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Synthesis and structural characterization of novel three carbon atom bridged *ansa*-bis(indenyl)zirconocene complexes: Applications in ethylene polymerization

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Dedicated to Professor Vukadin Leovac on the happy occasion of his 70th birthday.

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ABSTRACT

The *ansa* indenyl ligand precursors $CH_2CH_2CH_2(C_9H_6R)_2$ (R = Me (**7**), Et (**8**), Pr (**9**)) have been prepared by the reaction of the corresponding lithium indene, $Li(C_9H_6R\text{-}1)$ (R = Me (**4**), Et (**5**), Pr (**6**)), with 1,3-dibromopropane. Compounds **7**–**9** were converted, by the reaction with butyllithium, to the dilithium compounds, $Li_2\{CH_2CH_2CH_2(C_9H_5R\text{-}3)_2\}$ (R = Me (**10**), Et (**11**), Pr (**12**)). The three carbon atom bridge *ansa*-bis(indenyl)zirconium complexes, $[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5R\text{-}3)_2\}Cl_2]$ (R = Me (**13**), Et (**14**) Pr (**15**)) were synthesized from the reaction of **10**–**12** with zirconium tetrachloride. Compounds **13**–**15** have been tested as homogeneous catalysts in the polymerization of ethylene. The molecular structures of **14** and **15** have been determined by single-crystal X-ray diffraction studies.

1. Introduction

Since the discovery by Sinn and Kaminsky [1] that zirconocene complexes in the presence of MAO were able to polymerize olefins there has been a dramatic expansion in this field.

Group 4 metallocene complexes are now well known as excellent single site catalysts in olefin polymerization giving superior activity and selectivity with respect to other catalytic systems [2]. Crucial in the development of these catalysts has been the direct relationship found between complex structure and catalytic behavior [3]. Thus small changes in the structure of the metallocene complex have dramatic effects on the properties of the polymer obtained. Importance has thus been placed on understanding the influence that the differing cyclopentadienyl substituents in the metallocene catalyst have on the polymerization mechanism. The main focus of this research has therefore been centered on the molecular architecture of metallocene complexes as a means towards obtaining polyolefins with consumer defined properties. Despite the fact that many *ansa*-zirconocene complexes have been reported [2,3], few have been described that contain a three carbon alkyl bridge unit [4].

As a continuation of our work in this field [5], we present the synthesis of the three carbon atom bridged *ansa*-bis(indenyl)zirconocene complexes, $[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5R\text{-}3)_2\}Cl_2]$ (R = Me (**13**), Et (**14**), Pr (**15**)), and their structural characterization by single crystal X-ray diffraction studies. We also report the catalytic activity of **13**–**15** in the polymerization of ethylene.

2. Experimental

2.1. General manipulations

All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from sodium and degassed before use. Indene, CH_3I, CH_3CH_2Br, $CH_3CH_2CH_2Br$, 1,3-dibromopropane, $ZrCl_4$ and LiBu (1.6 M in hexane) were purchased from Aldrich and used directly. $C_9H_7R\text{-}1$ (**1**) (R = Me (**1**), Et (**2**), Pr (**3**)) were prepared by the reaction in THF of indene with CH_3I, CH_3CH_2Br, $CH_3CH_2CH_2Br$, respectively. ^1H NMR spectra were recorded on a Varian Mercury FT-400

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spectrometer. Microanalyses were carried out with a Perkin-Elmer 2400 or LECO CHNS-932 microanalyzer. Polymer molecular weights and distribution were determined by GPC (Waters 150C Plus or Alliance GPC-2000) in 1,2,4-trichlorobenzene at 150 °C, using standard polystyrene calibration.

