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## Coordination compounds of chromium (+3) and vanadium (+3) and (+5) with 2,6-bis(diphenylhydroxymethyl)pyridyl ligand: Synthesis and study of catalytic activity in the polymerization of ethylene

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## ABSTRACT

Coordination compounds of chromium (III) and vanadium (III) and (V) with 2,6-bis(diphenylhydroxymethyl)pyridine have been synthesized. Composition and properties of the obtained complexes have been evaluated by NMR, IR spectroscopy, X-ray diffraction, and elemental analysis. Depending on the nature of the metal and the synthesis conditions, there are various types of coordination state of the tridentate pyridine ligand in the obtained complexes: it can bind either as a dianionic, bisalkoxide, terdentate (compounds **5**, **7**, **8**, **9**), monoanionic, alkoxide/alkohol, terdentate (compounds **4**, **6**) or as a neutral, bisalkohol, terdentate ligand (compound **3**). Coordination compounds of chromium were found to be incapable of catalytic polymerization of ethylene. Catalytic activity of vanadium (III) and (V) complexes in this reaction varied between 85 and 578 kg PE/mol V h after activation with diethylaluminum chloride, depending on the V/Al ratio.

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## 1. Introduction

The vast majority of post-metallocene catalysts of olefin polymerization are coordination compounds of titanium, zirconium [1,2], iron, cobalt, or nickel [3,4]. Very little is known of the catalytic activity of vanadium and chromium derivatives for this reaction, but overall properties of such complexes seem to be very promising [5–17]. The interest in studying these complexes stems from their overall similarities to the coordination compounds of group IV metals. Indeed, the compounds of vanadium (III) are isoelectronic analogs of Ti, Zr, and Hf (IV) compounds which show the highest activity in polymerization. Although activity of vanadium catalysts is generally found to be lower than that of other systems, their major advantage is in their ability to form high- and ultra-high-molecular-weight polymers, as well as copolymers of ethylene with  $\alpha$ -olefins containing high amounts of the comonomer.

Application of currently available organoaluminum compounds as activators of vanadium-containing catalysts is yet another area worth investigating.

Chromium complexes demonstrate weak catalytic activity in common polymerization reactions; however they have a notable

activity in the di-, tri- and oligomerization of olefins [16]. Such their property makes it possible to use chromium complexes as a component of the tandem catalytic systems used in synthesis of elastomers.

Most works evaluating polyolefin synthesis used phenoxyimine [12,17] and 2,6-bis(imino)pyridyl [3] ligands, while systems with oxygen chelating ligands have been studied to much lesser extent [18–22].

One of the problems encountered when studying the vanadium-containing catalysts is that the metal easily converted to lower oxidation states; as a consequence, the catalytic activity may decline or disappear [8,23–27]. Nevertheless, it may be reasonably expected that the type of ligand environment, the number, size, and electronic properties of both a ligand and a central atom will affect not only the catalytic characteristics of the complexes but also their ability to withstand metal reduction.

In this study we use a ligand **1** combining pyridine core and two diphenylcarbinol fragments. Ligand **1** has very limited use in coordination chemistry. It has been used to prepare complexes of hypervalent pentacoordinated dimethyltin (IV) [28], germynes and stannylenes [29], different titanium complexes [30]. Only in our previous work [31] complexes of titanium and zirconium-based on ligand **1** have been proposed as catalysts for olefin polymerization.

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In this study we report synthesis of a new group of chromium (III) as well as vanadium (III) and (V) coordination compounds based on ligand **1**; and the investigation of their catalytic properties in polymerization of ethylene, using methylaluminoxane (MAO) and diethylaluminum chloride (DEAC) as catalyst activators.

## 2. Experimental

### 2.1. General methods

All manipulations were performed under an argon atmosphere by using standard Schlenk techniques. Toluene and THF were distilled from Na/benzophenone prior to use. Dichloromethane was distilled over calcium hydride. The water contents of these solvents were periodically controlled by Karl-Fischer coulometry by using a Methrom 756 KF apparatus. Argon and ethylene of special-purity grade were dried by purging through a column filled with 5 Å molecular sieves.

