



Short communication

Chromium complexes bearing pyrazolyl-imine-phenoxy/pyrrolide ligands: Synthesis, characterization, and use in ethylene oligomerization



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ABSTRACT

Chromium(III) complexes $[\text{NNZ}]\text{CrCl}_2(\text{THF})$ (**2a-d**) (NNZ = pyrazolyl-imine-phenoxy/pyrrolide) have been synthesized and characterized by elemental analysis and X-ray diffraction analysis. Upon activation with methylaluminoxane (MAO), chromium precatalysts **2a-b** showed moderate activity in ethylene oligomerization (TOF = 10.9 and 14.5×10^3 (mol ethylene)(mol Cr) $^{-1} \cdot \text{h}^{-1}$ at 80 °C, respectively), producing mostly oligomers (78.4–85.7 wt% of total products). On the other hand, under identical oligomerization conditions, **2c-d**/MAO behaved as a polymerization catalysts generating predominantly polyethylene (76.6 and 86.1 wt% of the total amount of products, respectively). Under optimized conditions, precatalyst **2a** led to TOF = 71,500 mol(C₂H₄)(mol(Cr)) $^{-1} \text{h}^{-1}$ and 95.6 wt% of oligomers.

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1. Introduction

The oligomerization of ethylene is one of the most important industrial processes to obtain linear α -olefins (LAOs), which are important commodity chemical for preparing detergents, lubricants, plasticizers, and oil field chemicals, or used as co-monomers for the production of linear low-density polyethylene (LLDPE) [1]. Among all the transition-metal-based oligomerization catalysts, chromium catalysts have received special attention since they provide both selective and nonselective ethylene oligomerization [2]. In this context, a number of selective homogeneous catalysts have been used in commercially viable tri- and tetramerization catalytic systems (Phillips [3], Mitsubishi [4], BP Chemicals [5], Sasol [6]). In addition, a considerable amount of research effort has been dedicated to nonselective ethylene oligomerization with the aim of improving the understanding of this industrially relevant catalytic process [7–8].

In the course of the past decade, several well-defined chromium catalysts bearing N⁺N⁺N [9], P⁺N⁺P [10], S⁺N⁺S [11], P⁺N [12], and N⁺N⁺P [13], ligands have been reported and their ethylene oligomerization behavior has been investigated. While, the vast majority of these ligands are used in the neutral form, just a few examples of anionic ligands have been utilized in the synthesis of active chromium species (Chart 1). [8] [14–16] For instance, Carpentier et al. described

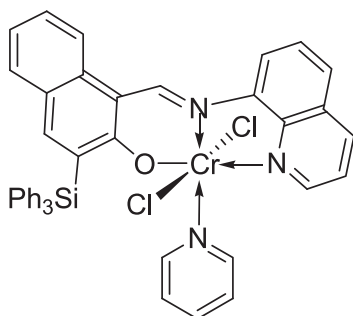
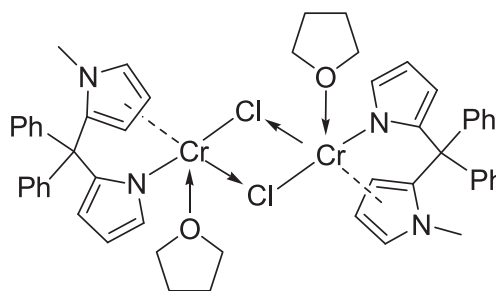
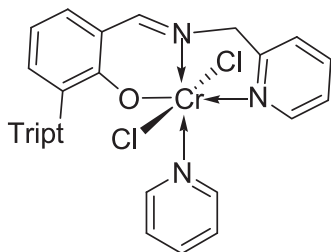
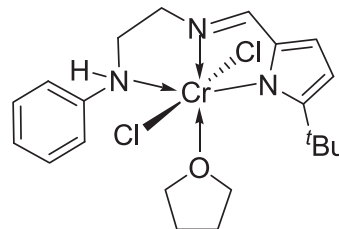
the synthesis of chromium complexes bearing sterically crowded naphthoxy-imine ligands; upon activation with MAO, high catalytic activities of up to 23,730 kg·mol⁻¹·h⁻¹, and high selectivity for linear α -olefins could be achieved [8].

