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Synthesis and characterization of novel chromium complexes based on β-enaminoketonato ligands and their application to ethylene polymerization

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ABSTRACT

A series of novel non-Cp-based chromium(III) complexes bearing tridentate β-enaminoketonato chelating ligands of type, $[R^2NC(CF_3)C(H)CR^1O]CrCl_2(thf)$ (**2a**: $R^1 = {}^tBu$, $R^2 = —C_6H_4OMe(o)$; **2b**: $R^1 = {}^tBu$, $R^2 = —C_9H_6N$; **2c**: $R^1 = {}^tBu$, $R^2 = —C_6H_4SMe(o)$; **2d**: $R^1 = Ph$, $R^2 = —C_9H_6N$; **2e**: $R^1 = Ph$, $R^2 = —C_6H_4SMe(o)$) have been prepared in high yields (e.g. 63–79%) from $CrCl_3(thf)_3$ by treating with 1.0 equiv. of the deprotonated ligands in tetrahydrofuran. These complexes were identified by IR, and mass spectra as well as elemental analysis. Structures for **2b**, **2c** and **2e** were further confirmed by X-ray crystallography. Non-Cp-based chromium(III) complexes have six-coordinate distorted octahedral geometry, and the heteroatom in the sidearm is coordinated to chromium. When activated by modified methylaluminoxane, complexes **2b** and **2c** exhibited high activities towards ethylene polymerization. These results indicated that both the donor atoms in side arm and the substituents in backbone significantly affected polymerization behaviors. In order to further explore the structure–reactivity relationship of the catalysts, we synthesized some novel half-sandwich chromium(III) complexes, $Cp[R^2NC(CF_3)C(H)CR^1O]CrCl$ (**3a**: $R^1 = {}^tBu$, $R^2 = —C_6H_4OMe(o)$; **3c**: $R^1 = {}^tBu$, $R^2 = —C_6H_4SMe(o)$; **3e**: $R^1 = Ph$, $R^2 = —C_6H_4SMe(o)$) and investigated their potential application in ethylene polymerization under the similar conditions. Complex **3c** adopts a three-legged piano stool geometry with a pseudo-octahedral coordination environment, and the heteroatom in the sidearm is not coordinated to chromium. These half-sandwich chromium complexes all displayed high activities for ethylene polymerization under the same conditions. Neither the donor atom in side arm nor the substituent in backbone significantly affected polymerization behaviors, in complete contrast to the results by non-Cp-based chromium catalysts.

1. Introduction

Polyolefins are by far the most important and the most produced synthetic polymers. One of the more interesting areas of chemical research in the past decade has been the discovery and development of new transition metal catalysts for olefin polymerization [1]. Among them, chromium-based catalysts play a significant role in ethylene polymerization and ethylene oligomerization [2]. Heterogeneous silica-supported systems, such as Phillips [3] or Union Carbide [4] catalysts, are the most important catalysts for the production of polyolefins and have been put to widespread commercial use. The ill-defined nature of these systems led to certain heterogeneities in the produced polymers, which might be not desirable for some applications. Therefore, more recent studies have focused on developing well-defined homogeneous chromium catalysts for improving catalytic activities and polymer properties [5–28]. The single-site half-sandwich chromium(III) complexes were found to exhibit high activities for the oligomerization, polymerization, and copolymerization of ethylene [5–12]. In addition, non-cyclopentadienyl chromium systems attracts considerable attention in the recent years. A variety of chromium complexes supported by anionic ligands and/or neutral ligands have produced effective polymerization catalysts, with the ligand structures exhibiting tremendous control over the catalytic behaviors [13–28].

We are interested in the design and synthesis of efficient chromium complexes for precise, controlled olefin polymerization [28]. We reported a series of novel non-Cp-based or half-sandwich chromium complexes bearing bidentate phosphine oxide-phenolate chelating ligands [O, P=O], which displayed