Ligand 2,6-bis(diphenylhydroxymethyl)pyridine was synthesized as described in [31]. Its physicochemical characteristics and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra match the published data. Phenylimidovanadium (V) chloride was prepared as described in [32].  $\text{VOCl}_3$ ,  $\text{VCl}_3 \cdot 3\text{THF}$ , and  $\text{CrCl}_3 \cdot 3\text{THF}$  as well as solutions of diethylaluminum chloride and butyllithium (Aldrich) were used. Polymethylaluminoxane (Witco) was used as a 10% solution in toluene.

NMR spectra were recorded on Bruker WP-600 and Bruker AMX-400 instruments. Deuterated solvents ( $\text{CD}_2\text{Cl}_2$ ,  $\text{CDCl}_3$ ) were degassed by freeze-thaw-vacuum cycles and stored over 3 Å molecular sieves. Chemical shifts are reported in ppm vs.  $\text{SiMe}_4$  and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz.

IR spectra were recorded on a Magna-IR 750 spectrophotometer. Elemental analysis was performed on Carlo Erba-1106 and Carlo Erba-1108 instruments.

The gel chromatograms of polymer samples were analyzed on a Waters GPCV-2000 chromatograph with the use of a PLgel 5  $\mu\text{m}$  MIXED-C column in 1,2,4-trichlorobenzene at 135 °C. Molecular masses were estimated using the universal calibration curve plotted relative to polystyrene standards.

The thermogravimetric analysis of samples was performed on a NETZSCHSTA-Jupiter449 C instrument. Measurements were carried out in a flow of argon (100 ml/min) in the temperature range 40–300 °C. The heating rate was 5 °C/min.

The experiments on the polymerization of ethylene were performed in a 100-ml reactor (Parr Instrument Co.).

X-ray diffraction data for the single crystals of **3**, **4**, **6**, and **8** were collected using a “Bruker SMART APEX2” CCD diffractometer. The obtained images were integrated [33]. The precise unit cell dimensions and errors were determined. The absorption correction was applied semiempirically using the  $\text{SADABS}$  program [34]. The details of X-ray data collection in the subsequent refinement are listed in Table 2. Initially spherical atom refinements were undertaken with  $\text{SHELXL PLUS 5.0}$  [35] using the full-matrix least-squares method. All non-hydrogen atoms were allowed to have an anisotropic thermal motion. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center with numbers CCDC 878807–878810. X-ray diffraction analysis of polymers was performed on a DRON-2 instrument (Cu  $K\alpha$  radiation, Ni filter, a scan rate of 1 deg ( $2\theta$ )/min). The degree of crystallinity  $\chi$  of samples was estimated from the ratio of the integral intensity of crystalline constituent and the total intensity.

### 2.2. Polymerization of ethylene

All operations on equipment preparation, the order and techniques of loading of gaseous ethylene and complexes, and the measurement of kinetic parameters of polymerization are similar to those described in [31].

The polymerization of ethylene was performed at a total pressure of ethylene and toluene vapors of 1.7 atm. Polymerization was carried out in a 100-ml reactor (PARR) equipped with a magnetic stirrer and inlets for loading components of catalytic systems and ethylene. Toluene (50 ml) and the necessary amount of a cocatalyst (DEAC or MAO) in the form of toluene solutions were successively loaded in the reactor together with the cocatalyst. The required amount of the precatalyst in the form of toluene solution was placed into a special syringe connected with the reactor. The reactor was heated to a specified temperature, and the reaction mixture was saturated with ethylene. Polymerization was started by precatalyst loading to the reaction mixture. The pressure of ethylene was maintained constant during polymerization. Polymerization was stopped through the addition of 10% HCl solution in ethanol to the reactor. The polymer was filtered off, washed several times with water-ethanol mixture, and dried under vacuum at 50–60 °C until a constant weight was achieved.

