



A new series of zirconium metallocenes derived from partially alkylated *s*-indacene with potential applications in the polymerization of ethylene



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ABSTRACT

This contribution describes the synthesis and characterization of a series of zirconium metallocenes derived from partially alkylated *s*-indacene. The complexes [Cp*ZrCl₂-*s*-Ic''H] **1**, [Cp*ZrCl₂-*s*-Ic''H] **3** and [CpZrCl₂-*s*-Ic''H] **4** (*s*-Ic''H = 2,6-diethyl-4,8-dimethyl-1-hydro-*s*-indacene; *s*-Ic''H = 2,6-dibutyl-4,8-dimethyl-1-hydro-*s*-indacene) were synthesized from the monolithiated salts of *s*-indacene (*s*-Ic''H or *s*-Ic''H) with one equivalent of C₅R₅ZrCl₃ (R = H, CH₃). All complexes here reported were characterized by means of ¹H and ¹³C NMR, mass spectrometry, elemental analysis. Complexes [Cp*ZrCl₂-*s*-Ic''H] **1** and [CpZrCl₂-*s*-Ic''H] **2** (previously reported by NMR analysis) were characterized by X-ray diffraction. In order to gain further knowledge about their catalytic behavior, the complexes were tested in the catalysis of ethylene polymerization showing a highest activity. Complex **4** presents the highest ethylene polymerization activity than complexes **1** and **2**, and **3** under the same working conditions.

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1. Introduction

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 [1]. 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 [2–4]. 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 [5–12] 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 [5,13,14]. The ability to modify the single-site catalytic center varying the ancillary ligands, open the

possibilities to obtaining new classes of polyolefin renewing the classical Ziegler–Natta polymerization.

It has been reported that the modification in nature and number of substituents on a cyclopentadienyl ring [15–18,14,19] may directly affect the catalytic activity and/or the stereoselectivity [20], allowing the use of these metallocenic catalysts in industrial processes on a macroscale level, registering catalytic activity values similar or superior to those obtained with the conventional Ziegler–Natta heterogeneous catalysts [21–25].

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 [26–33], we have reported obtaining of a new series of zirconium precatalysts using 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (Ic''H₂) and 2,6-dibutyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (Ic''H₂) as main ligand as well as cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) ligands. This contribution describes the general approach for the successful preparation of these molecular species were fully characterized by methods such as ¹H and ¹³C NMR spectroscopic analysis, elemental analysis, and mass spectrometry. Complexes **1** and **2** (previously synthesized [34]) were also characterized by X-ray diffraction. In addition, in order to gain further knowledge about their catalytic behavior, the complexes were tested in the catalysis of ethylene polymerization showing a high activity.

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2. Experimental

2.1. General

All manipulations were carried out under pure dinitrogen atmosphere using a vacuum atmosphere 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 ketyl (tetrahydrofuran, toluene, hexanes, pentane, diethyl ether). The starting compounds 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene [26], 2,6-dibutyl-4,8-dimethyl-1,5-dihydro-*s*-indacene [35], Cp*ZrCl₃ [36], CpZrCl₃·DME [37] and CpZrCl₂(2,6-diethyl-1-4,8-dimethyl-1-hydro-*s*-indacene) (**2**) [34] were prepared according to previously published methods. *n*-Butyllithium (1.6 M in hexanes) and C₆D₆ (C₆D₆ was dried with Na prior to use) were purchased from Aldrich. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker Avance 400 MHz. Mass spectra (EI, 70 eV) were recorded on HP-5889A spectrometer. Elemental analyses (C and H) were recorded on a Fisons EA 1108 microanalyzer. 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. Synthesis

2.2.1. General procedure for synthesis of the zirconium complexes derivated from partially alkylated *s*-indacene

A solution of 1,5-dihydro-2,6-diethyl-4,8-dimethyl-*s*-indacene (*s*-Ic''H₂) or 1,5-dihydro-2,6-dibutyl-4,8-dimethyl-*s*-indacene (*s*-Ic''H₂) in 30 mL of THF was cooled to -80 °C and one equivalent of *n*-BuLi 1.6 M was slowly added with vigorous stirring. Once the addition was complete, the solution was left to warm to room temperature, and after 2 h a clear dark red solution was obtained, then the THF was evaporated. To this solid was added a solution of Cp*ZrCl₃ or CpZrCl₃·DME in 20 mL of toluene. This mixture was then refluxed by 35 h giving a yellow solution, which was filtered and washed twice with toluene. The solvent was evaporated obtaining a gummy yellow solid, which was dissolved in hot hexanes, and the solution was filtered to eliminate the LiCl formed. This solution was then concentrated until the yellow a precipitate was formed. The solid was then filtered off and dried under vacuum giving a yellow solid.

