

Titanium and zirconium ketimide complexes: synthesis and ethylene polymerisation catalysis

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Abstract

The syntheses of ketimide titanium complexes of the type $\text{Ti}(\text{N}=\text{C}'\text{Bu}_2)_3\text{X}$ ($\text{X} = \text{Cl}, \text{Cp}, \text{Ind}$), $\text{Ti}(\text{N}=\text{C}'\text{Bu}_2)_4$ and the zirconium complex $\text{Cp}_2\text{Zr}(\text{N}=\text{C}'\text{Bu}_2)_2\text{Cl}$ are described. When activated by MAO, all compounds are ethylene polymerisation catalysts. In the conditions studied, the most active catalyst is $\text{Cp}_2\text{Zr}(\text{N}=\text{C}'\text{Bu}_2)_2\text{Cl}$, with an activity of $2.7 \times 10^5 \text{ kg}/(\text{molZr} [\text{E}] \text{ h})$. Titanium complexes are less active by about two orders of magnitude. The polyethylene produced is linear, as determined by NMR spectroscopy. Molecular structures of $\text{Ti}(\text{N}=\text{C}'\text{Bu}_2)_3\text{X}$ ($\text{X} = \text{Cl}, \text{Cp}, \text{Ind}$) and $\text{Ti}(\text{N}=\text{C}'\text{Bu}_2)_4$ were determined by X-ray single crystal diffraction. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

The search for non-metallocene olefin polymerisation catalyst has dominated the chemistry of Group 4 metal complexes over the past decades. Carbon-, nitrogen- and oxygen-based ligands have been replacing one or both Cp ligands of metallocenes, giving rise to new classes of compounds that have a wide range of activities towards the polymerisation of olefins [1]. Nitrogen-based ligands have, in particular, been given much attention over the past decade and, as a result, new support moieties for Group 4 complexes, many of which are active

catalysts in olefin polymerisation, have been reported [2–12].

Although known for several decades, ketimide ligands never played an important role in early transition metal chemistry. Recently, however, compounds $\text{Cp}'\text{Ti}(\text{N}=\text{CR}_2)\text{X}_2$ were patented by Nova Chemicals [13,14]. These are highly active olefin polymerisation catalysts, with reported activities of $10^8 \text{ g}/(\text{molTi} [\text{E}] \text{ h})$ and $10^7 \text{ g}/(\text{molTi} [\text{E}] \text{ h})$ for ethylene and propylene homopolymerisation, respectively [15]. $\text{Cp}_2\text{Zr}(\text{N}=\text{CR}_2)\text{Cl}$ was also reported recently [16,17] and tested as an olefin polymerisation catalyst, showing a slightly lower activity than Cp_2ZrCl_2 . Ketimide ligands are thus emerging as potential ancillary ligands in Group 4 chemistry.

In this paper, we report the syntheses of a new half-sandwich ketimide Zr(IV) complex and its behaviour in ethylene polymerisation catalysis. We also report the synthesis of new Ti(IV) complexes containing three

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and four ketimide ligands and their ethylene polymerisation activity.

2. Results and discussion

2.1. Synthesis and characterization

Treatment of TiCl_4 with two equivalents of $\text{LiN}=\text{C}^t\text{Bu}_2$ in toluene affords $\text{Ti}(\text{N}=\text{C}^t\text{Bu}_2)_3\text{Cl}$, **1** (Scheme 1). This non-stoichiometric product is obtained pure as a bright-red microcrystalline solid in the conditions described, in various reaction scales (see Section 3 for details). Changing reaction conditions such as the $\text{TiCl}_4:\text{LiN}=\text{C}^t\text{Bu}_2$ ratio or using $\text{TiCl}_4(\text{THF})_2$ in THF with 1:2 or 1:3 ratios affords **1**, in similar yields, as the major component of a mixture of compounds that we were unable to identify.

Proton and carbon NMR data for **1** are comparable to other Ti–ketimide complexes found in the literature [15,18,19]. Experimental values for elemental analysis are slightly lower than the theoretical ones, probably due to the compound's high sensitivity to air and moisture and so, its formulation was confirmed by high-resolution electron ionisation mass spectrometry (EI/FT ICR-MS). The spectrum shows a signal at $m/z = 503.33779$ corresponding to $[\text{C}_{27}\text{H}_{54}\text{N}_3\text{Cl}^{48}\text{Ti}]^-$ with the correct isotopic pattern.