2.2. Synthesis of compounds

2.2.1. Synthesis of Li(C_9H_6Me-1) (**4**)

LiBu (7.7 mL, 12.30 mmol, 1.6 M in hexane) was added dropwise to a solution of C_9H_7Me-1 (**1**) (1.63 g, 12.30 mmol) in Et_2O (40 mL) at −78 °C. The mixture was warmed to 25 °C and stirred for 4 h. Solvent was then removed *in vacuo* giving a white solid, which was washed with hexane (2 × 50 mL) and dried under vacuum to give the title compound as a white powder. Yield 1.57 g, 94%. $C_{10}H_9Li$ (136.1): Calc. C, 88.24; H, 6.66. Found: C, 87.93; H, 6.62%.

2.2.2. Synthesis of Li(C_9H_6Et-1) (**5**)

The preparation of **5** was carried out in an identical manner to that of **4**. C_9H_7Et-1 (**2**) (1.52 g, 10.40 mmol) and LiBu (6.5 mL, 10.40 mmol, 1.6 M in hexane). Yield 1.39 g, 89%. $C_{11}H_{11}Li$ (150.1): Calc. C, 87.99; H, 7.38. Found: C, 87.62; H, 7.31%.

2.2.3. Synthesis of Li(C_9H_6Pr-1) (**6**)

The preparation of **6** was carried out in an identical manner to that of **4**. C_9H_7Pr-1 (**3**) (1.82 g, 11.34 mmol) and LiBu (7.1 mL, 11.34 mmol, 1.6 M in hexane). Yield 1.69 g, 91%. $C_{12}H_{13}Li$ (164.1): Calc. C, 87.79; H, 7.98. Found: C, 87.48; H, 7.96%.

2.2.4. Synthesis of $CH_2CH_2CH_2(C_9H_6Me)_2$ (**7**)

1,3-Dibromopropane (0.99 g, 4.90 mmol) in THF (30 mL) was added to a solution of Li(C_9H_6Me-1) (**4**) (1.47 g, 10.80 mmol) in THF (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. Solvent was removed *in vacuo* and hexane (150 mL) was added to the resulting dark orange oil. The mixture was filtered and the solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow solid. Yield 1.21 g, 82%. $C_{23}H_{24}$ (300.4): Calc. C, 91.95; H, 8.05. Found: C, 91.87; H, 8.07%.

2.2.5. Synthesis of $CH_2CH_2CH_2(C_9H_6Et)_2$ (**8**)

The preparation of **8** was carried out in an identical manner to that of **7**. Li(C_9H_6Et-1) (**5**) (1.58 g, 10.50 mmol) and 1,3-dibromopropane (0.99 g, 4.90 mmol). Yield 1.04 g, 64%. $C_{25}H_{28}$ (328.5): Calc. C, 91.41; H, 8.59. Found: C, 91.32; H, 8.62%.

2.2.6. Synthesis of $CH_2CH_2CH_2(C_9H_6Pr)_2$ (**9**)

The preparation of **9** was carried out in an identical manner to that of **7**. Li(C_9H_6Pr-1) (**6**) (1.72 g, 10.45 mmol) and 1,3-dibromopropane (0.99 g, 4.90 mmol). Yield 1.27 g, 72%. $C_{25}H_{28}$ (356.5): Calc. C, 91.95; H, 9.05. Found: C, 91.89; H, 9.04%.

2.2.7. Synthesis of $Li_2\{CH_2CH_2CH_2(C_9H_5Me\text{-}3)_2\}$ (**10**)

LiBu (4.4 mL, 7.00 mmol, 1.6 M in hexane) was added dropwise to a solution of $CH_2CH_2CH_2(C_9H_6Me)_2$ (**7**) (1.01 g, 3.32 mmol) in Et_2O (40 mL) at −78 °C. The mixture was warmed to 25 °C and stirred for 4 h. Solvent was then removed *in vacuo* giving a white solid, which was washed with hexane (2 × 50 mL) and dried under vacuum to give the title compound as a white powder. Yield 0.97 g, 93%. $C_{23}H_{22}Li_2$ (312.3): Calc. C, 88.45; H, 7.10. Found: C, 88.29; H, 7.02%.