2.2.1.1. Cp*ZrCl₂(2,6-diethyl-1-hydro-4,8-dimethyl-*s*-indacene). [Cp*ZrCl₂-*s*-Ic''H] (**1**). In the same way, **1** was prepared using 0.40 g (1.68 mmol) of 1,5-dihydro-2,6-diethyl-4,8-dimethyl-*s*-indacene (*s*-Ic''H₂); 1.10 mL (1.68 mmol) of *n*-BuLi 1.6 M; 30 mL of THF; Cp*ZrCl₃ 0.56 g (1.68 mmol) in 20 mL of toluene. Yield: 0.47 g (52%).

Anal. Calc. for C₂₈H₃₆Cl₂Zr: C, 62.89; H, 6.79. Found: C, 63.21; H, 6.99%.

Mass spectroscopy results: MS (EI, m/z, %): M⁺532 (100%), [M-(Cp*ZrCl₂)]⁺ 238.

¹H NMR (C₆D₆): δ 0.96 (t, ³J = 7.5 Hz, 3H, C₍₂₎CH₂CH₃), 1.05 (t, ³J = 7.5 Hz, C₍₆₎CH₂CH₃), 1.75 (s, 15H, CH₃-Cp*), 2.14 (q, d, ³J = 7.5 Hz, 2H, C₍₆₎CH₂CH₃), 2.26 (s, 3H, CH₃-C₍₄₎), 2.33 (s, 3H, CH₃-C₍₈₎), 2.39 (q, d, ³J = 7.6 Hz, 2H, C₍₂₎CH₂CH₃), 2.90 (m, ²J = 23 Hz, H, C₍₁₎H_a), 3.10 (m, H, C₍₁₎H_b), 6.10 (d, ⁴J = 2.3 Hz, 1H, C₍₅₎H), 6.40 (d, ⁴J = 2.3 Hz, 1H, C₍₇₎H), 6.50 (dt, ³J = 3 Hz, 7H,

C₍₃₎H). ¹³C{¹H} NMR (C₆D₆): δ 1.03, 12.35, 12.48, 15.62, 16.27, 23.42, 24.63, 39.16, 103.19, 107.59, 118.98, 123.46, 123.82, 124.31, 132.26, 140.07, 143.31, 151.98.

2.2.1.2. Cp*ZrCl₂(2,6-dibutyl-1-hydro-4,8-dimethyl-*s*-indacene). [Cp*ZrCl₂-*s*-Ic''H] (**3**). In the same way, **3** was prepared using 0.20 g (0.70 mmol) of 1,5-dihydro-2,6-dibutyl-4,8-dimethyl-*s*-indacene (*s*-Ic''H₂); 0.51 mL (0.82 mmol) of *n*-BuLi 1.6 M; 30 mL of THF; Cp*ZrCl₃ 0.23 g (0.70 mmol) in 20 mL of toluene. Yield: 0.15 g (46%).

Anal. Calc. for C₃₂H₄₄Cl₂Zr: C, 65.05; H, 7.51. Found: C, 64.12; H, 7.15%.

Mass spectroscopy results: MS (EI, m/z, %): M⁺588 (100%), [M-(Cp*ZrCl₂)]⁺ 294.

¹H NMR (C₆D₆): δ 1.26 (t, ³J = 7.3 Hz, 3H, C₍₂₎-CH₂CH₂CH₂CH₃), 1.32 (t, ³J = 7.1 Hz, C₍₆₎-CH₂CH₂CH₂CH₃), 1.40 (m, 4H, C₍₆₎-CH₂CH₂CH₂CH₃), 1.45 (m, 4H, C₍₂₎-CH₂CH₂CH₂CH₃), 1.82 (s, 15H, Cp*), 2.22 (q, d, ³J = 7.1 Hz, 2H, C₍₂₎-CH₂CH₂CH₂CH₃), 2.26 (s, 3H, CH₃-C₍₄₎), 2.34 (s, 3H, CH₃-C₍₈₎), 2.76 (m, H, ²J = 22.4 Hz, C₍₁₎H_b), 2.90 (q, d, ³J = 7.3 Hz, 2H, C₍₆₎-CH₂CH₂CH₂CH₃), 3.01 (m, ²J = 22.4 Hz, H, C₍₁₎H_a), 6.12 (d, 1H, C₍₅₎H), 6.30 (d, H, C₍₇₎H), 6.56 (dt, H, C₍₃₎H). ¹³C{¹H} NMR (C₆D₆): δ 1.04, 14.00, 15.04, 22.59, 31.32, 31.50, 40.06, 104.21, 106.59, 124.72, 140.58, 140.68, 148.69, 151.97

