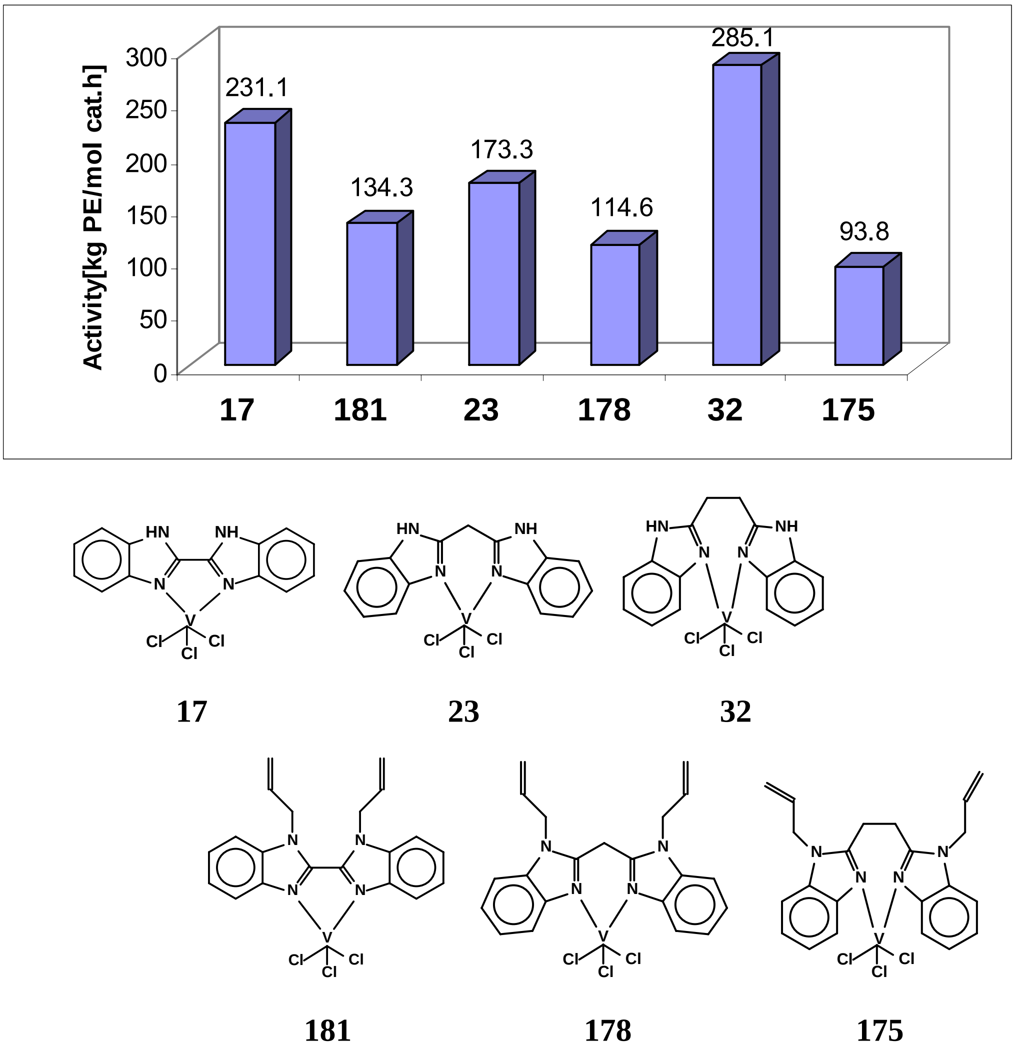
179 **176** **173**

180 **177** **174**

Scheme 91. Polymerization activities of N-allyl-bis(benzimidazolyl) titanium (**179**, **176**, **173**) and zirconium (**180**, **177**, **174**) complexes.

7.4.3. Polymerization activities of 1,2-bis(N-allyl-benzimidazolyl) ethane,1,1-bis(N-allyl-benzimidazolyl)methane and bis(benzimidazolyl)vanadium complexes

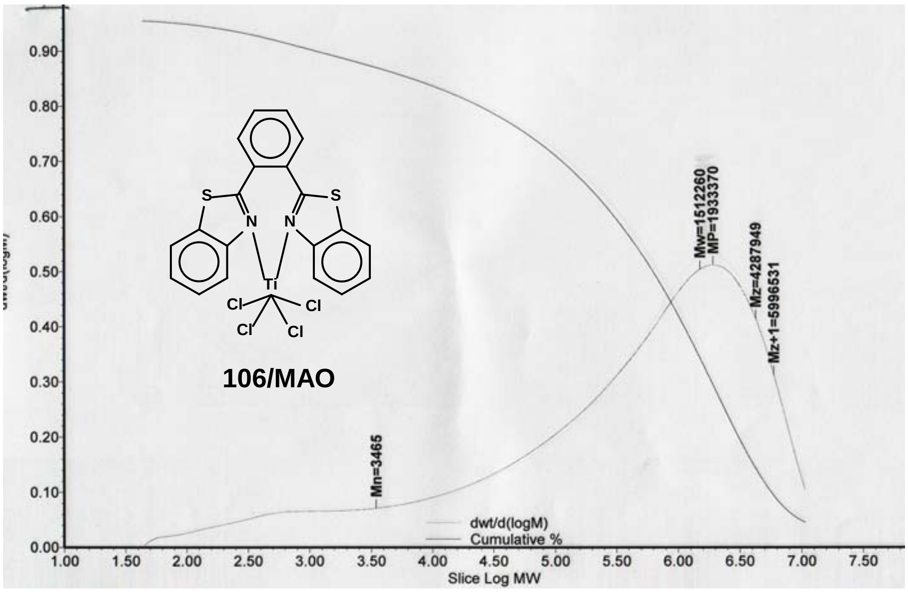
The vanadium complexes **175**,**178**, **181** with the title ligand systems showed different activities depending on the length of the connecting unit as in the case of the titanium complexes obtained from the same ligand system. The N-allyl substituted complexes showed lower activities compared to those containing N-H groups (Scheme 92). This can be explained in general by the observed behaviour of all complexes of this type that any factor increasing the electron density on the hetero atom (N, O, S) increases the activity and vice versa.



Scheme 92. Effect of the allyl group on the activities of bis-benzimidazolyl vanadium complexes.

