Inorganica Chimica Acta 396 (2013) 35–39

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Novel titanocene derived from a partially alkylated *s*-indacene: Synthesis, characterization and comparative study with its zirconium analog

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ARTICLE INFO

Article history:
Received 2 May 2012
Received in revised form 20 September 2012
Accepted 27 September 2012
Available online 12 October 2012

Keywords:
Titanocene
Zirconocene
Organometallic
DFT
Ethylene polymerization
Elechtrochemistry

ABSTRACT

The preparation of a novel titanium(IV) metallocene (**2**), including 2,6-diethyl-4,8-dimethyl-5-hydroindacenide (Ic′H) as ligand was successfully achieved and it was characterized by means of ^{1}H, ^{13}C NMR and elemental analysis. Cyclic voltammetry studies were performed for complex **2** as well as for its zirconium analog **1**. Both complexes were tested in the catalysis of ethylene polymerization, showing a considerable difference between their catalytic activities in a proportion of 625:1 between complex **1** and **2**. DFT calculations were performed in order to gain further knowledge about the geometry of the complexes and their electronic properties and therefore explain the difference between their reactivity.

1. Introduction

Since the isolation and later recognition of the ferrocene sandwich structure ($Fe(\eta^5\text{-}C_5H_5)_2$) in the beginning of the 1950 [1–5], metallocenes have constituted one of the most important subjects in organometallic chemistry, due to their current and potential applications in different fields of chemistry [6–9].

Metallocenes, in conjunction with methylaluminoxane (MAO) have positioned the polyolefin industry in a principal role, representing more than 50% of all polymers produced per year [10]. The most widely employed metallocene catalysts, include a group IV transition metal like titanium, zirconium or hafnium, were in particular the Zr-based compounds have been the center of academic and industrial attention [6–8]. The bent coordination mode of both cyclopentadienyl rings into such group IV metallocenes in addition to other features, has been of great relevance for olefin polymerization since its introduction as a new generation of Ziegler–Natta catalyst. These complexes have also shown a great potential in synthetic organic chemistry as well as in development of new materials [11–18] since the beginning of the 90s.

The novelty of such metallocenes acting as catalyst rely on the fact that they show only one kind of active sites during the catalytic process, resulting in polymers with higher molecular weight and narrow distribution [11,19,20]. The ability to modify the single-site catalytic center varying the ancillary ligands, open the possibilities to obtaining new classes of polyolefins renewing the classical Ziegler–Natta polymerization.

Normally, the proportion of the catalytic activity in ethylene polymerization between single-site metallocene catalyst of the lighter members of group IV, namely, Zr and Ti, is of 3:1 [21,22] which can vary according to the nature of the coordinating ligands.

As part of our current interest on metallocenes derived from the fused-ring ligand *s*-indacene which offers the potential ability to incorporate a second catalytic site [23–27], we have reported the obtention of a 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (*s*-Ic′H_2) complex of $[CpZrCl_2]^{1+}$, namely $[CpZrCl_2(s\text{-}Ic'H)]$ (**1**) [28] in order to modulate the coordination sphere of such center. With the aim to evaluate its catalytical activity comparing with its

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http://dx.doi.org/10.1016/j.ica.2012.09.032

lighter analog, herein we report the synthesis and characterization of a novel titanocene complex using (s-Ic′H_2) as supporting ligand, namely [CpTiCl_2(s-Ic′H)] (**2**) (Fig. 1), focusing on the comparison of catalytical and electrochemical properties. Additionally, we carry out DFT calculations with the aim to gain more insights into the chemical differences between these two compounds.

2. Experimental

2.1. General data

All manipulations were carried out under pure dinitrogen atmosphere using a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri-Train purifier or a vacuum line using standard Schlenk-tube techniques. Reagent grade solvents were distilled under dinitrogen from sodium/benzophenone (tetrahydrofuran, toluene, petroleum ether) or from P_2O_5 (dichloromethane). The starting compounds 2,6-diethyl-1,5-dihydro-4,8-dimethyl-s-indacene (Ic′H_2) [23], $CpTiCl_3$ [29], [CpZrCl_2(Ic′H)] (**1**) [28] were prepared according to published methods. Elemental analyses (C and H) were made with a Fisons EA 1108 microanalyzer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-400 and Bruker AC-200P Spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane. All peaks reported are singlets, unless otherwise specified. All voltammetries were performed employing dry CH_2Cl_2 as solvent, with 0.1 M tetrabutylammonium tetrafluroborate as supporting electrolyte, and all complexes in a 5×10^{-4} M concentration. Working Electrode: Platinum Disc; Counter Electrode: Platinum Wire; potentials listed versus SCE. Polymerization reactions were carried out in a 30 mL Parr stainless steel autoclave (in a glovebox under an inert nitrogen atmosphere) with toluene and the desired amount of co-catalyst (MAO/toluene 10%) and the complexes were dissolved in toluene. The autoclave was sealed, brought out of the glovebox and connected to a mechanical stirrer, a temperature controller and an ethylene consumption control. The reaction was ended by the addition of HCl/methanol (20% v/v). The polymer was isolated by filtration, washed with acetone and dried overnight at room temperature.