2.2.8. Synthesis of $Li_2\{CH_2CH_2CH_2(C_9H_5Et\text{-}3)_2\}$ (**11**)

The preparation of **11** was carried out in an identical manner to that of **10**. $CH_2CH_2CH_2(C_9H_6Et)_2$ (**8**) (1.00 g, 3.01 mmol) and LiBu (4.0 mL, 6.40 mmol, 1.6 M in hexane). Yield 0.90 g, 88%. $C_{25}H_{26}Li_2$ (340.4): Calc. C, 88.22; H, 7.70. Found: C, 87.81; H, 7.67%.

2.2.9. Synthesis of $Li_2\{CH_2CH_2CH_2(C_9H_5Pr\text{-}3)_2\}$ (**12**)

The preparation of **12** was carried out in an identical manner to that of **10**. $CH_2CH_2CH_2(C_9H_6Pr)_2$ (**9**) (0.92 g, 2.55 mmol) and LiBu (3.5 mL, 5.60 mmol, 1.6 M in hexane). Yield 0.79 g, 84%. $C_{27}H_{30}Li_2$ (368.4): Calc. C, 88.02; H, 8.21. Found: C, 87.83; H, 8.17%.

2.2.10. Synthesis of $[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5Me\text{-}3)_2\}Cl_2]$ (**13**)

A solution of $Li_2\{CH_2CH_2CH_2(C_9H_5Me\text{-}3)_2\}$ (**10**) (0.76 g, 2.44 mmol) in THF (40 mL) was added to $ZrCl_4$ (0.57 g, 2.44 mmol) in THF at 0 °C. The reaction mixture was stirred under reflux for 18 h. Solvent was removed in vacuum and a toluene:hexane mixture (9:1) (125 mL) added to the resulting solid. The mixture was filtered and the filtrate concentrated (20 mL) and cooled to −30 °C to yield crystals of the title complex. Yield 0.54 g, 48%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.84 (2H), 2.60 (4H) (m, CH_2CH_2-CH_2), 3.28 (s, 6H, 2 × CH_3), 6.42 (2H), 7.00–7.40 (8H) (m, 2 × C_9H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 22.1 ($CH_2CH_2CH_2$), 25.8 (CH_3), 30.6 ($CH_2CH_2CH_2$), 105.8, 115.3, 121.0, 123.5, 126.1, 126.7, 126.9, 127.2, 128.7, 129.3 (2 × C_9H_5). $C_{23}H_{22}Cl_2Zr$ (460.6): Calc. C, 59.98; H, 4.81. Found: C, 59.49; H, 4.74%.

2.2.11. Synthesis of $[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5Et\text{-}3)_2\}Cl_2]$ (**14**)

The preparation of **14** was carried out in an identical manner to that of **13**. $Li_2\{CH_2CH_2CH_2(C_9H_5Et\text{-}3)_2\}$ (**11**) (0.60 g, 1.76 mmol) and $ZrCl_4$ (0.41 g, 1.76 mmol). Yield 0.28 g, 33%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 (m, 6H, 2 × CH_2CH_3), 2.47 (4H), 2.74 (2H) (m, $CH_2CH_2CH_2$), 3.05 (m, 4H, 2 × CH_2CH_3), 5.99 (2H), 7.11 (2H), 7.24 (2H), 7.52 (4H) (m, 2 × C_9H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.2 ($CH_2CH_2CH_2$), 22.7 (CH_2CH_3), 26.8 (CH_2-CH_3), 36.9 ($CH_2CH_2CH_2$), 103.5, 113.3, 120.7, 123.9, 127.1, 127.8, 128.2, 128.6, 129.7, 130.3 (2 × C_9H_5). $C_{25}H_{26}Cl_2Zr$ (488.6): Calc. C, 61.45; H, 5.36. Found: C, 61.09; H, 5.29%.