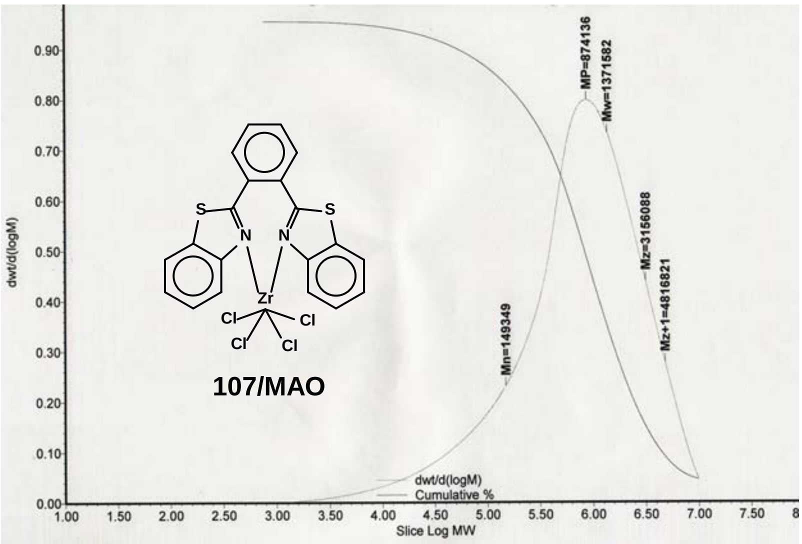
7.5. Polymer analysis

GPC analysis of the polyethylenes produced by benzimidazole based complexes revealed that the symmetric catalysts systems were capable to produce resins with very high molecular weights associated with broad or even bimodal molecular weight distributions. The bimodality may arise from the fact that the MAO counterion induces the necessary dissymmetry of the active sites in the activation process[113]. For example, the catalyst system **106/MAO** produced a resin with M_w= 1512260 g/mol in a bimodal fashion (PD = 436) (Scheme 93)

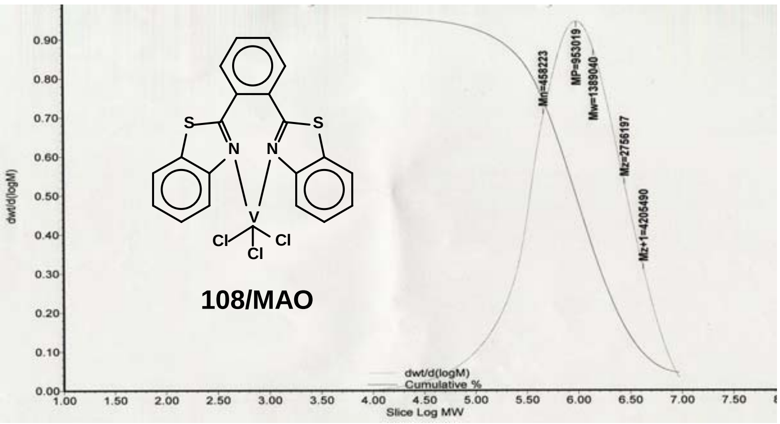


Scheme 93. GPC spectrum of polyethylene produced with **106** /**MAO**.

Schemes 94 and 95 show the GPC-spectra of polyethylenes produced with the catalyst systems **107/MAO** and **108/MAO.** The molecular weight M_w of the polymer produced with **107**/**MAO** was determined to be 1371582g/mol, (PD= 9.18). The catalyst system **108**/**MAO** produced polyethylene with M_w= 1389040g/mol (PD= 3.03).

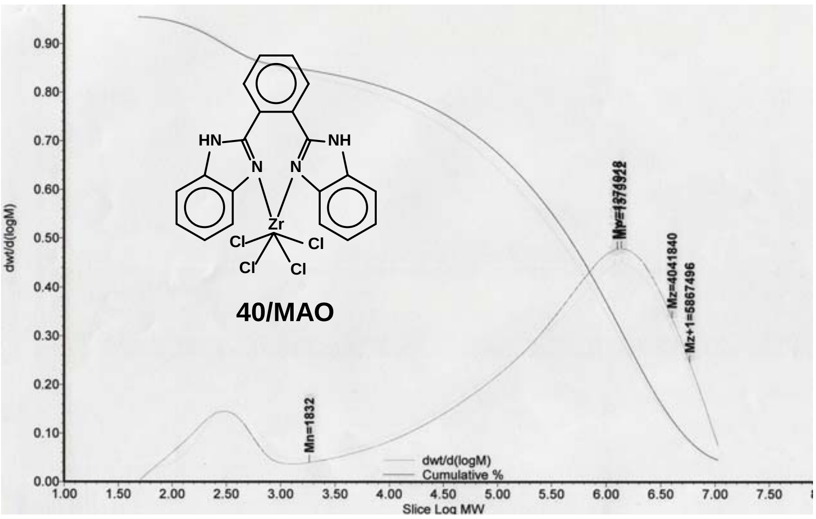


Scheme 94. GPC spectrum of polyethylene produced with **107 /MAO**.

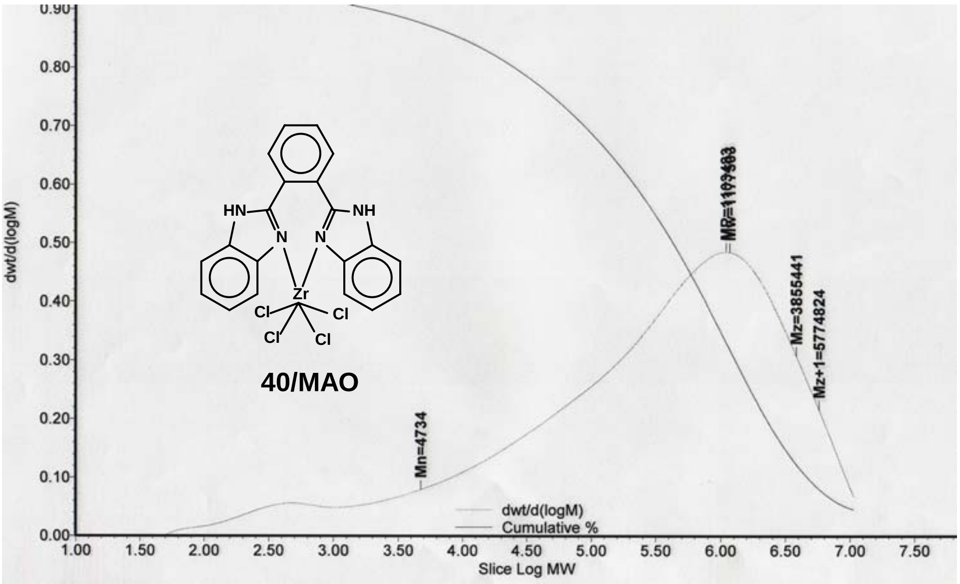


Scheme 95. GPC spectrum of polyethylene produced with **108** /**MAO**.

