



Titanium, zirconium and vanadium complexes of 2-(benzimidazolyl, benzothiazolyl, and benzoxazolyl) pyridine as catalyst precursors for ethylene polymerization



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Dedicated to Professor Dr. Uwe Rosenthal on the occasion of his 65th birthday (April 23).

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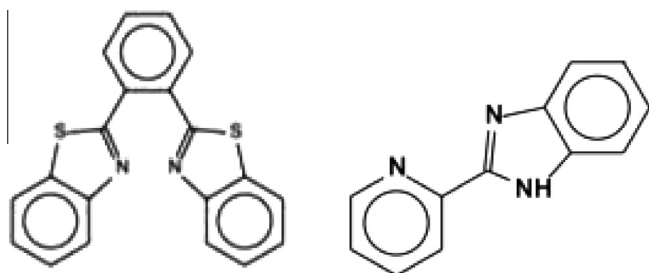
ABSTRACT

Dissymmetric chelating complexes of Ti, Zr and V with 2-(benzimidazolyl, benzothiazolyl, and benzoxazolyl) pyridine ligands were synthesized and characterized. After activation with methylalumoxane (MAO) in solution, these complexes could be applied as ethylene polymerization catalysts. Their activities depend on the metal and the substituents at the pyridine ring and the heterocycle. Structure–property-relationship studies revealed that the titanium and vanadium catalyst systems showed higher polymerization activities than the zirconium analogues. The benzoxazolyl moiety containing vanadium complex **29**, with a methyl substituent in the 6-membered ring in meta position to the nitrogen atom in the 5-membered ring, and an unsubstituted pyridine ring showed the highest activity (1154.8 kg PE/mol cat h). The produced polyethylenes exhibited high molecular weights and broad molecular weight distributions. Obviously different active sites are generated in the course of these polymerization reactions.

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1. Introduction

Recently we reported the synthesis and the characterization of 2,6-bis-(benzimidazolyl, benzothiazolyl, and benzoxazolyl) benzene complexes with the metals, titanium, zirconium and vanadium [1,2]. These complexes could be activated with methylalumoxane (MAO) in solution and be applied as catalysts for homogeneous ethylene polymerization. Now we modified these ligands in a way that we removed one heterocyclic moiety and the bridging unit and instead placed a pyridyl substituent on the carbon atom of the heterocyclic 5-membered ring.



2,6-Bis-(benzimidazolyl) [3–7], 2,6-bis(benzothiazolyl) pyridine [8] and 2,6-bis(benzoxazolyl) pyridine [9,10] already have been reported as ligands for several transition metals in order to investigate the complexes for their structures and properties. In polyolefin chemistry, an increasing interest has been focused on the development and design of homogeneous transition metal catalysts as a result of an increasing demand for polyethylene [11–15 and references therein]. So far, vanadium complexes with bis-(benzimidazole) amine as tridentate [N, N, N] ligands were described as active ethylene polymerization catalysts after activation with alkylaluminum compounds [16]. 2,6-Bis(2-benzimidazolyl) pyridine zirconium dichloride/MAO polymerizes methylacrylate [17]. Now we report the first titanium(IV), zirconium(IV) and vanadium(III) complexes with the title ligands together with their use as catalysts for ethylene polymerization after activation with methylalumoxane (MAO).

2. Results and discussion

2.1. Synthesis of the pyridine derivatives 1–8

The compounds 1–8 were synthesized according to Scheme 1 via the polyphosphoric acid method [18]. Condensation reactions of 2-pyridine carboxylic acid, or 6-methyl-2-pyridine carboxylic

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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 ($\geq 85\%$). The Phillip's modified method [19,20] failed to give any of the desired products.

2.2. Synthesis of the coordination compounds

The complexes **9–32** were synthesized according to Scheme 2 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 over night. The products were obtained in very good yields.

2.3. Characterization

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

The compounds **1–8** were characterized by ^1H NMR and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of compound **3** (Fig. 1) shows seven sets of signals. The broad signal with low intensity at $\delta = 9.88$ ppm belongs to the NH proton, a doublet at $\delta = 8.25$ ppm [1H , $^3J_{\text{H,H}} = 7.5$ Hz] can be assigned to the pyridine ring proton H3, a virtual triplet at $\delta = 7.82$ ppm [1H , $^3J_{\text{H,H}} = 7.5$ Hz] to H2. The multiplets at $\delta = 7.72$ – 7.68 and 7.27 – 7.25 ppm belong to an AA'BB' spin system and can be assigned to the phenyl protons H4, H7 and H5, H6. H1 appears at $\delta = 7.38$ ppm [d, 1H , $^3J_{\text{H,H}} = 7.5$ Hz]. The methyl protons are found as a singlet at $\delta = 2.58$ ppm.

The ^{13}C NMR spectrum of compound **3** (Fig. 2) shows ten signals. The signal at $\delta = 159.1$ ppm corresponds to C1, the signal at $\delta = 150.2$ ppm to C5. The signals at $\delta = 146.0$ and 138.6 ppm can be assigned to C12 and C3. The signal at $\delta = 137.2$ ppm arises from the two carbon atoms of the phenyl ring (C6, C11). The carbon

atom C2 of the pyridine ring appears at $\delta = 125.9$ ppm, C8 and C9 at $\delta = 124.4$ ppm. The signal at $\delta = 120.1$ ppm corresponds to C4, while C7 and C10 are observed at $\delta = 115.9$ ppm. At $\delta = 24.7$ ppm, the methyl carbon atom (C13) can be detected.