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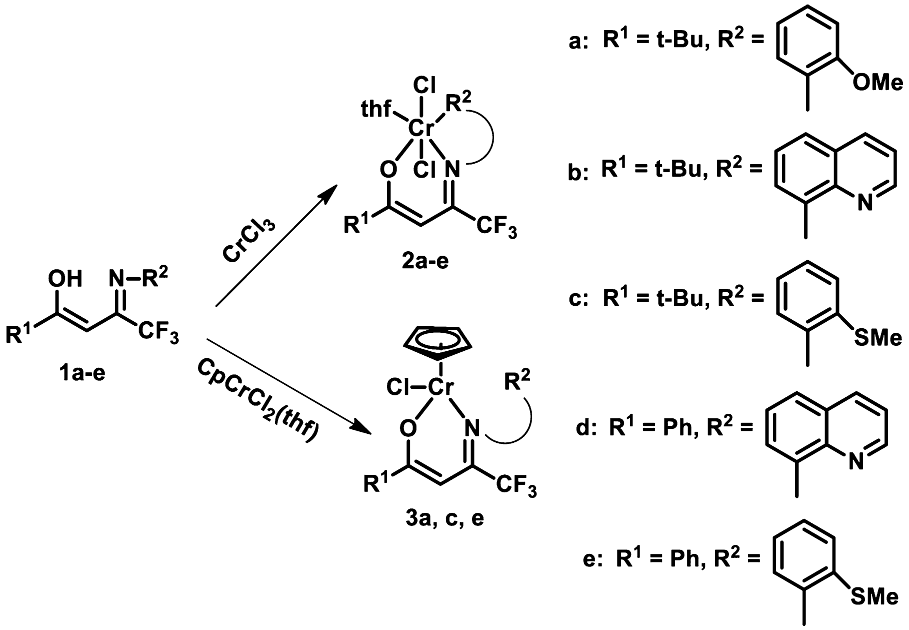

Scheme 1.

moderate activities towards ethylene polymerization [28a,28d]. Recent search on transition metal catalysts indicated that sidearm approach was an efficient strategy for stabilizing the active species [29,30]. As an extension of our investigation of transition-metal complexes with tridentate chelating ligands, [ONX]-type β-enaminoketonato derivatives were prepared and coordinated to titanium metal center. These titanium complexes showed high activity for ethylene (co)polymerization [31]. We became attracted to building on this platform to prepare non-Cp-based or half-sandwich chromium complexes containing β-enaminoketonato chelating ligands. Herein, we reported the synthesis and characterization of the new chromium complexes bearing an additional heteroatom such as O, N and S donors as a bulky side arm on the β-enaminoketonato system (Scheme 1), and explored their preliminary performance on ethylene polymerization. The polymerization behaviors were significantly influenced by catalyst structures.

2. Experimental

2.1. General procedures and materials

All manipulation of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. The NMR data of the ligands used were obtained on a Bruker-300 MHz spectrometer at ambient temperature, with CDCl$_3$ as the solvent (dried by MS 4 Å). The NMR data of the copolymers were obtained on a Bruker-400 MHz spectrometer at 135 °C, with *o*-C$_6$D$_4$Cl$_2$ as a solvent. Mass spectra were obtained using electron impact (EI-MS). Elemental analyses were recorded on an elemental Vario EL spectrometer. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The weight-average molecular weights (M_ws) and the polydispersity indices (PDIs) of polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10-μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd.). The 2.20 M *n*-butyllithium solution in hexane was purchased from Acros. CrCl$_3$(thf)$_3$ was purchased from Aldrich. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Commercial ethylene was directly used for polymerization without further purification.

2.2. Procedure for ethylene polymerization

High-pressure polymerization experiments were performed in a mechanically stirred 200 mL stainless steel reactor, equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. The reactor was baked under nitrogen flow for 24 h at 150 °C and subsequently cooled to the temperature of polymerization. The reagents were transferred via a gastight syringe to the evacuated reactor. Ethylene was introduced into the reactor, and the reactor pressure was maintained at prescribed ethylene pressure throughout the polymerization run by continuously feeding the ethylene gas. After proceeding for 10 min, the polymerization was stopped by turning the ethylene off and relieving the pressure. The reaction mixture was poured into a solution of hydrochloric acid/ethanol (10 vol%) to precipitate the polymer. The polymer was isolated by filtration, washed with ethanol, and dried under vacuum at 60 °C for 24 h in a vacuum oven.

2.3. Synthesis of compounds *1a*–*e*

Various tridentate β-enaminoketonato chelating ligands bearing different substituent on R^1 and R^2 positions, R^{2}NC(CF$_3$)C(H)CR^{1}OH (**1a**: R$_1$ = ^{t}Bu, R^2 = —C$_6$H$_4$OMe(*o*); **1b**: R^1 = ^{t}Bu, R^2 = —C$_9$H$_6$N; **1c**: R^1 = ^{t}Bu, R^2 = —C$_6$H$_4$SMe(*o*); **1d**: R^1 = Ph, R^2 = —C$_9$H$_6$N; **1e**: R^1 = Ph, R^2 = —C$_6$H$_4$SMe(*o*)) were prepared according to literature procedures [31].

2.4. Synthesis of non-Cp-based chromium complexes

2.4.1. [(2-OMeC$_6$H$_4$)NC(CF$_3$)C(H)C(^{t}Bu)O](thf)CrCl$_2$ (*2a*)

To a stirred solution of **1a** (0.60 g, 2.00 mmol) in dried THF (20 mL) at −78 °C, a 2.20 M *n*-butyllithium hexane solution (0.91 mL, 2.00 mmol) was added dropwise over 5 min. The mixture was allowed to warm to room temperature and stirred for 2.5 h. The