2.2.1.3. CpZrCl₂(2,6-dibutyl-1-hydro-4,8-dimethyl-*s*-indacene). [CpZrCl₂-*s*-Ic''H] (**4**). In the same way, **4** was prepared using 0.30 g (1.02 mmol) of 1,5-dihydro-2,6-dibutyl-4,8-dimethyl-*s*-indacene (*s*-Ic''H₂); 0.67 mL (1.07 mmol) of *n*-BuLi 1.6 M; 30 mL of THF; CpZrCl₃·DME 0.36 g (1.02 mmol) in 20 mL of toluene. Yield: 0.18 g (45%).

Anal. Calc. for C₂₇H₃₄Cl₂Zr: C, 62.28; H, 6.58. Found: C, 64.12; H, 7.15%.

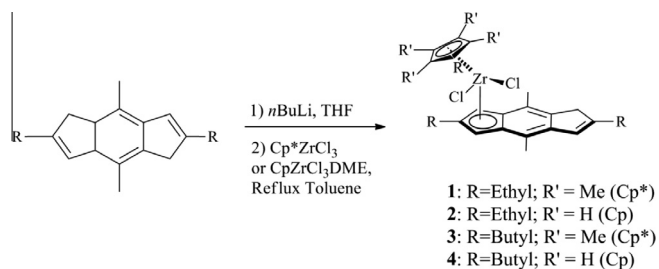
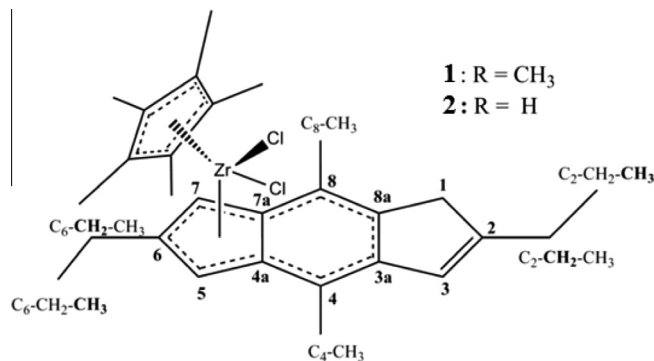
Mass spectroscopy results: MS (EI, m/z, %): M⁺518 (100%), [M-(CpZrCl₂)]⁺ 224.

¹H NMR (C₆D₆): δ 1.26 (t, ³J = 7.3 Hz, 3H, C₍₂₎CH₂CH₂CH₂CH₃), δ 1.32 (t, ³J = 7.1 Hz, C₍₆₎CH₂CH₂CH₂CH₃), δ 1.40 (m, 4H, C₍₆₎CH₂CH₂CH₂CH₃), δ 1.45 (m, 4H, C₍₂₎CH₂CH₂CH₂CH₃), 2.22 (q, d, ³J = 7.1 Hz, 2H, C₍₂₎CH₂CH₂CH₂CH₃), 2.26 (s, 3H, CH₃-C₍₄₎), 2.34 (s, 3H, CH₃-C₍₈₎), 2.66 (m, H, C₍₁₎H_b), 2.76 (q, d, ³J = 7.3 Hz, 2H, C₍₆₎CH₂CH₂CH₂CH₃), 3.01 (m, ²J = 22.4 Hz, H, C₍₁₎H_a), 5.93 (s, 5H, Cp), 6.12 (d, H, C₍₅₎H), δ 6.30 (d, H, C₍₇₎H), 6.56 (dt, H, C₍₃₎H). ¹³C{¹H} NMR (C₆D₆): δ 14.03, 15.10, 22.62, 31.32, 31.49, 40.03, 104.27, 106.40, 116.08, 124.70, 140.63, 140.73, 148.69.