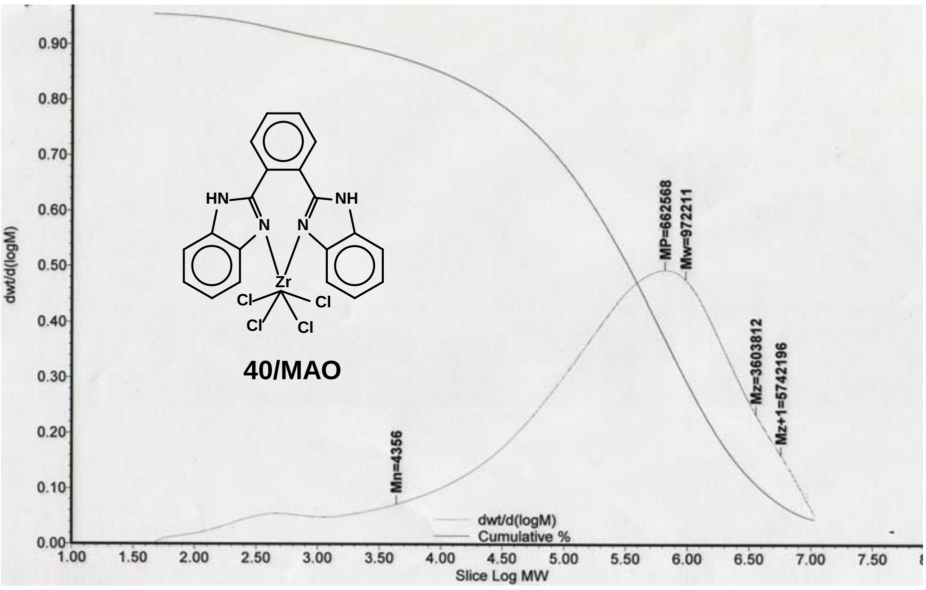
The effect of the polymerization temperature on both molecular weights and polydispersities of the polymers produced with the catalyst system **40**/**MAO** was investigated. At 20°C (Scheme 96) the molecular weight M_w was found to be 1271018g/mol, and the polydispersity index (PDI) = 693. At 40°C (Scheme 97), M_w was 1177503g/mol (PD= 248), at 60°C (Scheme 98), M_w = 972211g/mol, (PD = 223). It is clear that the temperature affects both molecular weights and polydispersities. This effect is pronounced in the polydispersity index. The higher the temperature, the lower the polydispersity. This catalyst effect can be explained by a rotation along the axis of the imino carbon atom: the faster the rotation, the lower the polydispersity.



Scheme 96. GPC spectrum of polyethylene produced with **40**/MAO at 20°C.



Scheme 97. GPC spectrum of polyethylene produced with **40**/**MAO** at 40°C.



Scheme 98. GPC spectrum of polyethylene produced with **40**/**MAO** at 60°C.

GPC analysis for the polyethylenes produced with complexes derived from 1,1-bis(benzimidazolyl, benzothiazolyl and benzoxazolyl)methane and 1,2-bis(benzimidazolyl, benzothiazolyl and benzoxazolyl)ethane shows high molecular weights and their polydispersities were found to be narrower than those produced with 1,2-bis(benzimidazolyl, benzothiazolyl and benzoxazolyl)benzene complexes which can be accounted for structurally. For example, the catalyst system **23/MAO** produces a resin with molecular weight M_w = 424279g/mol (PD = 3.2) and the catalysts **83** and **85/MAO** produce resins with molecular weights M_w = 362916 and 356538g/mol (PD = 4.3 and 3.3). For the catalyst 33/MAO the molecular weight Mw was determined to be 444669g/mol, PD = 9.1). the catalyst system **94/MAO** produce polymer with (M_w = 373250g/mol, PD = 5.3) and similarly the catalyst **97/MAO** (M_w = 633535g/mol, PD = 7.5). In most cases, the polyethylenes produced with 2- (benzimidazolyl, benzothiazolyl and benzoxazolyl)pyridine complexes 136-159 were of very high molecular weights and variable polydispersities depending on the nature of the hetero atom, substitution patteren and the individual metal center. For example, the catalyst system **136/MAO** produce polyethylene with molecular weight (M_w = 1765524g/mol, PD = 4.4) and the catalyst **148/MAO** shows molecular weight (M_w = 1685769g/mol, PD = 5.7) and the molecular weight and the polydispersity of the resin produced with 156/MAO (M_w = 2876365g/mol, PD = 1.6).

8. Experimental

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 aluminum hydride. Methylene chloride was dried with phosphorus pentoxide and calcium hydride. Methanol and ethanol were dried over molecular sieves.

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.

8.1 NMR spectroscopy

The spectrometers Bruker ARX 250 and VARIAN INOVA 300/ 400 MHz 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 $CDCl_3$, $\delta = 39.0$ ppm for DMSO-D_6).

8.2 Mass spectrometry

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

8.3 GC/MS

GC/MS spectra were recorded with a HP 5890 gas chromatograph in combination with a HP 5971A mass detector. A 12 m J&W Scientific fused silica column (DB1, diameter 0,25 mm, film 0,33 µm, flow 1ml/min) respectively 25 m J&W Scientific fused silica column (DB5ms, diameter 0,25 mm, film 0,33 µm, flow 1ml/min) were used, helium (4.6) was applied as carrier gas. Using a 12 m column, the routinely performed temperature program started at 70°C (2 min). After a heating phase of eleven minutes (20K/min, final temperature 290 °C) the end temperature was held for a variable time (plateau phase). At the Zentrale Analytik of the University of Bayreuth, GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector.

8.4 Gel permeation chromatography (GPC)

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

8.5 Elemental analysis

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).

8.6 Syntheses

8.6.1 Synthesis of the 1,2-bis(benzoimidazoles) 1-14

Method A: 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 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.

Method B: The diamine 0.05mol was added to 0.025 mol of di-carboxylic acid or acid anhydride in 100 ml of 5N hydrochloric acid. The reaction mixture was then refluxed for 10 hours, cooled and allowed to stand. The precipitate was filtered and extracted with hot diluted ammonium hydroxide solution and then washed with ethanol and air dried.

8.6.2. Synthesis of bis-benzothiazoles and bis-benzoxazoles

Only method A was applicable, in place of o-phenylene diamine, either 2-aminothiophenol, 2-hydroxyaniline, 2-hydroxy-4-methylaniline, 2-hydroxy-5-methylaniline were used respectively.

8.6.3 Synthesis of (2-benzimidazolyl, 2-benzothiazolyl and 2-benzoxazolyl) pyridine

Method A was used for the synthesis of the above mentioned compounds. Pyridine -2-carboxylic acid and the diamine or 2-aminothiophenol and 2-hydroxyaniline were used in equimolar quantities.