2.2. Computational details

Geometry optimization and properties were performed using density functional theory (DFT) in the Amsterdam density functional package (ADF 2008.01) [30] including the scalar relativistic corrections by means of the Hamiltonian ZORA. [31,32] We employed triple-ζ Slater basis set plus polarization function (STO-TZP). Geometry optimizations of both complexes were performed via the analytical energy gradient method implemented by Verluis and Ziegler [33], and the nonlocal correction of the exchange and correlation (XC) incorporated via the general gradient approximation (GGA) within the functional PW91 proposed by Perdew–Wang [34]. The excitation energies were estimated through the incorporation of an oscillating time-dependent perturbation to the DFT (TD-DFT) [35,36], employing as GGA the functional SAOP, which is specially designed for the calculation of optical properties [37].

2.3. Synthesis of [CpTiCl_2(2,6-diethyl-4,8-dimethyl-5-hydroindacenide)] (**2**)

To a solution of Ic′H_2 (0.50 g, 2.10 mmol) in tetrahydrofuran (THF, 15 mL) at −80 °C, was added drop wisely a hexane solution of n-butyllithium (n-BuLi, 1.6 mol L^{-1}, 1.32 mL, 2.10 mmol) with constant stirring. The reaction mixture was allowed to warm to room temperature and stirred for 30 min, producing the consequent lithiated salt of the s-indacene ligand. Then the mixture was once again cooled to −80 °C, and a solution of $CpTiCl_3$ (0.46 g, 2.10 mmol) [31] in tetrahydrofuran (20 mL) was added via syringe. The solution was allowed to warm to room temperature and stirred for 24 h and then the solvent was removed under vacuum. The solid residue was extracted with toluene, filtering out the lithium chloride precipitate and washed three times with toluene. The filtrate was then reduced to ~5 mL and 20 mL of pentane were added, then the solution was cooled to −80 °C for optimal precipitation and filtered off. The resulting brown powder corresponding to complex **2** is unstable to air, and was obtained in a moderated yield (yield 0.40 g, 45%).

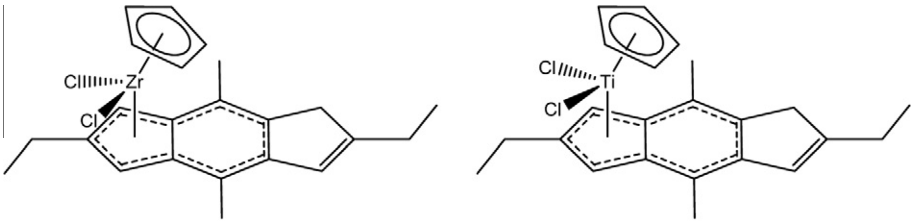
^{1}H NMR (400 MHz, C_6D_6) δ ppm = 0.98 (t, 3H, C$\boldsymbol{H_3}$–CH_2–C($_6$), J_{H-H} = 7.4 Hz); 1.09 (t, 3H, C$\boldsymbol{H_3}$–CH_2–C($_2$), J_{H-H} = 7.4 Hz); 2.15 (q, 2H, CH_3–C$\boldsymbol{H_2}$–C($_6$)), 2.23 (s, 3H, C$\boldsymbol{H_3}$–C($_4$)); 2.27(s, 3H, C$\boldsymbol{H_3}$–C($_8$)); 2.69 (q, 2H, CH_3–C$\boldsymbol{H_2}$–C($_2$), $^3J_{H-H}$ = 7.4 Hz); 2.80; 2.87 (s, 2H, C($_5$)H_2); 5.82 (s, 5H, Cp), 6.42 (s, 2H, C($_{1,3}$)H); 6.12 (s, 1H, C($_7$)H).

^{13}C NMR (100 MHz, C_6D_6) δ ppm = 12.83 ($\boldsymbol{C}H_3$–CH_2–C($_6$)); 14.68 ($\boldsymbol{C}H_3$–CH_2–C($_2$)); 15.54 ($\boldsymbol{C}H_3$–C($_8$)); 15.89 ($\boldsymbol{C}H_3$–C($_4$)); 24.95 (CH_3–$\boldsymbol{C}H_2$–C($_6$)); 26.07 (CH_3–$\boldsymbol{C}H_2$–C($_2$)); 39.41 (C($_5$)H_2); 108.75, 112.92 (C($_{1,3}$)H); 119.95 (C($_{Cp}$)); 143.36 (C($_2$)); 123.91 (C($_7$)); 126.74 (C($_{7a}$)); 129.08 (C($_{3a}$)); 130.67 (C($_{8a}$))134.13 (C($_{4a}$)); 141.20 (C($_4$)); 144.74 (C($_8$)); 154.14 (C($_6$)). *Anal.* Calc. for $C_{23}H_{26}Cl_2Ti$: C, 66.35; H, 7.15. Found: C, 66.52; H, 7.31%.

3. Results and discussion

3.1. Synthesis and characterization of titanocene derivative

The synthesis of the desired titanium(IV) complex containing an alkylated s-indacene ligand began with the selection of an appropriate half sandwich compound that would undergo salt metathesis to generate a mixed-ligand titanocene dichloride, as is presented in Scheme 1. The mixed-sandwich compound was achieved by using $CpTiCl_3$ [29] as source of $[CpTiCl_2]^+$ moiety, and 2,6-diethyl-4,8-dimethyl-1,5-dihydro-s-indacene (s-Ic′H_2) in its monodeprotonated form obtained by reacting the neutral (s-Ic′H2) with n-butyl-lithium (n-BuLi) as a strong base. Moreover, this ligand has the advantage that has a controlled deprotonation of its acidic vinylic protons, allowing the control in the formation of the target product. The



(1) (2)

Fig. 1. Zirconocene **1** previously reported [28] (left) and its titanium analog **2** (right).