



Dichlorovanadium(IV) diamine-bis(phenolate) complexes for ethylene (co)polymerization and 1-olefin isospecific polymerization

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ABSTRACT

Two vanadium complexes bearing amine-bis(phenolate) ligands with the amino side-arm donor, $[V\{Me_2NCH_2CH_2N(CH_2-2-O-3,5-tBu_2-C_6H_2)_2\}Cl_2]$ (**1**) and $[V\{Me_2NCH_2CH_2N(CH_2-2-O-3,5-tBu_2-C_6H_2)(CH_2-2-O-C_6H_4)\}Cl_2]$ (**2**), were synthesised and characterized by FTIR and 1H NMR spectroscopy. Upon activation with $Al(iBu)_3/Ph_3CB(C_6F_5)_4$, these complexes became active catalysts for 1-octene polymerization giving highly stereoregular polymers (*mmmm* ~ 90%) having regioirregularly arranged units. The catalytic activity of the catalysts in ethylene homo- and copolymerization, and their ability to incorporate a comonomer were highly dependent on both the activator type and the complex structure. **1**/EtAlCl₂ exhibited very high activity (up to $3.3 \cdot 10^7$ g/(mol_V h)) in ethylene polymerization and produced copolymers with the highest comonomer content (up to 9.1 mol%), moderate molecular weight and narrow chemical composition distribution (CCD). Both vanadium complexes, when combined with trityl borate activator, led to ethylene copolymers with lower 1-octene content and broad CCD. In addition, the copolymers were characterized by very high molecular weight ($\sim 1 \cdot 10^6$ g/mol) and narrow dispersity ($M_w/M_n = 1.4-2.0$).

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1. Introduction

The use of complexes which contain multidentate ligands as precatalysts is one of the most important trends which are observed nowadays in the catalytic polymerization of olefins. Their structures, that can be easily modified, make essential determinants for the properties of a catalytic system, inclusive of its activity, stereospecificity and ability to incorporate comonomer molecules, and for the properties of the obtained products as well. The type of the metal center makes a factor which is not less essential for the catalytic performance of a complex. Apart from the group 4 metal complexes, inclusive of those which offer a number of interesting properties – complexes with phenoxy-imine, salan and amine-bis(phenolate) ligands with an additional donor in the side arm [1–3], which are studied most frequently, the vanadium complexes attract more and more interest in the past years. The classical vanadium catalysts which are based on simple vanadium compounds (e.g. VCl₄, VOCl₃) play a meaningful role in the catalytic polymerization of olefins. They are capable of producing polyethylene with a very high molecular weight and narrow molecular weight distribution, syndiotactic polypropylene, amorphous

ethylene-propylene copolymer with homogeneous composition, ethylene/propylene/dien (EPDM) copolymers, or ethylene/cyclic olefin (COC) copolymers [4]. The main disadvantage of this type of vanadium catalysts is their low activity due to quick deactivation through reduction which yields a catalytically inactive vanadium(II) species [4,5]. The introduction of a mono- or multidentate ligand to a vanadium compound help to stabilize the metal oxidation state but reduction of vanadium is still observed which can be connected with migration of that ligand to the organoaluminium activator [5]. This problem can be overcome by using a mild oxidizing agent such as Cl₃CCO₂Et (ETA) or chlorinated hydrocarbons which reactivate the inactive vanadium (II) centers to the active vanadium(III) species [4].

In recent years a number of vanadium(III) and -(IV) complexes of O,N-chelating ligands have been developed. These complexes bearing one or two β-enaminoketonato and salicylaldehyde ligands exhibit high catalytic activities in the presence of Et₂AlCl and ETA in ethylene homopolymerization and in its copolymerization with 1-olefins and norbornene [6–10]. The results also showed that the presence of two O,N-ligands in the complex stabilized the active species better than one ligand and maintained the single-site catalytic behavior of the vanadium catalyst, regardless of the reaction conditions [9]. Nevertheless, the amount of research works involved in investigation of catalytic properties of vanadium