8.6.4 Synthesis of N-allyl substituted bis-benzoimidazole and benzoimidazolyl pyridine compounds

The general procedure for the reaction of N-allylation was as follows: Benzimidazolyl pyridine (5g, 25.6 mmol) was dissolved in 10 ml anhydrous DMF. Then K_2CO_3 (1.4 equiv) was added to the solution at room temperature. Shortly afterwards (20 min), allylbromide (25.6 mmol) was added in portions to the reaction mixture. The reaction was stirred at room temperature for two days. The inorganic salt was removed by filtration and rinsed twice with dichloromethane. The solution was poured into water and extracted with dichloromethane (2 x 50 ml). The combined organic layers were washed with brine, dried over anhydrous sodium sulphate, filtered, and concentrated in vacuo resulting in a viscous oil. Addition of water resulted in the formation of the product in 85% yield. Other N-allyl substituted compounds were prepared similarly.

Table20. Elemental analysis data of representative compounds.

Compound No.	**Calculated**			**Found**		
	C	**H**	**N**	**C**	**H**	**N**
3	72.58	4.84	22.58	72.75	4.77	22.48
10	77.42	4.52	18.06	77.38	4.49	18.13
60	69.77	3.49	8.14	69.74	3.52	8.11
67	72.73	4.55	10.61	72.85	4.50	10.47
72	77.65	4.71	8.23	77.71	4.73	8.41
128	67.92	3.77	13.21	67.87	3.81	13.16
132	78.84	4.61	21.34	78.86	4.58	21.45
134	74.28	4.76	13.33	74.32	4.78	13.36
160	76.59	5.53	17.87	76.61	5.55	17.83
161	76.73	5.37	17.90	76.70	5.42	17.79
163	77.19	6.43	16.37	77.22	6.37	16.29

8.6.5 General procedures for the synthesis of the complexes

8.6.5.1 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.

8.6.5.2 Zirconium complexes

To 0.45g (1.2mmol) $ZrCl_4(THF)_2$ in dichloromethane was added 1.2 mmol of the solid ligand. The reaction mixture was stirred over night at room temperature, filtered and washed several times with dichloromethane, then with pentane, dried under vacuum and weighed.

8.6.5.3 Vanadium complexes

To 0.41g (2.6 mmol) VCl_3 in ether was added 2.6 mmol of the ligand. The reaction mixture was stirred over night at room temperature, filtered and washed several times with ether and pentane, dried under vacuum and weighed.

8.6.6 Synthesis of titanium and zirconium tetrachloride THF adducts

The titanium and zirconium adducts were synthesized via published procedures[114]. A 250 ml Schlenk flask equipped with a magnetic stirring bar was charged with 5.0g (26 mmol) titanium tetrachloride dissolved in 50 ml dichloromethane. Anhydrous tetrahydrofuran (7.62g,.010mol) was added dropwise, and the solution was stirred at room temperature for 15 minutes. Dry pentane (50ml) was added, and the solution was chilled to -25° for 1 hour, filtered on a medium fritted funnel and the residue was washed with dry pentane.

Table 21. Elemental analysis data of representative complexes.

Complex No.	**Calculated**			**Found**		
	C	**H**	**N**	**C**	**H**	**N**
23	44.40	2.96	13.83	43.86	2.81	13.40
35	48.32	4.03	12.53	48.48	4.24	11.98
37	35.51	3.20	8.84	36.85	3.15	8.96
43	46.23	3.15	9.81	47.06	3.23	8.97
48	42.25	2.76	9.86	42.02	2.87	9.76
53	49.51	3.93	11.00	48.75	3.92	10.97
83	34.95	1.94	5.38	35.04	2.00	5.38
90	46.90	3.22	6.44	47.12	3.30	6.51
95	36.29	2.27	5.29	37.31	2.49	5.36
99	45.61	2.85	6.65	44.75	2.67	6.53
102	48.00	3.56	6.22	47.68	3.53	6.18
107	41.59	2.08	4.58	41.97	2.01	4.66
124	45.42	2.19	8.37	45.63	2.25	8.41
125	48.51	2.34	8.94	48.31	2.33	8.90
138	40.91	2.56	11.93	40.68	2.54	11.86
141	42.62	3.01	11.48	42.16	2.97	11.35

Complex No.	Calculated			Found		
	C	H	N	C	H	N
149	32.36	1.80	6.29	32.07	1.78	6.24
151	37.31	2.11	7.25	37.01	2.32	6.99
152	33..57	1.86	6.53	33.93	2.04	6.74
157	39.00	2.50	7.00	39.37	2.66	7.31
167	38.46	2.78	8.97	38.30	2.77	8.94
168	45.92	3.32	10.71	45.23	3.27	10.55
169	54.74	3.83	12.77	55.11	3.92	12.45
173	49.62	4.14	10.53	49.36	4.23	10.78
174	45.91	3.83	9.74	45.34	3.92	9.78
178	51.96	4.12	11.55	52.10	4.25	11.34
179	47.62	3.57	11.11	48.21	3.62	11.21

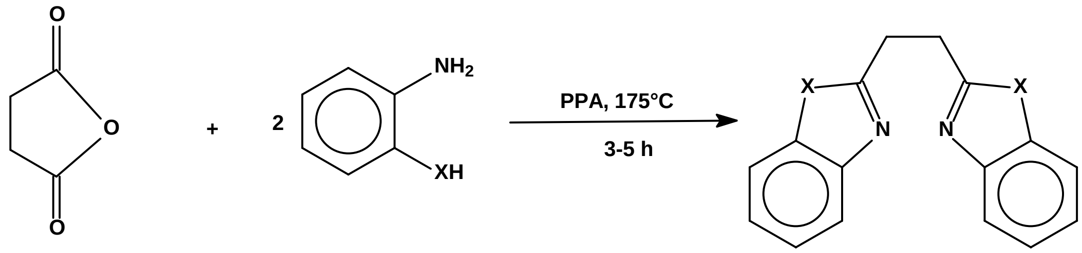
8.7 Polymerization of ethylene in a 1l Büchi autoclave

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

Summary

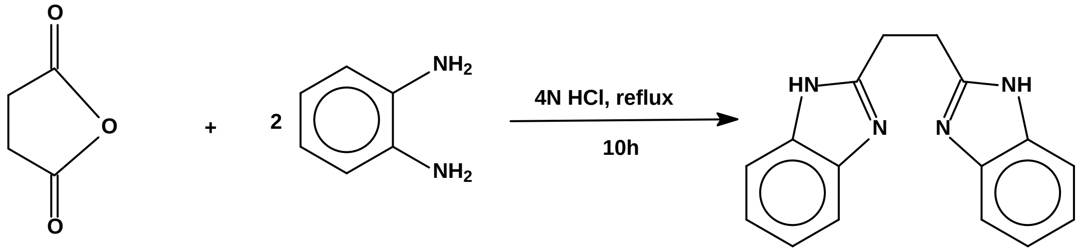
The synthesis of titanium, zirconium and vanadium complexes with bis(benzimidazole)s, bis(benzothiazole)s and bis(benzoxazole)s is a main objective of this study. Their catalytic performance towards ethylene polymerization reactions was also studied.