3. Results and discussions

3.1. Synthesis of the complexes

In order to properly produce zirconocene complexes containing an alkylated *s*-indacene ligand, the synthetic studies began with an appropriate half sandwich compound that would undergo salt metathesis with an alkali metal salt of the alkylated *s*-indacene ligand to generate a mixed-ligand zirconocene dichloride, as presented in Scheme 1. As previously mentioned, in our case the chosen ligand corresponds to 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (*s*-Ic''H₂) or 2,6-dibutyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (*s*-Ic''H₂) which were selectivity monodeprotonated with a strong base such as *n*-Butyllithium. The reaction of the lithiated salt *s*-Ic''HLi or *s*-Ic''HLi with Cp*ZrCl₃ or CpZrCl₃·DME gave the desired zirconocene dichloride complexes in moderately good yields. These compounds were isolated as yellow crystalline solids from hexanes.

Scheme 1. Synthetic route for complexes **1**, **2**, **3** and **4**.Chart 1. NMR assignment of the tetraalkylated *s*-indacene ligand for the reported complexes.

3.2. NMR considerations

The characterization of these organometallic complexes was carried out by ^1H and ^{13}C NMR spectroscopy and were assigned using 2D NMR tools. For complexes **1**, **3** and **4**, the signals match with the legend shown in Charts 1 and 2. Typical signals that corroborate the presence of the desired product are described below.

Complex $[\text{Cp}^*\text{ZrCl}_2\text{-}s\text{-Ic}^*\text{H}]$ **1** shows that protons 5 and 7 appear as different signals at 6.10 ppm and 6.40 ppm. In addition, both protons from carbon 1 appear as two different signals (doublet of doublets at 2.9 and 3.1 ppm). This spectroscopic behavior is completely different from the other mononuclear *s*-indacene complexes with late transition metals developed in our laboratory [27,29–32,38], which present a singlet for both protons 5 and 7 and a broad singlet for protons 1. A possible explanation could rely on the chlorine atoms. One chlorine is located beneath the benzene ring, while the another one is perpendicular to the *s*-indacene,

making protons 5 and 7 diastereotopic, with a coupling constant of 2.3 Hz. Furthermore, these protons appear deshielded compared to proton 3 at 6.5 ppm. Complex **1** shows similar spectroscopic behavior than its analog complex **2** [34].

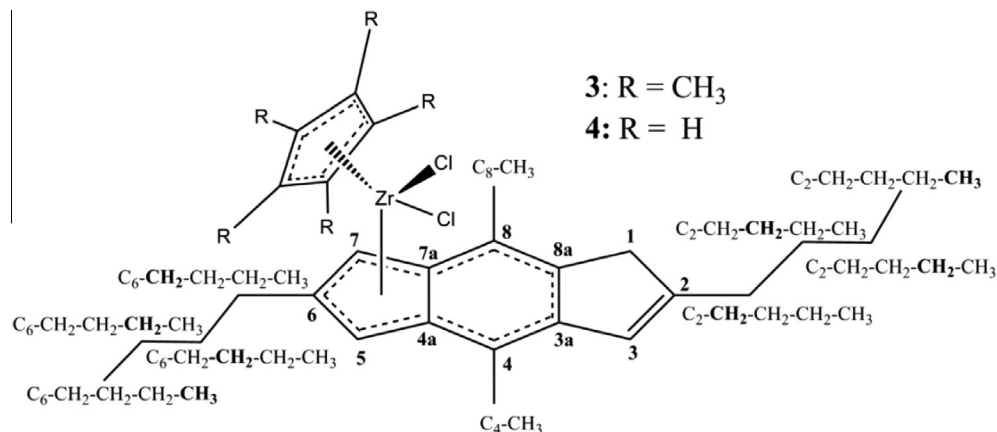
A similar effect was observed for the complexes **3** and **4**, where the same protons 5 and 7 of the five-membered ring of the *s*-indacene ligand appear as different signals, due to explanation given above.

Studies at different temperatures were carried out between -30°C and 80°C , in order to elucidate the behavior of the complexes in solution compared to the X-ray structure in the solid state (*vide infra*). Fig. 1 shows no decomposition of complex **1** in the ^1H NMR spectra between -30°C and 80°C . The signals corresponding to protons 5 and 7 are not affected by the temperature change, just an insignificant shift was observed for these signals. From these studies, it is possible to deduce that the Zr complex presents a degree of rigidity due to the steric hindrance around the zirconium center, restricting the rotation of the metallic moiety. This same behavior was observed for the complexes **2**, **3** and **4**.

