



Short communication

# Acetyl-hydroxy-fulvene: A new ligand for chromium-catalyzed polymerization of ethylene at room temperature. Crystal structures of the ligands and chromium complex

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## ABSTRACT

In the field of transition metal catalysts for olefin polymerization, the discovery of new chelating ligands has attracted significant interest. This paper reports on the polymerization of ethylene with new chromium based catalysts containing an acetyl-hydroxy-fulvene ligand. A parallel method was applied to screen eleven metal salts versus two different functionalized fulvene ligands. A direct visual analysis showed solid PE formation only in vials containing a chromium salt after 1 h of polymerization at 35 °C and 15 bar. This preliminary screening was followed by optimization studies to obtain high activities (up to 5 tPE/(mol·h)). ORTEP structures of the corresponding ligands and of the best catalysts were reported.

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## 1. Introduction

Polyolefins are among the most widely produced polymers today. The catalytic polymerization of ethylene and  $\alpha$ -olefins, using single site transition metal catalysts, is an active field of research as it can yield structurally uniform polyolefins, in contrast with Ziegler Natta or Philips catalytic systems [1]. The discovery of the single site metallocene family marked considerable progress in this domain [2]. More recently, the discovery of “post-metallocene” catalysts involving heteroatoms, such as N, P and O atoms, has attracted growing attention. For instance, catalysts based on  $\alpha$ -diimine [3], salicylaldiminato [4] or phosphine-sulfonato ligands [5] have the opportunity to tune the catalytic activity by playing with steric hindrance and/or electronic properties of the chelating ligands. Extensive studies and surveys were reported [6] on the modifications of the previous ligands to demonstrate the corresponding impact on both the yield of the synthesis and the physical properties of the polyolefins, as well as to improve their stability for potential application in industrial processes [7].

In addition to the modification of these [N, N], [N, O] or [P, O] chelating ligands [6], the discovery of new types of chelating ligands, such as phosphine-oxazoline [8] or pyridine-phosphine [N, P] [9] ligands, is also an active area of research. Acetyl-hydroxy-fulvene [O, O] ligands [10], well known in transition metal coordination chemistry [11], present an interesting potential for olefin polymerization. These molecules

combine a fulvene backbone, which imposes a planar shape on the structure, with conjugated acetyl and hydroxyl chelating functionalities. Delocalization of the electrons around the cyclopentadiene with acetyl and hydroxyl groups might also confer an original electronic property to these molecules which might be modulated by the diversity of the substituents.

Here we report new chromium-based catalysts with hydroxy-acetyl-fulvene ligands for the selective polymerization of ethylene. A catalyst was isolated and characterized by X-ray diffractometry.

## 2. Experimental

## 2.1. Screening test

Under inert atmosphere in a dry glove box, eleven solutions (0.040 M) of each metal salt, and solutions (0.080 M) of each ligand were prepared in THF. 1 mL tubes were disposed in 96 well-plates. Each tube of row A was charged with 50  $\mu$ L of the ligand **1** (4.0  $\mu$ mol). Each tube of row B was charged with 50  $\mu$ L of the ligand **2** (4.0  $\mu$ mol). Ligands **1** and **2** were also deprotonated with an equimolar amount of NaH in THF during 1 h. Each tube of row C was charged with 50  $\mu$ L of the deprotonated ligand **1**<sup>−</sup> (4.0  $\mu$ mol). Each tube of row D was charged with 50  $\mu$ L of the deprotonated ligand **2**<sup>−</sup> (4.0  $\mu$ mol).

Then, each tube, from columns 1–11, was first charged with 50  $\mu$ L of the appropriate metal salt solutions (2.0  $\mu$ mol). The solvent was rapidly evaporated under reduced pressure, and 20  $\mu$ L of THF was charged in each tube to get ~0.1 M metal concentration. The library was allowed

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to react for 2 h at room temperature. Then, the solvent was evaporated under reduced pressure overnight and the library of complexes was used without further purification for the polymerization test.

To the previously described library were added 325  $\mu\text{L}$  of MAO solution (30 wt.% in toluene, 1000 equivalents) and 175  $\mu\text{L}$  of toluene in each tube. The tubes were placed in 15 bars of ethylene at 35  $^{\circ}\text{C}$  for 3 h. After 3 h a direct observation of the reaction medium volume allowed the detection of active catalysts for oligomerization of ethylene. Otherwise, reaction mediums were quenched with 4 mL of acidic methanol solution (5% HCl). Polymers were filtered and dried under vacuum overnight.

## 2.2. Polymerization of ethylene

In a Schlenk tube under argon, 20  $\mu\text{mol}$  of metal salt and 40  $\mu\text{mol}$  of ligand were introduced with 200  $\mu\text{L}$  of THF. Prior to complexation, the ligands can also be deprotonated with an equimolar amount of NaH in THF during 1 h. The solution was stirred 2 h at room temperature. The solvent was eliminated under reduced pressure. The metallic catalyst components were activated with 3.25 mL of MAO (30 wt.% in toluene, 1000 equivalents). The solution was stirred for 5 min and then diluted with 1.75 mL of toluene. The reactor was dried under nitrogen at a temperature of 110  $^{\circ}\text{C}$  for a period of time of 30 min. The reactor was brought to a polymerization temperature of 35  $^{\circ}\text{C}$  and 50 mL of toluene were added to the reactor under nitrogen. A scavenger solution consisting of 1 mL of MAO (30 wt.% in toluene) and 4 mL of toluene were added to the reactor and the solution was stirred for a few minutes. The solution of activated catalyst was added to the reactor under nitrogen. The flux of nitrogen was interrupted; the reactor was purged and placed under an ethylene pressure of 15 bars otherwise mentioned. It was placed under stirring for a period of time of 1 h. The reactor was purged and the polymerization was stopped by adding a 10% solution of MeOH/HCl. The polymer was washed three times with 30 mL of MeOH and 3 times with 30 mL of acetone. The polymer was dried under a vacuum overnight at room temperature.