The ligand systems mentioned above were synthesized via condensation reactions using polyphosphoric acid which acts as solvent, oxidizing and dehydration agent. The condensation reactions proceeded readily to produce high yield products.

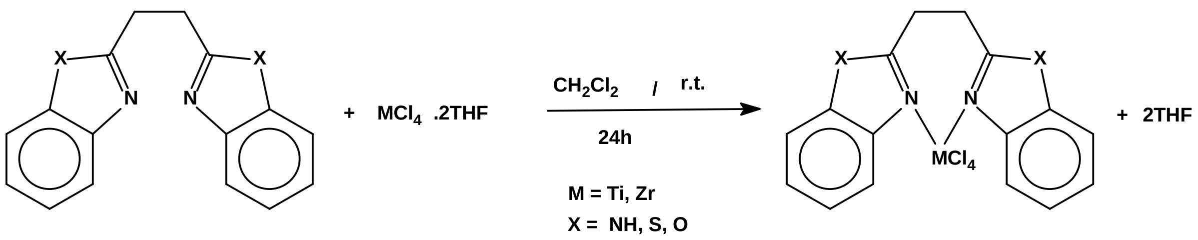


X = NH, S, O

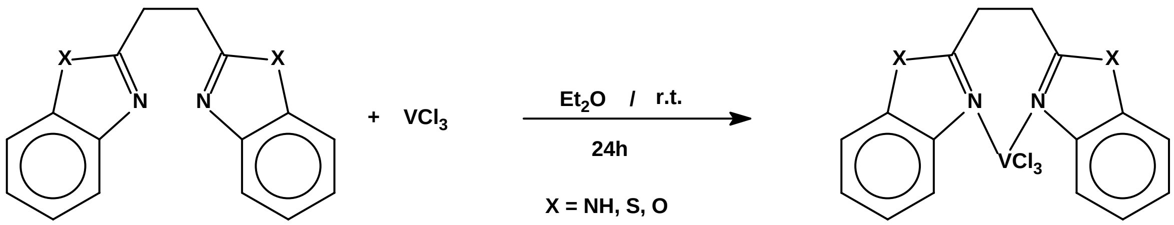
Bis(benzimidazole)s can also be prepared by refluxing the reactant in 4 N hydrochloric acid for ten hours or longer.



The organic compounds mentioned above, when reacted with the tetrahydrofuran adducts of titanium and zirconium tetrachloride, are capable to produce 1:1 complexes via ligand displacement in very good yields.

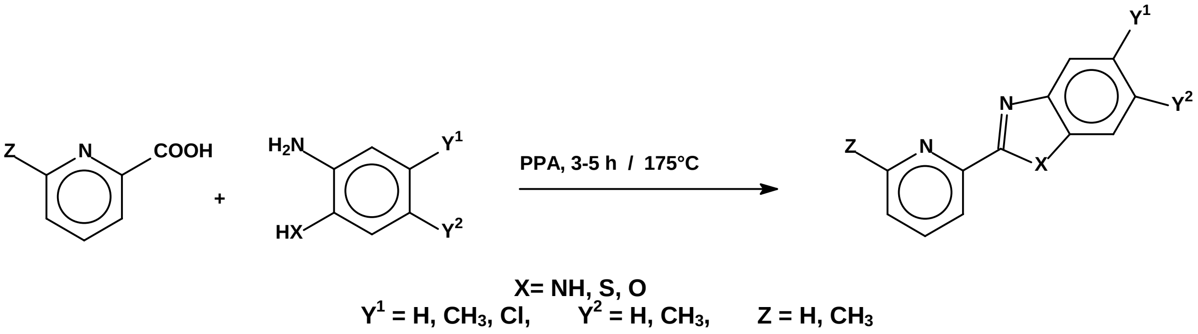


The vanadium complexes were prepared using the vanadium trichloride salt in diethylether.

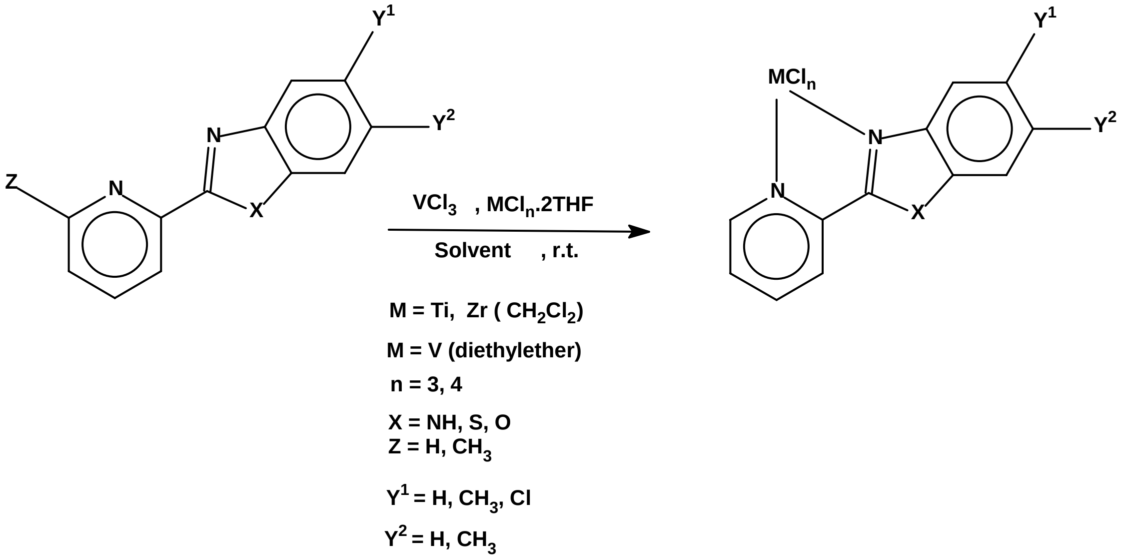


Secondly, titanium, zirconium and vanadium complexes derived from 2-(benzimidazolyl)pyridine, 2-(benzothiazolyl)pyridine and 2-(benzoxazolyl)pyridine were prepared and used as olefin polymerization catalysts upon activation with MAO.

The potential ligand precursors were obtained in high yields and very good purity.