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complexes supported by tetradentate ligands is very limited. The vanadium(II-V) complexes bearing the ancillary amino-bis(phenolate) ligand with the additional amine donor were tested in combination with EtAlCl₂, in homo- and copolymerization of ethylene [11]. They produced poly(ethylene-co-1-hexene) and poly(ethylene-co-norbornene) with the moderate comonomer contents and at moderate yields. Vanadium(IV) complexes of this type tetradentate ligand and additional azido and isopropoxo groups ([V{Me₂NCH₂CH₂N(CH₂-2-O-3,5-Me₂-C₆H₂)₂}X₂], where X = OiPr, N₃) were obtained in direct reaction of a metal precursor, V(NMe₂)₂(N₃)₂ or V(OiPr)₄, with a ligand, and the chlorovanadium complex was obtained by replacement of isopropoxo groups by chloride atoms coming from Me₃SiCl [12]. Other studies involved oxovanadium(V) complexes which contained amine pyridine bis(phenolate) [13] and amine trihydroxy ligands [14]. In the presence of Et₂AlCl as an activator and ETA as a reactivating agent, these complexes displayed good thermal stability and activity in ethylene polymerization, and they efficiently promoted ethylene/NBE copolymerization. The ethylene polymerization study was also conducted with the oxovanadium(V) complex which contained the *trans*-1,2-dithiacyclohexane-bridged bis(phenolato) ligand [15]. However, the activity of the complex with the O,S,S,O-chelating ligand was significantly lower than those of the complexes bearing tetradentate ligands with the O and N donor atoms. This might be due to both the ligand structure itself and the type of activator used which was MAO.

Taking into account that the catalytic properties of the vanadium complexes, especially of vanadium(IV), with tetradentate ligands were not actually recognized, two dichlorovanadium(IV) complexes containing ancillary diamine bis(phenolate) ligand were synthesized and their catalytic properties in ethylene homo- and copolymerization were studied. In addition, since there are only a few vanadium postmetallocene systems known which lead to higher 1-olefin polymers, their activity and stereospecificity in 1-octene polymerization were tested and the results were compared to those obtained for the corresponding group 4 transition metal complexes.

2. Experimental section

2.1. Materials

All manipulations of air- and/or moisture sensitive compounds were done under an inert atmosphere of argon or nitrogen, using the vacuum/argon line, a glove box and the standard Schlenk technique. Tetrahydrofuran, hexane and toluene were refluxed over and distilled from sodium/benzophenone and sodium, respectively. 1-Octene (98%, Aldrich), and C₆D₆ were dried under argon over 4A molecular sieves. Ethylene (3.0 grade, Linde Gas) and nitrogen (Messer) were used after having been passed through a column with sodium metal supported on Al₂O₃. Argon (5.0 grade, Air Liquide), methylaluminoxane (MAO) (10.0 wt.%, Aldrich), EtAlCl₂ (1.8 M, Aldrich) and Al(*i*Bu)₃ (1.0 M, Aldrich), Ph₃CB(C₆F₅)₄ (min. 97%, Strem Chemicals), B(C₆F₅)₃ (min. 97%, Strem Chemicals), NaH (60% in mineral oil, Aldrich), VCl₄ (99%, Aldrich) were used as received. Ligand Lig¹H₂ was prepared according to a known synthesis procedure [16]. ¹H NMR (400 MHz, C₆D₆, δ): 9.87 (s, 2H, HO–Ar), 7.51 (d, 2H, Ar–H), 6.99 (d, 2H, Ar–H), 3.40 (s, 4H, NCH₂Ar), 2.20 (t, 2H, CH₂), 1.92 (t, 2H, CH₂), 1.92 (s, 6H, N(CH₃)₂), 1.68 (s, 18H, C(CH₃)₃), 1.35 (s, 18H, C(CH₃)₃). Ligand Lig²H₂ was prepared according to literature procedure [17] and characterized by X-ray crystallography [18]. ¹H NMR (400 MHz, C₆D₆, δ): 9.93 (br, 2H, HO–Ar), 7.48 (d, 1H, Ar–H), 6.95 (d, 1H, Ar–H), 7.19–6.76 (Ar–H), 3.40 (s, 2H, NCH₂Ar), 3.23 (s, 2H,

NCH₂Ar), 2.14 (t, 2H, CH₂), 1.92 (t, 2H, CH₂), 1.92 (s, 6H, N(CH₃)₂), 1.60 (s, 9H, C(CH₃)₃), 1.36 (s, 9H, C(CH₃)₃).