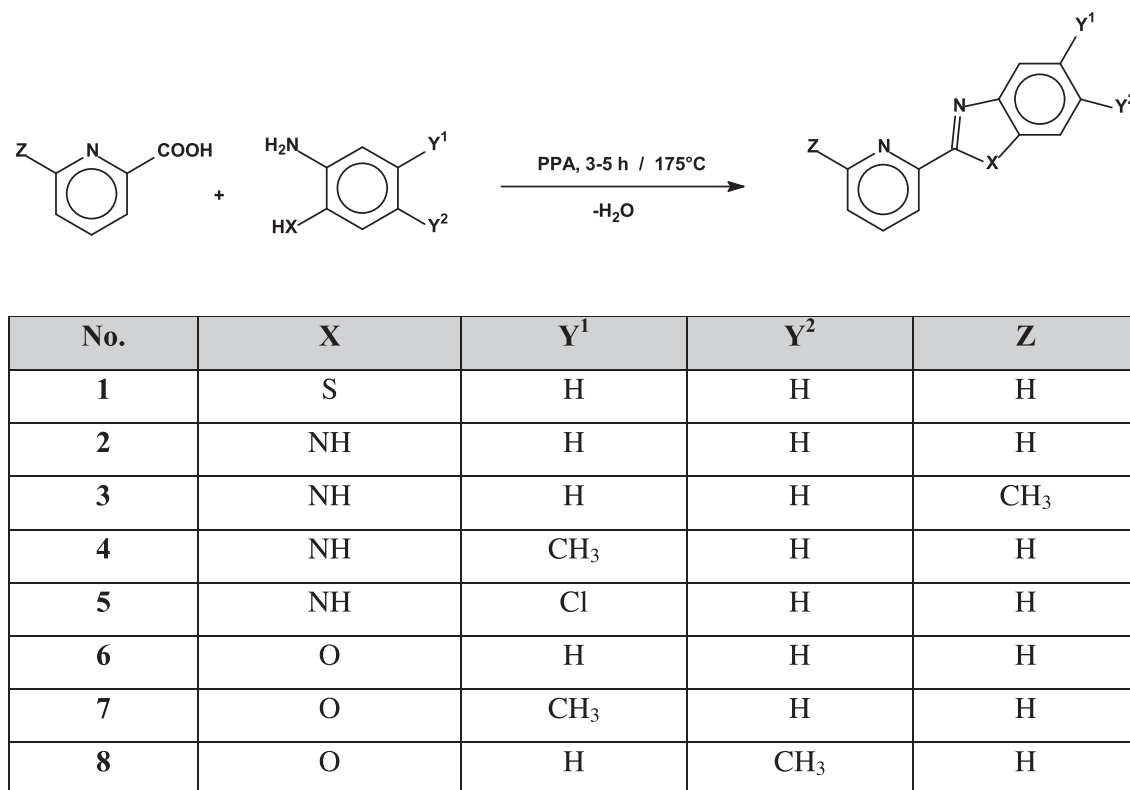
Complexes **9–32** were characterized by ^1H NMR and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of complex **19** (Fig. 3) shows six resonance signals: the super imposed doublets at $\delta = 8.84$ ppm correspond to H1 and H4. The virtual triplets at $\delta = 8.19$ and 7.68 ppm [$^3J_{\text{H,H}} = 7.5$ Hz] belong to H3 and H2. H5 and H6 form an AB pattern at $\delta = 7.62$ and 7.35 ppm [$^3J_{\text{H,H}} = 8.5$ Hz], and H7 a singlet at $\delta = 7.56$ ppm. The protons of the methyl group can be observed at $\delta = 2.02$ ppm.

The ^{13}C NMR spectrum of complex **19** (Fig. 4) shows 13 resonance signals: the signal at $\delta = 151.1$ ppm can be assigned to C12. C1 appears at $\delta = 147.2$ ppm while the signals at $\delta = 142.6$, 139.0 and 137.2 ppm belong to C5, C11 and C6. The signals at $\delta = 133.6$ and 130.5 ppm derive from C3 and C8. The signals at $\delta = 128.7$ and 128.1 ppm were assigned to C9 and C2. Further signals at $\delta = 124.6$, 114.6 , and 114.3 ppm belong to C7, C4 and C10. The methyl carbon (C13) signal is found at $\delta = 21.9$ ppm.

2.3.2. Mass spectrometry

The compounds **1–8**, in addition to their ^1H NMR and ^{13}C NMR spectra, were characterized by mass spectrometry. The mass spectrum of compound **3** 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 Fig. 5).

In addition to their NMR spectra, the complexes **9–32** were characterized by mass spectrometry. The mass spectrum of complex **19** (Fig. 6) shows an incomplete fragmentation pattern. The reason is the fact that the n-donor bonds in the complex do not survive the ionization process. A molecular ion cannot be observed. The peak at $m/z = 209$ can be assigned to the free ligand.



Scheme 1. Synthesis of the potential ligand **1–8**.

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