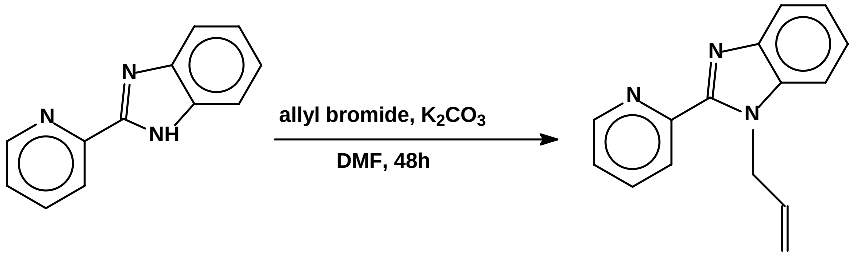


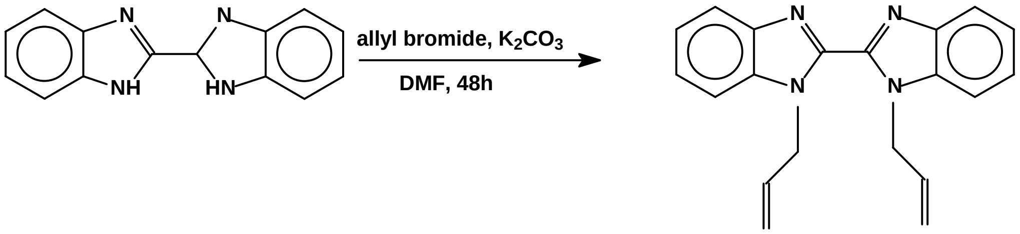
The titanium, zirconium and vanadium complexes were synthesized as described earlier.



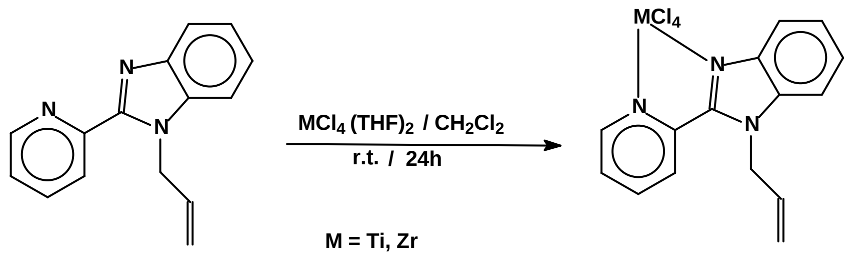
The synthesis of titanium, zirconium and vanadium complexes with N-allyl substituted benzimidazoles was one of the study goals. These complexes were tested for ethylene polymerization reactions. Their ability of self immobilization was also investigated.

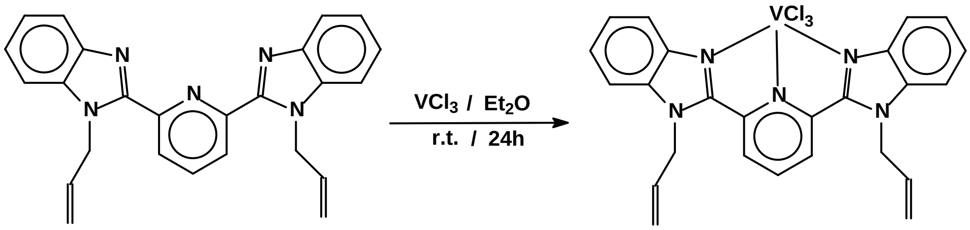
The ligands were synthesized by the reaction of allylbromide with benzimidazole in the presence of potassium carbonate and DMF as a solvent.





The titanium, zirconium and vanadium complexes were synthesized as described earlier.





The titanium, zirconium and vanadium complexes after activation with methylaluminoxane (MAO) were used for the homogeneous polymerization of ethylene. They showed good to moderate catalytic activities towards ethylene polymerization reactions. The vanadium complexes showed the highest activities, followed by titanium complexes, while zirconium complexes showed the lowest activities.

The catalytic activities seem to depend on several factors but the substitution patterns and types played significant roles in addition to the ligand structures and the natures of the metal ions. It was observed that both electron withdrawing and electron releasing groups *meta* to the imino nitrogen atom reduced the activities compared to the unsubstituted complexes. However, complexes with electron releasing groups showed higher activities compared to those with electron withdrawing groups. The nature of the hetero atoms (N, O and S) also influenced the catalytic activities of the complexes.

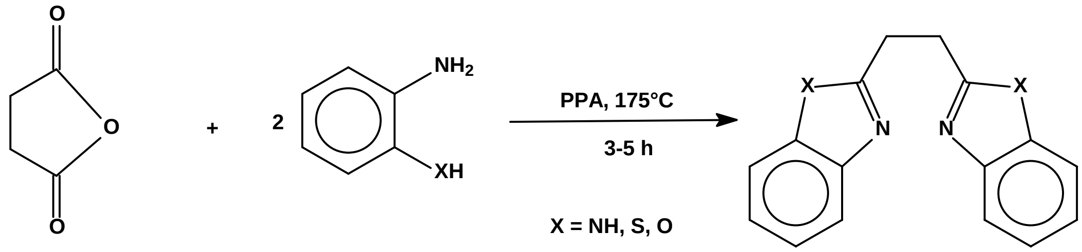
The introduction of one allyl substituent in 2-(benzimidazolyl)pyridine complexes increased the activities of the complexes compared to unsubstituted ones. However, the activity of the vanadium complex was increased by a factor of 20.

The introduction of two allyl substituents in 1,2-bis(benzimidazole) complexes lowered the activities compared to the unsubstituted complexes and to those with only one allyl group.

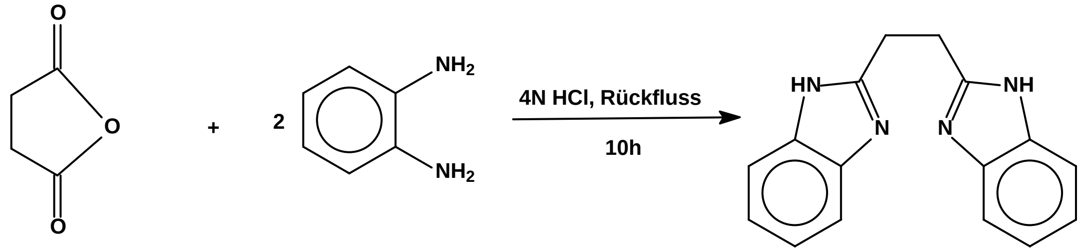
The polyethylenes produced by the above mentioned complexes as catalysts were in most cases of higher molecular weights (> 1000000g/mol) associated with broad and/or bimodal molecular weight distributions. The bimodality was thought to arise from the presence of more than one isomer (diastereomer) for each complex in addition to the different active centres resulting from different kinds of interactions with the cocatalyst MAO.