### 2.3. Synthesis

#### 2.3.1. [2,6-(CPh<sub>2</sub>OH)<sub>2</sub>Py]CrCl<sub>3</sub> (**3**)

A two-necked flask equipped with a magnetic stirrer was successively charged in a flow of argon with ligand **1** (221.5 mg, 0.5 mmol), toluene (10 ml), and  $\text{CrCl}_3 \cdot 3\text{THF}$  (187 mg, 0.5 mmol). The reaction mixture was stirred at 40 °C for 100 h. The precipitated green crystals were filtered off and washed with methylene chloride and toluene.

Yield 0.09 g (32%); *Anal. Calc.* for  $\text{C}_{31}\text{H}_{25}\text{Cl}_3\text{NO}_2\text{Cr}$ : C, 61.80; H, 4.10; Cl, 17.69; N, 2.33; Cr, 8.64. Found: C, 61.75; H, 3.95; Cl, 17.73; N, 2.32; Cr, 8.66%. IR,  $\nu$ ,  $\text{cm}^{-1}$ : ( $\text{OH}_{\text{bound}}$ ) 3480, (Cr–O) 657 and (Cr–N) 583.

#### 2.3.2. [2,6-(CPh<sub>2</sub>O)<sub>2</sub>Py]Cr[2-(CPh<sub>2</sub>O)-6-(CPh<sub>2</sub>OH)-Py] (**4**)

A two-necked flask equipped with a magnetic stirrer was successively charged in a flow of argon with ligand **1** (221.5 mg, 0.5 mmol) dissolved in toluene (5 ml) and  $\text{CrCl}_3 \cdot 3\text{THF}$  (93.5 mg, 0.25 mmol) dissolved in tetrahydrofuran (5 ml). The reaction mixture was stirred at 40 °C for 100 h. Precipitated blue crystals were filtered off and washed with tetrahydrofuran and toluene.

Yield, 0.21 g (45%); *Anal. Calc.* for  $\text{C}_{62}\text{H}_{47}\text{N}_2\text{O}_4\text{Cr}$ : C, 79.55; H, 5.06; Cr, 5.55; N, 2.99. Found: C, 79.27; H, 5.42; Cr, 5.29; N, 2.44%. IR,  $\nu$ ,  $\text{cm}^{-1}$ : ( $\text{OH}_{\text{bound}}$ ) 3440, (O–Cr–O) 750, (Cr–O) 620, and (Cr–N) 560.

#### 2.3.3. [2,6-(CPh<sub>2</sub>O)<sub>2</sub>Py]CrCl (**5**)

A two-necked flask equipped with a magnetic stirrer was charged in a flow of argon with compound **1** (221.5 mg, 0.5 mmol) and toluene (10 ml); then, at –78 °C, 2.5 M solution of butyllithium in *n*-hexane (0.44 ml, 1.1 mmol) was added dropwise. The reaction solution was slowly heated to room temperature, stirred for 4 h and cooled to –78 °C.  $\text{CrCl}_3 \cdot 3\text{THF}$  (187 mg, 0.5 mmol) dissolved in tetrahydrofuran (3 ml) was added, and the resulting mixture was stirred for 96 h at room temperature. The brown precipitate was filtered off, the organic solvents were evaporated, and the product formed was recrystallized from methylene chloride.

Yield, 0.11 g (80%);  $T_{\text{melt}} = 307$  °C; *Anal. Calc.* for  $\text{C}_{31}\text{H}_{23}\text{NO}_2\text{CrCl}$ : C, 70.39; H, 4.38; Cl, 6.70; Cr, 9.83; N, 2.65. Found: C, 69.50; H, 5.03; Cl, 6.15; Cr, 9.40; N, 2.50%. IR,  $\nu$ ,  $\text{cm}^{-1}$ : (Cr–O) 689 and (Cr–N) 547.

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