



## The role of the ionic radius in the ethylene polymerization catalyzed by new group 3 and lanthanide scorpionate complexes

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### ABSTRACT

A series of new monomeric group 3 and lanthanide [N,N,N]-heteroscorpionate triflate-complexes [Ln(OTf)<sub>2</sub>(cybpamd)(THF)] {Ln = Sc (**2**), Y (**3**), La (**4**), Nd (**5**), Sm (**6**), Dy (**7**), Yb (**8**); OTf = SO<sub>3</sub>CF<sub>3</sub>; cybpamd = N,N'-dicyclohexyl-2,2-bis-(3,5-dimethyl-pyrazol-1-yl)-acetamidinate} has been synthesized and characterized. The behavior of **2–8** as catalysts in olefin polymerization was investigated after proper activation with methylaluminoxane and the comparative results are reported. The activity of the catalytic systems towards ethylene polymerization is affected by the nature of the metal center and linearly grows with the ionic radius, with the exception of the scandium derivative. From DFT calculations it was possible to correlate the activity data with computed properties of the metal–alkyl bonds of the catalytically active species. The very narrow polydispersivities showed that all the considered systems act as single-site catalysts and high-weight linear polyethylene polymers were always obtained.

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### 1. Introduction

In addition to the first examples of scandium, yttrium, lanthanum and f-block metals homoleptic hydrotris(pyrazolyl)borate complexes, MTP<sub>3</sub> [1], homo- and heteroscorpionate ligands have shown to be very interesting species for the synthesis of a wide range of stable group 3 elements and lanthanide derivatives [2]. As a result of the variable size of the Ln(III) ions, the predominant ionic bonding and the well-known oxophilicity of these metals, the usual coordinative unsaturation of their complexes, the presence of hard donor atoms and the ligand charge are critical factors in controlling the coordination number, the geometry and the architecture of their complexes and the isolation of well-defined molecular species. Scorpionates represent an attractive and versatile choice, due to the fine-tuning of the electronic and steric properties of these ligands and consequently the control of the metal coordination sphere.

Polyolefins can be obtained in the presence of several neutral and cationic alkyl complexes of the rare-earth metals, stabilized by both cyclopentadienyl- and non-cyclopentadienyl ancillary lig-

ands [3] and the expected electrophilicity of group 3 metals makes them attractive as homogeneous catalysts for Ziegler-Natta polymerization. From a catalytic point of view the preparation of new scorpionate derivatives of early-d and f-block elements is a currently active field of research, as this type of complexes showed to be, among all, potentially interesting non-cyclopentadienyl Ziegler-Natta homogeneous catalysts in olefin polymerization, as observed for Sc, Y and lanthanides derivatives with substituted tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands [4].

Our recent research interest in the fields of organometallic chemistry and olefin polymerization has been mainly devoted to group 3 and lanthanide-based catalysts with polydentate ligands containing nitrogen-donor groups [5]. We have recently extended our studies to heteroscorpionate bis-pyrazol-1-yl-acetamidinate anionic ligands, whose lithium, magnesium and zinc derivatives have recently shown to be active initiators for the ring-opening polymerization of cyclic esters [6].

In the last few years group 3 metal triflates have been received great attention for their ability to promote a wide variety of organic reactions [7]. In this paper we report the synthesis of a series of new neutral group 3 and lanthanide triflate-complexes with the [N,N,N]-scorpionate ligand N,N'-dicyclohexyl-2,2-bis-(3,5-dimethyl-pyrazol-1-yl)-acetamidinate (cybpamd), together with the comparison of their catalytic behavior towards ethylene polymerization.

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## 2. Experimental

### 2.1. Materials and methods

All inorganic manipulations were carried out under oxygen- and moisture-free atmosphere in a Braun MB 200 glove-box with a purifying unity G-II and equipped with apparatus for high and low temperature reactions. All the solvents were thoroughly deoxygenated and dehydrated under argon by refluxing over suitable drying agents, while NMR deuterated solvents (Euriso-Top products) were kept in the dark over molecular sieves. The anhydrous triflate salts  $\text{Ln}(\text{OTf})_3$  {Ln = Sc, Y, La, Nd, Sm, Dy, Yb;  $\text{OTf} = \text{SO}_3\text{CF}_3$ } and  $\text{YCl}_3$  (Strem, Aldrich) and the organic compounds 3,5-dimethylpyrazole and *N,N'*-dicyclohexylcarbodiimide (Aldrich) were used as received. Butyllithium (1.6 M solution in hexanes) was purchased from Aldrich. Bis(3,5-dimethyl-pyrazol-1-yl)methane was synthesized from 3,5-dimethylpyrazole and dichloromethane on the basis of a reported procedure [8] and purified by crystallization from hot cyclohexane solutions.