Zusammenfassung

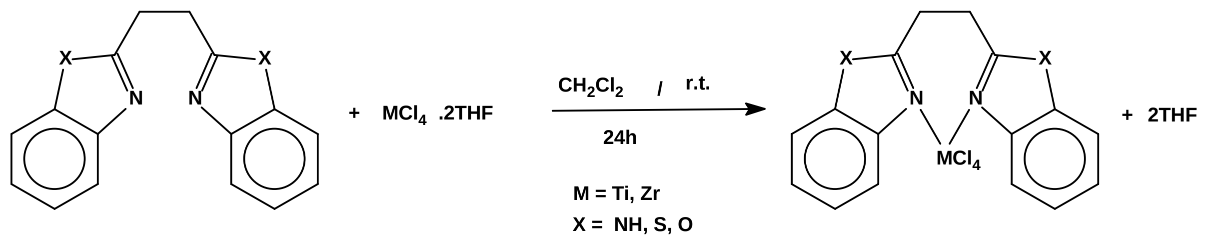
Die Darstellung von Titan-, Zirkonium- und Vanadiumkomplexen mit Bis(benzimidazole)-, Bis(benzothiazol)- und Bis(benzoxazol)verbindungen ist eines der Hauptziele der vorliegenden Arbeit. Des Weiteren wurden deren katalytische Eigenschaften hinsichtlich der Polymerisation von Ethen untersucht. Die oben erwähnten Ligandsysteme wurden durch Kondensationsreaktionen dargestellt. Hierfür diente Polyphosphorsäure als Lösungs-, Oxidations- und Dehydrierungsmittel. Diese einfache Reaktion lieferte die gewünschten Produkte in hohen Ausbeuten.



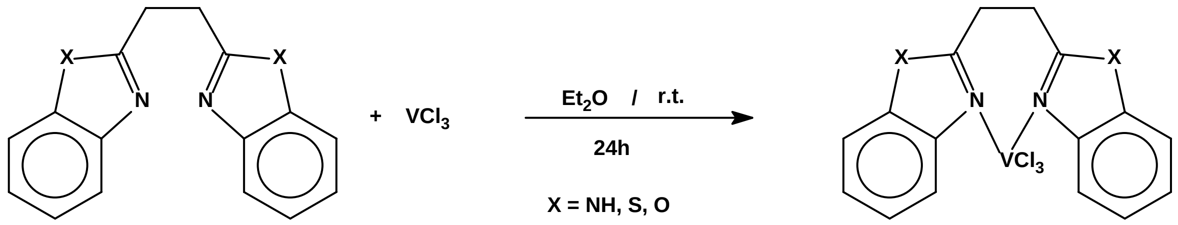
Bis(benzimidazol)verbindungen können alternativ durch zehnstündiges Rühren unter Rückfluss in 4 molarer Salzsäure dargestellt werden.



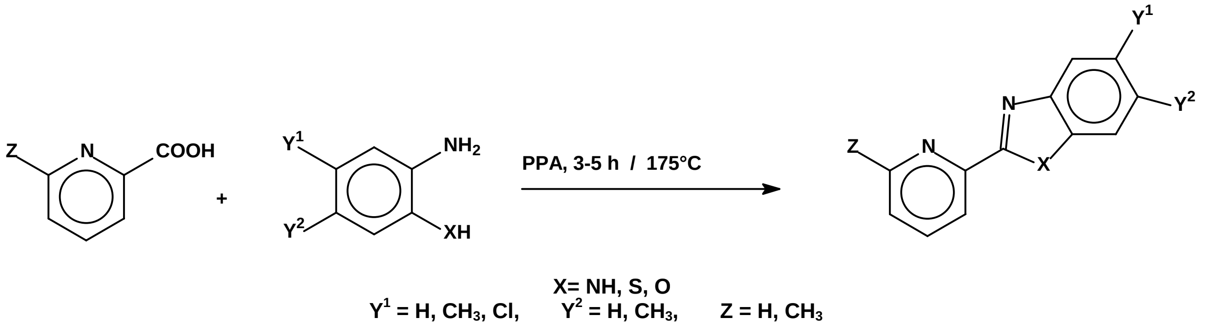
Diese organischen Verbindungen wurden mit dem THF-Addukt des Titan- und Zirkoniumtetrachlorids umgesetzt und produzierten die gewünschten 1:1 Komplexe durch Ligandaustausch in sehr guten Ausbeuten.



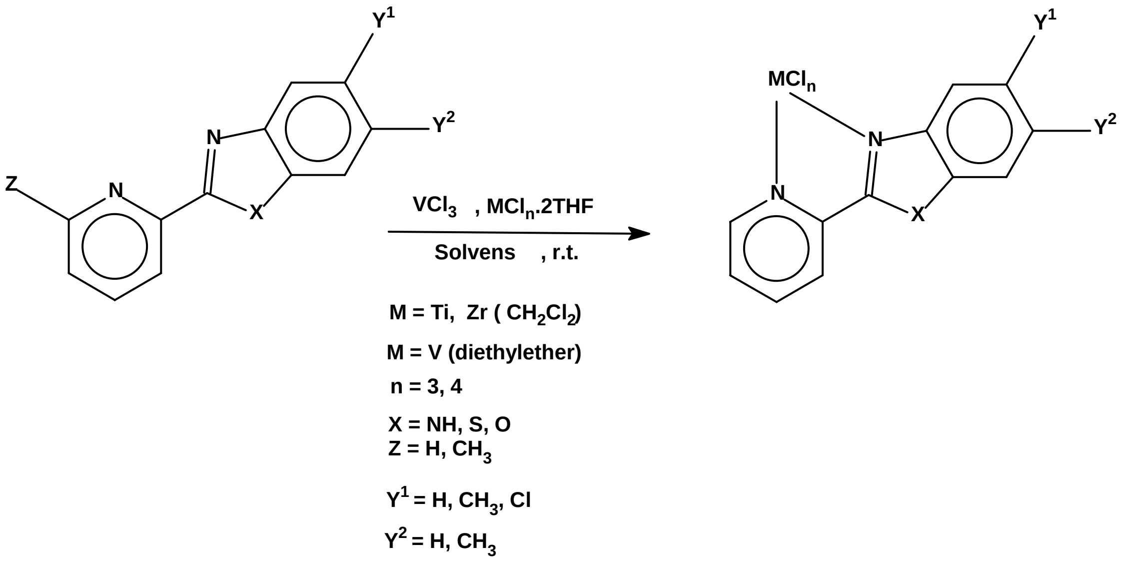
Die entsprechenden Vanadiumkomplexe wurden durch die Verwendung von Vanadiumtrichlorid in Diethylether dargestellt.



Zweitens wurden die Titan-, Zirkonium- und Vanadiumkomplexe ausgehend von 2-(Benzimidazolyl)pyridin, 2-(Benzothiazolyl)pyridin und 2-(benzoxazolyl)pyridin dargestellt und nach deren Aktivierung mit MAO als Polymerisationskatalysatoren eingesetzt. Die potentiellen Liganden wurden in großen Ausbeuten mit hoher Reinheit erhalten.