3.3. Description of crystal structure

X-ray data (Table 1) were collected on an Enraf Nonius diffractometer at 294(2) K for complex **2** and on a Bruker SMART diffractometer at room temperature for compound **1**. All data for both structures represented in this paper were collected with graphite-monochromated Mo $K\alpha$ radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied [39,40]. The structures were solved by direct methods, using SHELXS-9740 and refined using the least-squares method on F^2 [41]. All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model.

Monocrystals were obtained by solvent diffusion techniques. Complex **1** was obtained from diffusion of hexanes into toluene and two molecular units were present in the unit cell. Suitable crystal of **2** for X-ray diffraction were obtained from diffusion of pentanes into diethyl ether. Figs. 2 and 3 show the crystalline structures for complexes **1** and **2** respectively. The solid-state structure analysis shows that both compounds crystallize in a triclinic space group $P\bar{1}$ with two molecules in a unit cell. The cyclopentadienyl fragment from the *s*-indacene ligand displays a pentahapto bonding motif towards zirconium. Complex **1** presents a Cl–Zr–Cl angle of $94.7(1)^\circ$ and a $\text{C}_g(\text{Cp}^*)\text{-Zr-C}_g(\text{Ic})$ angle value of 134° , both values being slightly larger than for those analogues in complex **2**, presenting a Cl–Zr–Cl and $\text{C}_g(\text{Cp})\text{-Zr-C}_g(\text{Ic})$ angle values of $93.530(9)^\circ$ and 130° , respectively. This difference may be due to

Chart 2. NMR assignment of the tetraalkylated *s*-indacene ligand for complexes **3** and **4**.

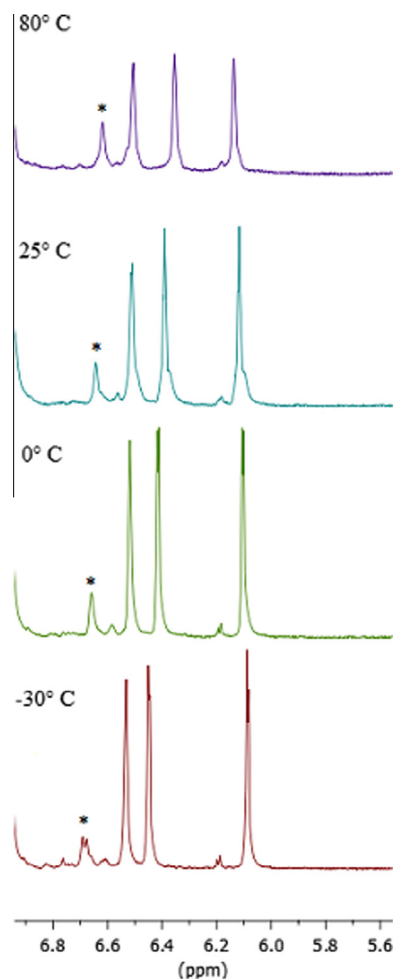


Fig. 1. $^1\text{H-NMR}$ spectra at different temperatures for complex $[\text{Cp}^*\text{ZrCl}_2\text{-s-Ind}]\text{1}$ in $\text{tol-}d_8$ (range 5.6–7.8 ppm). (*Impurity of the free ligand).

the steric hindrance produced by the methyl groups of the Cp group in complex **1**, forcing the ethyl group in position 6 to face away from the metallic fragment.

The experimental angles and bond lengths for these new zirconium compounds are similar to other previously reported group IV complexes [42,43]. All intramolecular Zr–C distances concerning those to the *s*-indacene ligand as well as the Cp or Cp* ligand vary from 2.2 to 2.6 Å, ratifying the η^5 hapticity of Zr in both complexes.

As mentioned in the $^1\text{H NMR}$ studies, it is worth to highlight that the structure of the compound does not correspond to the traditionally observed in the majority of zirconium metallocenes, possibly explained to the large bulky ligand tetraalkylated *s*-indacene, forcing the complex to adopt a bent and more rigid structure, despite the fact that these complexes are not ansa-metallocenes. Also, this property results as a promising feature in homogenous catalysis, particularly in the polymerization of ethylene, as these catalytic systems have mostly been carried out successfully by bridged ansa-metallocenes [44,45].