All the polymerization operations were carried out under nitrogen atmosphere by using conventional Schlenk-line techniques. Methylaluminoxane (10% in toluene, Witco) was used as a solid after distillation of solvent. Ethylene (>98%), was purchased from Aldrich.

### 2.2. Characterizations

Microanalyses (C, H, N, Cl) of ligands and complexes were made at the Istituto di Chimica Inorganica e delle Superfici, CNR, Padova.  $^1\text{H}$  NMR, homodecoupled  $^1\text{H}$  NMR,  $^1\text{H}$  COSY,  $^1\text{H}$  NOESY,  $^{13}\text{C}$  { $^1\text{H}$ } NMR,  $^{13}\text{C}$  APT, HSQC and HMBC spectra were recorded at 298 K on a Bruker Avance 300 spectrometer operating at 300 MHz ( $^1\text{H}$ ) and 75 MHz ( $^{13}\text{C}$ ) and referred to internal tetramethylsilane. The SwaN-MR and MestRe-C software packages were used for NMR spectroscopic data treatment [9]. Mass spectra (E.I., 70 eV) of lanthanum derivative and of the paramagnetic compounds were recorded on a Finnigan Trace GC-MS equipped with a probe controller for the sample direct inlet. The assignments were done by comparison between theoretical and experimental isotopic clusters and the most intense signals of each characterized cluster are reported.

Semi-empirical computational geometry optimizations were carried out with the MOPAC2007 software package [10]. In all the calculations the PM6 Hamiltonian [11] was used and the paramagnetic lanthanides ions were simulated using the sparkle model [12]. Calculations were carried out without symmetry constraints. Scandium, yttrium and lanthanum derivatives were also optimized with the restricted EDF1 DFT functional [13] in combination with the ECP-based LACVP\* basis set [14]. Charges derived from Mulliken population analysis [15]. The software used was Spartan '08 [16]. All the calculations were carried out on a Intel Core i7-based x86-64 computer.

The samples of polyethylene for  $^{13}\text{C}$  NMR analysis were prepared by dissolving polymer sample (40 mg) into tetrachloro-dideutero-ethane (0.5 mL). The spectra were recorded at 100 °C using hexamethyldisiloxane (HMDS) as internal chemical shift reference. The Gel Permeation Chromatography (GPC) analysis of the samples were carried out at 135 °C by Waters instrument GPCV 2000 equipped with refractive index and viscosimeter detectors, using four PSS columns set consisting of, 105, 104, 103, 102 Å (pore size) – 10 μm (particle size). *o*-Dichlorobenzene was the carrier solvent used with a flow rate of 1.0 mL/min. The calibration curve was established with polystyrene standards. Differential Scanning Calorimetry analysis have been carried out on a DSC 2920 apparatus manufactured by TA Instruments, calibrated against an indium standard ( $T_m = 156.6$  °C), with heating scans from –10 to 200 °C,

at a 10 °C/min heating rate, under a flowing nitrogen atmosphere. Specimens were sealed in aluminum pans.

### 2.3. Synthesis of *N,N'*-dicyclohexyl-2,2-bis-(3,5-dimethyl-pyrazol-1-yl)-acetamide (cybpamd-H) ( $\text{C}_{24}\text{H}_{38}\text{N}_6$ , $M_W = 410.60$ )

A solution of bis(3,5-dimethyl-pyrazol-1-yl)methane (2.000 g, 9.8 mmol) in anhydrous THF (50 mL) was cooled to –70 °C, then a 1.6 M solution in hexanes of butyllithium (6.1 mL) was added dropwise during about half an hour by maintaining the temperature as constant as possible. The resulting solution was allowed to slowly reach –10 °C and then maintained at this temperature for 20 min. The reaction mixture was cooled again at –70 °C and a solution of *N,N'*-dicyclohexylcarbodiimide (2.02 g, 9.8 mmol) in 20 mL of THF was slowly added. Once the addition was ended, the system was allowed to reach room temperature and left 4 h under stirring. Cold water (30 mL) was added to quench the reaction and THF was quite completely removed by evaporation under reduced pressure. The crude product was extracted with diethylether (3 × 50 mL) and the resulting organic fraction was dried over  $\text{MgSO}_4$ . The solvent was then removed under reduced pressure and the residual oil was purified by chromatography on silica gel, using a 1:1 mixture of hexane–ethyl acetate as eluent. After *in vacuo* removal of the solvents the residue was dissolved in pentane (20 mL) and the resulting solution was passed on filter paper to remove eventual traces of unreacted bis(3,5-dimethyl-pyrazol-1-yl)methane. Pentane was finally removed by evaporation under reduced pressure and the product was collected as white microcrystals. Yield = 3.550 g, 88%.