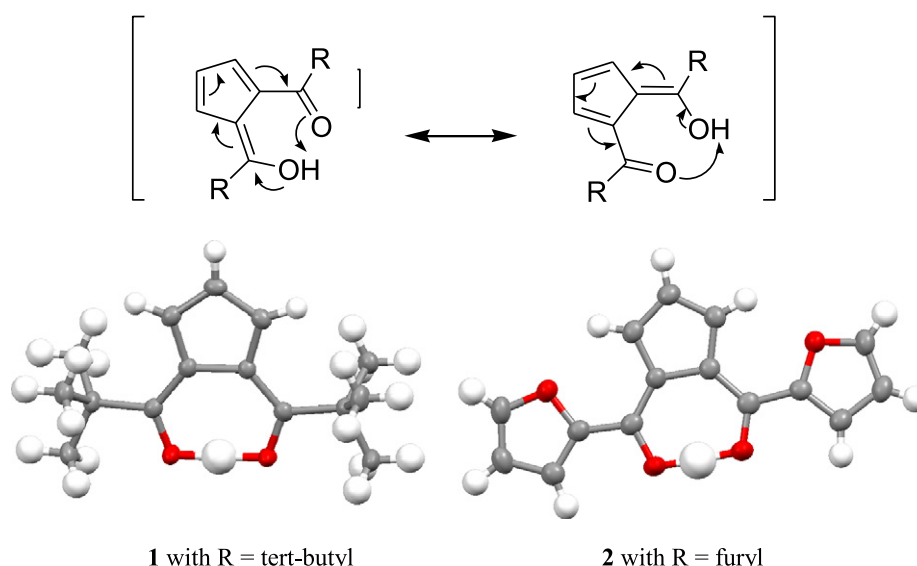
## 3. Results and discussion

Two acetyl-hydroxy-fulvene ligands were investigated (Scheme 1). Ligand **1** presents two bulky tert-butyl substituents around the oxygen pincer moiety. Ligand **2**, with two furan substituents, was also chosen to study a potential chelating effect with the furan oxygen atoms, in addition to inducing a different electronic effect on the acetyl-hydroxy-

fulvene pincer in comparison with the inductive effect on the alkyl tert-butyl substituents of ligand **1**.

This electronic effect is illustrated by the different chemical shift in the  $^{13}\text{C}$  NMR spectrum for the acetyl-hydroxy-fulvene carbon atoms directly linked to the alkyl or furan substituents. They were observed at 199 ppm for ligand **1** and 169 ppm for ligand **2**, respectively. For both ligands, only one signal was observed for the acetyl and hydroxy-fulvene carbon atoms, due to the conjugation effect of the keto-enol delocalized systems [12]. Hydroxy-acetyl-fulvenes may be used just as neutral ligands to coordinate transition metals through a L2 chelating mode ([O, OH]). Hydroxy-acetyl-fulvenes may also be used, after deprotonation of the hydroxyl function, to coordinate transition metals with a LX chelating mode ([O, O $^{-}$ ]).

To test the catalytic systems for the polymerization of ethylene, we have used a parallel approach. The synthesis of the library of potential catalysts was performed, with a combination of different metal salts (M) and hydroxy-acetyl-fulvene ligands **1** and **2**, using a multi-vial plate format. The complexation reactions were performed in 1 mL vials in tetrahydrofuran (THF) at room temperature for 2 h with metallic precursors that have a potential for catalysis (CrCl<sub>3</sub>, CrCl<sub>2</sub>, CoCl<sub>2</sub>, Co(OAc)<sub>2</sub>, CuCl<sub>2</sub>, Cu(OAc)<sub>2</sub>, FeCl<sub>2</sub>, Fe(OAc)<sub>2</sub>, FeCl<sub>3</sub>, NiBr<sub>2</sub> and Ni(OAc)<sub>2</sub>). After drying the solutions, the complexes were activated with MAO (1000 equivalents), and the polymerizations of ethylene were carried out in toluene at 35  $^{\circ}\text{C}$  for 3 h in a 15 bar ethylene atmosphere. Activities with the neutral and deprotonated hydroxyl-acetyl-fulvene ligands were qualitatively analyzed in a parallel way, by visual evaluation, to check solid formation and/or oligomer formation. This screening test revealed that in our conditions only chromium based catalysts, in the presence of either the neutral or deprotonated hydroxyl-acetyl-fulvene ligands, allowed the production of significant amounts of solid polyethylene. By comparison, the other metal salt-ligand combinations showed no solid polymer formation, potentially indicating no metal-ligand interaction to generate the corresponding complexes and/or no polymerization activity for these potential catalysts. However, in the case of Ni(OAc)<sub>2</sub>, a significant increase of the volume of liquid was observed. The preferential formation of liquid oligomers versus solid polyethylene was then checked for both precursor Ni(OAc)<sub>2</sub> and the combination ligand **1**/Ni(OAc)<sub>2</sub> in a conventional reactor in the same pressure and temperature conditions than the screening test. For both experiments the high selectivity for oligomerization process was confirmed (580 kg Olig/mol h versus 1.05 kg of solid PE/mol h for Ni(OAc)<sub>2</sub>; 641 kg Olig/mol·h versus 1.55 kg of solid PE/mol·h for ligand **1**/Ni(OAc)



Scheme 1. Schemes and molecular structure of acetyl-hydroxy-fulvene ligands **1** and **2**.

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