3.4. Catalytic study

In order to investigate the catalytic properties of the zirconocene complexes in olefin polymerization, the ethylene polymerization behavior of **1**, **2**, **3** and **4** were explored. The results are summarized in Table 2.

Table 2 shows the results obtained at same Al/Zr ratios and same concentration values of $3.5 \cdot 10^{-7}$ mol/L of zirconocene complexes. It is noteworthy to mention that studies at concentration at $8.5 \cdot 10^{-7}$ mol/L for these complexes were not carried out, because these complexes forms such a large quantity of polymeric product, that makes impossible to continue stirring the reactor.

Complex **4** displayed activity value of 52,883 (kg PE/mol Zr bar h), showing higher activity and yield (18.6 g) than the others complexes. For complex **2** shows a similar activity (49,574 kg PE/mol Zr bar h) and yield (17.5 g) than the complex **4** and both present higher values compared with **1** and **3** at the same Al/Zr ratio and concentration (34,498 and 14,574 kg PE/mol Zr bar h respectively) whom present lower catalytic activity in this conditions.

Table 1
Summary of crystallographic data for compounds **1** and **2**.

	$[\text{Cp}^*\text{Zr-Ind}]\text{1}$	$[\text{CpZr-Ind}]\text{2}$
Empirical formula	$\text{C}_{56}\text{H}_{72}\text{Cl}_4\text{Zr}_2$	$\text{C}_{23}\text{H}_{26}\text{Cl}_2\text{Zr}$
Formula weight	1069.38	464.56
<i>T</i> (K)	298(2)	294(2)
λ (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	<i>P1</i>	<i>P1</i>
Unit cell dimensions		
<i>a</i> (Å)	9.5735(15)	7.081(3)
<i>b</i> (Å)	15.209(2)	11.976(3)
<i>c</i> (Å)	18.742(3)	12.503(3)
α (°)	96.797(3)	91.88(3)
β (°)	91.705(3)	94.39(4)
γ (°)	108.071(3)	93.52(3)
<i>V</i> (Å ³)	2569.7(7)	1054.3(6)
<i>Z</i>	2	2
<i>D</i> _{calc} (Mg/m ³)	1.382	1.463
Absorption coefficient (mm ⁻¹)	0.65	0.779
<i>F</i> (000)	1112	476
Crystal size (mm ³)	$0.73 \times 0.14 \times 0.12$	$0.25 \times 0.12 \times 0.10$
Theta range for data collection (°)	2.2–28.0	1.6–25.0
Index ranges	$-12 \leq h \leq 12, -19 \leq k \leq 19, -24 \leq l \leq 24$	$-8 \leq h \leq 8, -14 \leq k \leq 14, 0 \leq l \leq 14$
Independent reflections	11,102	3712
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	11,102/0/577	3712/0/239
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.059, <i>wR</i> ₂ = 0.142	<i>R</i> ₁ = 0.0719, <i>wR</i> ₂ = 0.1244
Largest difference peak and hole (e Å ⁻³)	0.65 and -0.30	0.445 and -0.725

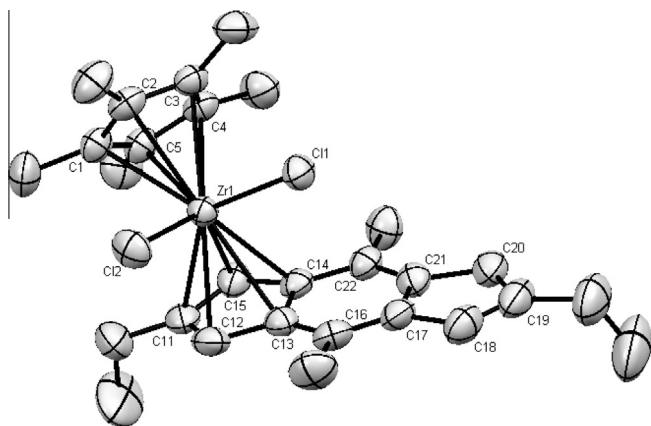


Fig. 2. ORTEP representation for complex $[Cp^*ZrCl_2-s-Ic'H]$ **1** at the 50% probability level for the thermal ellipsoids. (Hydrogen atoms omitted for clarity). Selected distances (Å) and angles ($^\circ$): Zr–Cl₁ 2.424(1), Zr–Cl₂ 2.433(1), Zr–C₁ 2.526(4), Zr–C₂ 2.493(4), Zr–C₃ 2.548(5), Zr–C₄ 2.564(5), Zr–C₅ 2.520(4), Zr–C₁₁ 2.488(4), Zr–C₁₂ 2.511(5), Zr–C₁₃ 2.530(5), Zr–C₁₄ 2.615(4), Zr–C₁₅ 2.579(5), Cl₁–Zr–Cl₂ 94.7(1), C_g(Cp^{*})–Zr–C_g(Ic) 134.