Elemental analysis: found (%): C 69.9, H 9.30, N 20.4. Calcd. for  $\text{C}_{24}\text{H}_{38}\text{N}_6$  (%): C 70.20, H 9.33, N 20.47.

### 2.4. Synthesis of $[\text{YCl}_3(\text{cybpamd-H})]$ (**1**) ( $\text{C}_{24}\text{H}_{38}\text{Cl}_3\text{N}_6\text{Y}$ , $M_W = 685.86$ )

A solution of cybpamd-H (0.410 g, 1.0 mmol) in THF (15 mL) was added at room temperature to a suspension of anhydrous  $\text{YCl}_3$  (1.0 mmol, 0.195 g) in 15 mL of THF. The resulting reaction mixture was allowed to react overnight at room temperature, then the solvent was removed by *in vacuo* evaporation and dichloromethane (30 mL) was added. The  $\text{CH}_2\text{Cl}_2$  solution was centrifuged and subsequently concentrated to ca. 10 mL under reduced pressure. Hexane was slowly added until the product separated as solid, which was collected by filtration after about 1 h under stirring, washed with *n*-hexane and dried *in vacuo*. Yield = 0.522 g, 86%.

Elemental analysis: found (%): C 47.4, H 6.30, N 13.8, Cl 17.5. Calcd. for  $\text{C}_{24}\text{H}_{38}\text{N}_6$  (%): C 47.58, H 6.32, N 13.87, Cl 17.55.

### 2.5. Synthesis of $[\text{Ln}(\text{OTf})_2(\text{cybpamd})(\text{THF})]$ {Ln = Sc, $\text{C}_{30}\text{H}_{45}\text{F}_6\text{N}_6\text{O}_7\text{S}_2\text{Sc}$ , $M_W = 824.79$ (**2**); Ln = Y, $\text{C}_{30}\text{H}_{45}\text{F}_6\text{N}_6\text{O}_7\text{S}_2\text{Y}$ , $M_W = 868.74$ (**3**); Ln = La, $\text{C}_{30}\text{H}_{45}\text{F}_6\text{LaN}_6\text{O}_7\text{S}_2$ , $M_W = 918.74$ (**4**); Ln = Nd, $\text{C}_{30}\text{H}_{45}\text{F}_6\text{N}_6\text{NdO}_7\text{S}_2$ , $M_W = 924.08$ (**5**); Ln = Sm, $\text{C}_{30}\text{H}_{45}\text{F}_6\text{N}_6\text{O}_7\text{S}_2\text{Sm}$ , $M_W = 930.20$ (**6**); Ln = Dy, $\text{C}_{30}\text{H}_{45}\text{F}_6\text{N}_6\text{O}_7\text{S}_2\text{Dy}$ , $M_W = 942.34$ (**7**); Ln = Yb, $\text{C}_{30}\text{H}_{45}\text{F}_6\text{N}_6\text{O}_7\text{S}_2\text{Yb}$ , $M_W = 952.88$ (**8**); $\text{OTf} = \text{SO}_3\text{CF}_3$ }

The same synthetic approach was applied for the preparation of all the **2–8** complexes. In a typical synthesis a solution of cybpamd-H (0.410 g, 1.0 mmol) in THF (15 mL) was added at room temperature to a THF solution (15 mL) containing 1.0 mmol of the proper anhydrous triflate salt  $\text{Ln}(\text{OTf})_3$  {Ln = Sc, Y, La, Nd, Sm, Dy, Yb}. After 20 min 12.5 mL of a 0.08 M solution of butyllithium in hexane and THF, prepared by diluting with THF the commercial solution, was added dropwise in about 15 min. The resulting mixture was allowed to react at room temperature for 12 h, then the

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