Duchateau and co-workers have shown that activation of Cr(III) complex bearing dipyrrole-based ancillary ligand with MAO in methylcyclohexane led to a highly active oligomerization system with production of a statistical distribution of oligomers [14]. Gibson et al. showed that Cr(III) complexes based on tridentate bulky ortho-triptycenylyl substituted salicylaldimines containing pendant pyridyl methyl or quinolyl donors are thermally robust catalysts which oligomerize ethylene to give predominantly linear α -olefins [15]. We recently communicated on tridentate pyrrolide-imino-amine/ether complexes of Cr(III), which the steric effects in the pyrrole moiety play a pronounced role in controlling the oligomer/PE ratio while tuning of electronic effects, using either a phenylamine or a phenoxy unit, has a higher impact on the catalytic activity [16].

Over the past seventeen years, several classes of pyrazolyl-based ligands have been used to generate efficient catalysts for oligo- and polymerization of ethylene [17–19]. As an extension of our studies focused on the synthesis and use of pyrazolyl-based metal complexes in ethylene oligomerization, we present here the synthesis and characterization of chromium (III) complexes bearing pyrazolyl-imine-phenoxy/pyrrolide ligands, and their application in ethylene oligomerization. Our aims were also to evaluate the role of the ligand, and the experimental parameters on the activity and on the product distribution.

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Carpentier et al.⁸Duchateau et al.¹⁴Gibson et al.¹⁵Casagrande et al.¹⁶**Chart 1.** Examples of chromium complexes based on anionic ligands applied in ethylene oligo- and polymerization.

2. Results and discussion

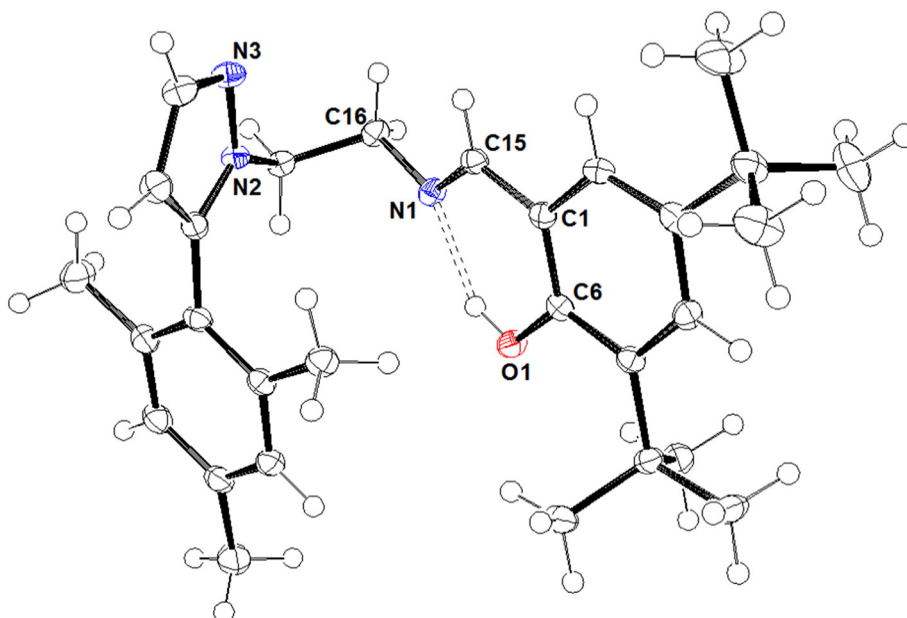
2.1. Synthesis of chromium complexes bearing pyrazolyl-imine-phenoxy/pyrrolide ligands

The monoproteo pyrazolyl-imine-phenoxy/pyrrolide proligands were readily synthesized by Schiff base condensations between the pyrazolyl amines and the corresponding aldehyde. The identity of this class of proligands was established by elemental analysis, ¹H and ¹³C NMR spectroscopy, and by an X-ray diffraction study for **1a**.

The ¹H NMR spectra of **1a–d** in CDCl₃ at room temperature exhibit resonances in the region 8.05–7.61 ppm assigned to the imine proton

(HC=N), with the corresponding ¹³C NMR resonances for the carbons of the imine moieties at ca. δ 168–160 ppm. Single crystals of **1a** suitable for crystal X-ray diffraction analysis were obtained by slow evaporation from pentane solution. The molecular geometry and atom-labeling scheme is shown in Fig. 1.

The molecular structure of **1a** shows that the geometry around the C=N bond is essentially co-planar, with phenoxy unit trans to the pyrazolyl moiety. Intramolecular hydrogen bonding occurs between the phenol proton and the nitrogen of the nitrogen of the imine group. The distance between N(1)...H-O(1) (1.847 Å) is comparable to that one in [3,5-dimethyl-1-pyrazolyl-C₂H₄-(N=CH)-2,4-tertbutyl-2-(OH)C₆H₂] [20].

**Fig. 1.** Molecular structure of **1a** (thermal ellipsoids drawn at 50% probability level).

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