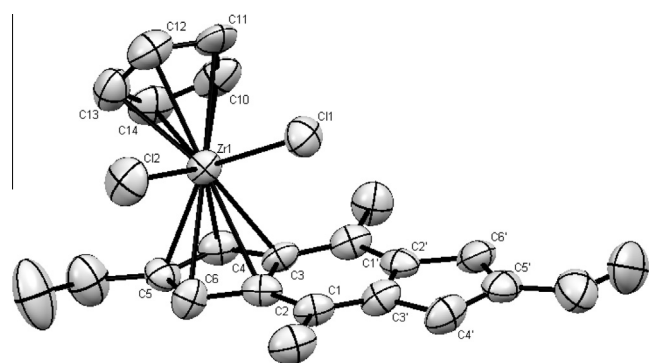


Fig. 3. ORTEP representation for complex $[CpZrCl_2-s-Ic'H]$ **2** at the 50% probability level for the thermal ellipsoids. (Hydrogen atoms omitted for clarity). Selected distances (Å) and angles ($^\circ$): Zr–Cl₁ 2.428(3), Zr–Cl₂ 2.434(3), Zr–C₁₀ 2.470(1), Zr–C₁₁ 2.518(9), Zr–C₁₂ 2.490(1), Zr–C₁₃ 2.480(1), Zr–C₁₄ 2.510(1), Zr–C₂ 2.613(9), Zr–C₃ 2.539(8), Zr–C₄ 2.463(9), Zr–C₅ 2.493(9), Zr–C₆ 2.544(9), Cl₁–Zr–Cl₂ 93.530(9), C_g(Cp)–Zr–C_g(Ic) 130.

Table 2
Ethylene polymerization result for complexes **1**, **2**, **3** and **4**.^a

Precatalyst ^b	Yield ^c	A ^d
1	12.1	34,498
2	17.5	49,574
3	3.6	14,574
4	18.6	52,883

^a Polymerizations were carried out in a 30 mL metallic Parr reactor, equipped with a temperature, stirring and internal pressure control system. Ethylene polymerization: Ratio Al/Zr = 6,000, Toluene = 25 mL, T = 60 °C, P = 2 bar, t = 0.5 h.

^b [Zr] 3.5×10^{-7} mol/L.

^c Grams.

^d Activity in (KgPE/molZr bar h).

Based on the considerations above, we propose that the increase in activity of complexes **4** and **2** is mainly due to one factor. The lower steric hindrance of the cyclopentadienyl ancillary ligand in comparison to the pentamethylcyclopentadienyl ligand, allowing an easier coordination of the olefin. Apparently changing the alkyl chain on the *s*-indacene ligand does not influence the catalytic activity.

4. Conclusion

In summary we have synthesized and characterized a new series of zirconium precatalysts using 1,5-dihydro-2,6-diethyl-4,8-dimethyl-*s*-indacene (*s*-Ic^H₂) and 1,5-dihydro-2,6-dibutyl-4,8-dimethyl-*s*-indacene (*s*-Ic^H₂) ligand as well as cyclopentadienyl and pentamethylcyclopentadienyl ligand.

The large bulky ligand tetraalkylated *s*-indacene, forcing the complex to adopt a bent and more rigid structure, despite the fact that these complexes are not ansa-metalloenes. This property results as a promising feature in homogenous catalysis, particularly in the polymerization of ethylene as has been shown for the catalytic tests.

The results have demonstrated that the complexes have applications in homogeneous catalysis, with high catalytic activities for ethylene. The differences in catalytic activities could be attributed to the steric hindrance and the electronic effects of the methyl groups in the pentamethylcyclopentadienyl ligand.

Further attempts to improve the catalytic activity of zirconocenes derived from tetraalkylated *s*-indacene will be performed in the future (different concentration of precatalyst and Al/Zr ratio). We also have the intention of performing the synthesis of new homo- and heterobimetallic systems in order to get insights on the cooperative effects between metals, catalytic properties and material science applications of these complexes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2015.05.011>.

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