Suitable crystals for X-ray single crystal analysis were grown overnight from a concentrated hexane solution at 4 °C. The molecular structure of **1** is shown in Fig. 1. Selected bond lengths and angles are presented in Table 1. The titanium coordination is best described as distorted tetrahedral, with angles ranging from 105.8(3)° to 113.6(3)°. The ketimide ligands are arranged around

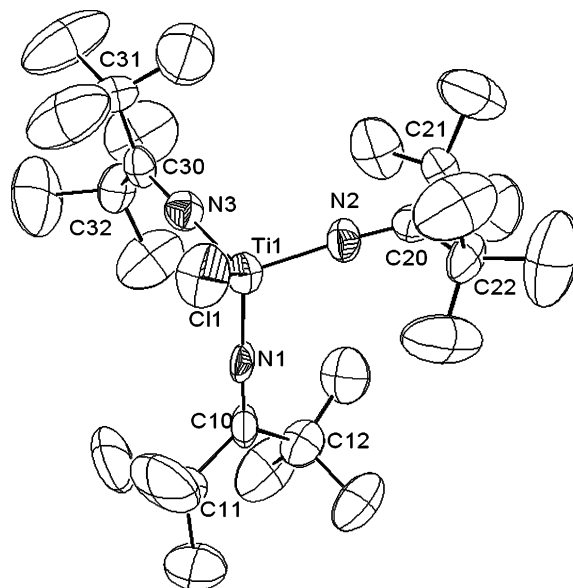
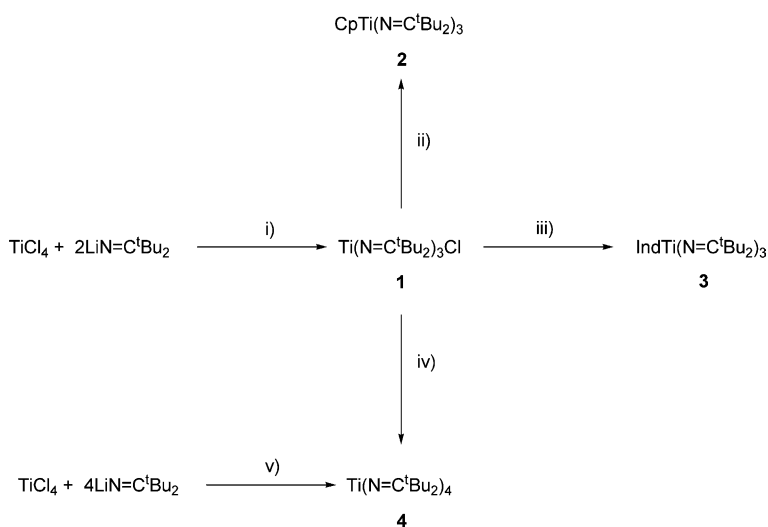


Fig. 1. Molecular structure of **1** showing atom-labeling scheme. Hydrogen atoms are omitted for clarity (thermal ellipsoids at 40% probability level).

the Ti–Cl axis in a propeller-like fashion, with angles between the Ti–Cl axis and the axis defined by the quaternary carbons of the ketimide ligands between 36.06(30)° and 46.02(38)°. The Ti–N=C angles are nearly linear, varying from 170.8(7)° to 175.6(7)°. This is a common feature of Group 4 ketimide complexes [15,16,19] and implies that the N atom has an sp hybridization. The Ti–N bond has therefore some π character, as reflected by the Ti–N distances. The values encountered for this complex (between 1.817(12) and 1.836(8) Å) are typical of titanium–ketimide complexes [15,19] and lay between Ti=N–R distances (average of 1.722 Å [20]) and Ti–NR₂



Scheme 1. (i) Toluene, –80 °C to R.T., (ii) NaCp, THF, R.T., (iii) NaInd, THF, R.T., (iv) $\text{LiN}=\text{C}^t\text{Bu}_2$, toluene, –50 °C to R.T.; (v) Toluene, –80 °C to R.T.

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