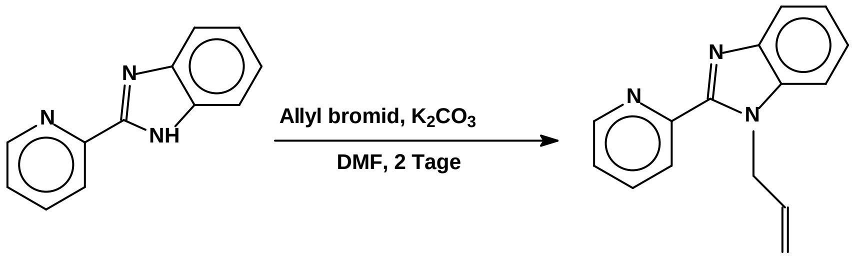


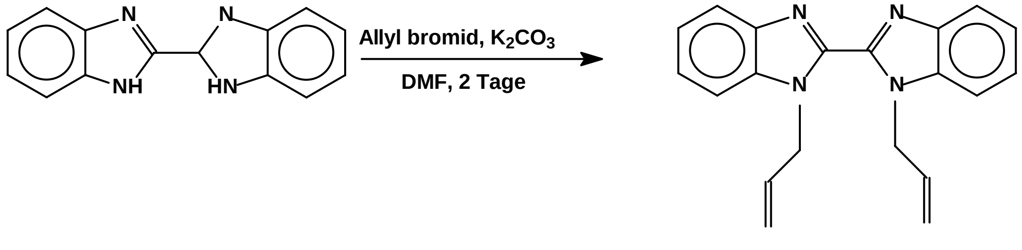
Ausgehend von diesen organischen Verbindungen wurden die Titan-, Zirkonium- und Vanadiumkomplexe wie schon erwähnt dargestellt.



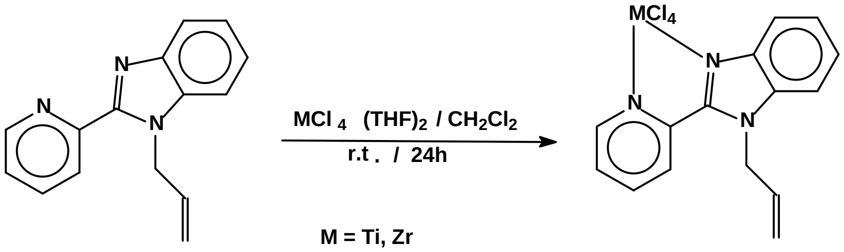
Ein weiteres Ziel dieser Arbeit war die Darstellung von N-allyl substituierten Benzimidazolen und deren Umsetzung zu den entsprechenden Titan-, Zirkonium- und Vanadiumkomplexen, sowie deren Test zur katalytischen Polymerisation von Ethen. Ebenso wurde deren Fähigkeit zur Selbstimmobilisierung untersucht.

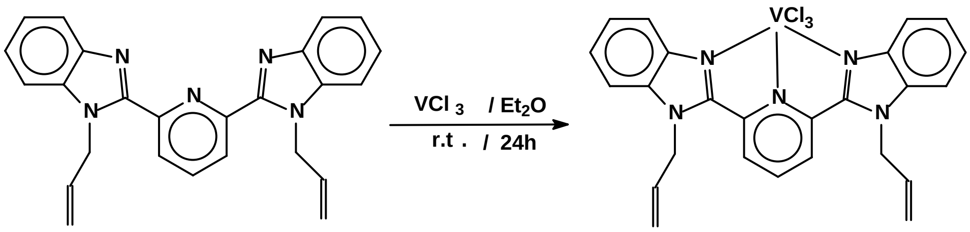
Die potentiellen Liganden wurden durch die Reaktion von Allylbromid und Benzimidazol in Anwesenheit von Kaliumcarbonat und DMF als Lösungsmittel erhalten.





Die anschließende Umsetzung zu den Titan-, Zirkonium- und Vanadiumkomplexen erfolgte wie schon vorher beschrieben.





Nach der Aktivierung mit Methylaluminoxan (MAO) wurden die Titan-, Zirkonium- und Vanadiumkomplexe für die homogene katalytische Polymerisation von Ethen getestet. Sie wiesen mäßige bis hohe katalytische Aktivitäten auf. Die Aktivitäten stiegen in der Reihe von Zirkonium über Titan zu Vanadium an.

Die Aktivitäten schienen von verschiedenen Faktoren abhängig zu sein. Zum einen spielen Substitutionsmuster und –typ zusätzlich zu der Ligandstruktur eine große Rolle, zum anderen das Zentralmetall. Es konnte beobachtet werden, dass sowohl elektronenziehende als auch –schiebende Substituenten an der meta-Position des Imino-Stickstoffs die Aktivitäten im Vergleich zu den unsubstituierten Komplexen verminderten, wobei die Aktivitäten der Komplexe mit elektronenschiebenden Gruppen im direkten Vergleich mit denen der Komplexe mit elektronenziehenden Gruppen größer waren. Ebenso beeinflusste die Natur des Heteroatoms (N, O, S) die katalytische Aktivitäten der unterschiedlichen Komplexe.

Die Einführung eines Allyl-Substituenten in 2-(Benzimidazolyl)pyridin Komplexe erniedrigte die Aktivität der Komplexe im Vergleich zu den unsubstituierten. Bei der Verwendung von Vanadium als Zentralmetall konnte eine Verminderung um den Faktor 20 beobachtet werden.

Eine weitere Gruppe mit Allyl-Substituenten in 1,2-Bis(benzimidazol) Komplexen zeigte wiederum eine geringere Aktivität im Vergleich zu den unsubstituierten und den monosubstituierten Komplexen.

Das mit den hier vorgestellten Komplexen produzierte Polyethylen wies in allen Fällen ein hohes Molekulargewicht auf (>1000.000 g/mol), verbunden mit breiter und/oder bimodaler Molekulargewichtsverteilung. Die Ursache für die Bimodalität scheint in der Anwesenheit von Diastereomeren für jeden Komplex zu suchen sein. Außerdem können verschiedenartige aktive Zentren gebildet werden, bedingt durch die unterschiedlichen Wechselwirkungen des jeweiligen Katalysators mit dem Cokatalysator MAO.

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Erklärung

Hiermit erkäre ich, dass ich die vorliegende Arbeit selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benützt habe.

Ferner erkläre ich, dass ich nicht anderweitig mit oder ohne Erfolg versucht habe eine Dissertation einzureichen oder mich der Doktorprüfung zu unterziehen.

Bayreuth.........................