2.2. Synthesis of vanadium complexes

Complexes **1** and **2** were synthesized according to literature procedure reported for titanium and zirconium complexes bearing the same diamino-bis(phenolate) ligands [19,20].

2.2.1. Complex 1

A solution of Lig¹H₂ (1.980 g, 3.77 mmol) in tetrahydrofuran was added dropwise to a suspension of NaH (0.302 g, 7.54 mmol) in THF at room temperature. The stirring was continued for 2 h, and to the obtained clear colorless solution was added dropwise solution of VCl₄ (3.77 mmol) in THF. The obtained deep dark green solution was stirred overnight, filtered and then the solvent was removed *in vacuo* to give a dark green solid. Yield: 2.09 g (86%). ¹H NMR (400 MHz, C₆D₆, ppm): δ 7.49 (2H, Ar–H); 6.90 (2H, Ar–H); 4.10 (d, 2H, J = 14.4 Hz, NCH₂Ar); 3.00 (d, 2H, J = 12.4 Hz, NCH₂Ar); 2.39 (s, 6H, N(CH₃)₂); 1.87 (m, 2H, CH₂); 1.82 (s, 18H, C(CH₃)₃); 1.56 (m, 2H, CH₂); 1.35 (s, 18H, C(CH₃)₃).

2.2.2. Complex 2

Complex **2** was prepared according to the same procedure as that of complex **1** except that Lig²H₂ (1.17 g, 2.84 mmol) was used instead of Lig¹H₂, and the other reagents were used in the appropriate amounts (NaH: 0.302 g, 7.54 mmol, VCl₄: 3.77 mmol). A dark green solid was obtained. Yield: 1.42 g (94.7%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.36 (1H, Ar–H); 6.99 (1H, Ar–H); 7.33–7.10, 7.02–6.88 (m, Ar–H); 4.48 (1H, NCH₂Ar); 4.45 (1H, NCH₂Ar); 3.43 (1H, NCH₂Ar); 3.36 (1H, NCH₂Ar); 2.97, 2.73 (m, 2H, CH₂); 2.42, 2.02 (m, 2H, CH₂); 2.85 (s, 3H, N(CH₃)₂); 2.52 (s, 3H, N(CH₃)₂); 1.65 (s, 9H, C(CH₃)₃); 1.31 (s, 9H, C(CH₃)₃).

2.3. General procedure for ethylene polymerization

Ethylene polymerization was carried out in a 500 mL Büchi glass reactor ecoclave 150 equipped with the magnetic stirrer and heating-cooling jacket. Hexane (150 mL) and an aluminium compound were introduced into the nitrogen-purged reactor and stirred. After the required temperature level had been reached, the solution of vanadium complex and Ph₃CB(C₆F₅)₄ (if it was used as activator) were added to the reactor. Polymerization was started by the addition of the ethylene and its pressure equal 5 bar as well as the reaction temperature were kept constant throughout the run. After the prescribed time, polymerization was quenched by adding a dilute solution of hydrochloric acid in methanol. The polymer was filtered, washed a few times with methanol and dried in vacuum oven.

2.4. General procedure for ethylene/1-octene copolymerization

The ethylene/1-octene copolymerization followed the same procedure as ethylene homopolymerization and the only difference was that 1-olefin was charged to the reactor after a solvent had been added there.

2.5. General procedure for 1-octene polymerization

Polymerization was carried out in a 100 mL flask equipped with a magnetic stirring bar to which monomer and organoaluminium activator were charged at room temperature. After the intended temperature level had been reached, the vanadium complex was added to the reaction mixture. If Ph₃CB(C₆F₅)₄ was used as an activator, it was added as the last ingredient. The mixture was stirred for the specified time and then the reaction was terminated by

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