2.2.12. Synthesis of $[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5Pr\text{-}3)_2\}Cl_2]$ (**15**)

The preparation of **15** was carried out in an identical manner to that of **13**. $Li_2\{CH_2CH_2CH_2(C_9H_5Pr\text{-}3)_2\}$ (**12**) (0.50 g, 1.36 mmol) and $ZrCl_4$ (0.32 g, 1.36 mmol). Yield 0.27 g, 39%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.83 (m, 6H, 2 × $CH_2CH_2CH_3$), 1.36 (m, 4H, 2 × $CH_2CH_2CH_3$), 2.30 (4H), 2.79 (2H) (m, $CH_2CH_2CH_2$), 3.00 (m, 4H, 2 × $CH_2CH_2CH_3$), 6.04 (2H), 7.13 (2H), 7.27 (2H), 7.55 (4H) (m, 2 × C_9H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.2 ($CH_2CH_2CH_2$), 21.7, 23.9, 31.3 ($CH_2CH_2CH_3$), 37.4 ($CH_2CH_2CH_2$), 100.2, 117.4, 121.4, 125.3, 128.6, 129.1, 130.5, 131.1, 134.0, 138.3 (2 × C_9H_5). $C_{27}H_{30}Cl_2Zr$ (516.7): Calc. C, 62.77; H, 5.85. Found: C, 62.31; H, 5.81%.

2.3. Data collection and structural refinement of **14** and **15**

The data of **14** and **15** were collected with a CCD Oxford Xcalibur S (λ(Mo Kα) = 0.71073 Å) using ω and φ scans mode. Semi-empirical from equivalents absorption corrections were carried out with SCALE3 ABSPACK [6]. All the structures were solved by direct methods [7]. Structure refinement was carried out with SHELXL-97 [8]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated with the riding model and refined isotropically. Table 1 lists crystallographic details and refinement details.

2.4. Ethylene polymerization

A 1 L glass autoclave was heated to 60 °C. Under an inert N_2 atmosphere, the zirconocene catalyst ([Zr] = 3 × 10^{-5} mol L^{-1}), and MAO (10% in toluene, [Al] = 3 × 10^{-2} mol L^{-1}) and toluene

Table 1
Crystallographic data of **14** and **15**.

Formula	$C_{25}H_{26}Cl_2Zr$	$C_{27}H_{30}Cl_2Zr$
Formula weight	488.58	516.63
T (K)	150(2)	130(2)
Crystal system	monoclinic	monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
a (Å)	10.4635(2)	15.0415(5)
b (Å)	12.5147(2)	8.2515(4)
c (Å)	15.6988(2)	19.3276(8)
α (°)	90	90
β (°)	96.7680(10)	97.805(4)
γ (°)	90	90
V (Å^3)	2041.39(6)	2376.62(17)
Z	4	4
D_{calc} (Mg m^{-3})	1.590	1.444
μ (mm^{-1})	0.809	0.699
$F(000)$	1000	1064
Crystal dimension (mm)	0.4 × 0.3 × 0.25	0.2 × 0.15 × 0.05
θ range (°)	2.55–30.51	2.68–25.35
hkl ranges	$-14 \leqslant h \leqslant 14$	$-18 \leqslant h \leqslant 18$
	$-17 \leqslant k \leqslant 17$	$-9 \leqslant k \leqslant 9$
	$-22 \leqslant l \leqslant 22$	$-23 \leqslant l \leqslant 23$
Collected reflections	57944	43510
Independent reflections	6225 [R_{int} = 0.0283]	4340 [R_{int} = 0.0982]
Completeness	99.9	99.9
Data/restraints/parameters	6225/0/255	4340/0/273
Goodness-of-fit on F^2	1.089	1.089
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0320	R_1 = 0.0630
	wR_2 = 0.0940	wR_2 = 0.1947
Final R indices (all data)	R_1 = 0.0409	R_1 = 0.1087
	wR_2 = 0.1017	wR_2 = 0.2118
Largest difference in peak and hole (e Å^{-3})	1.576 and −0.633	1.851 and −1.004

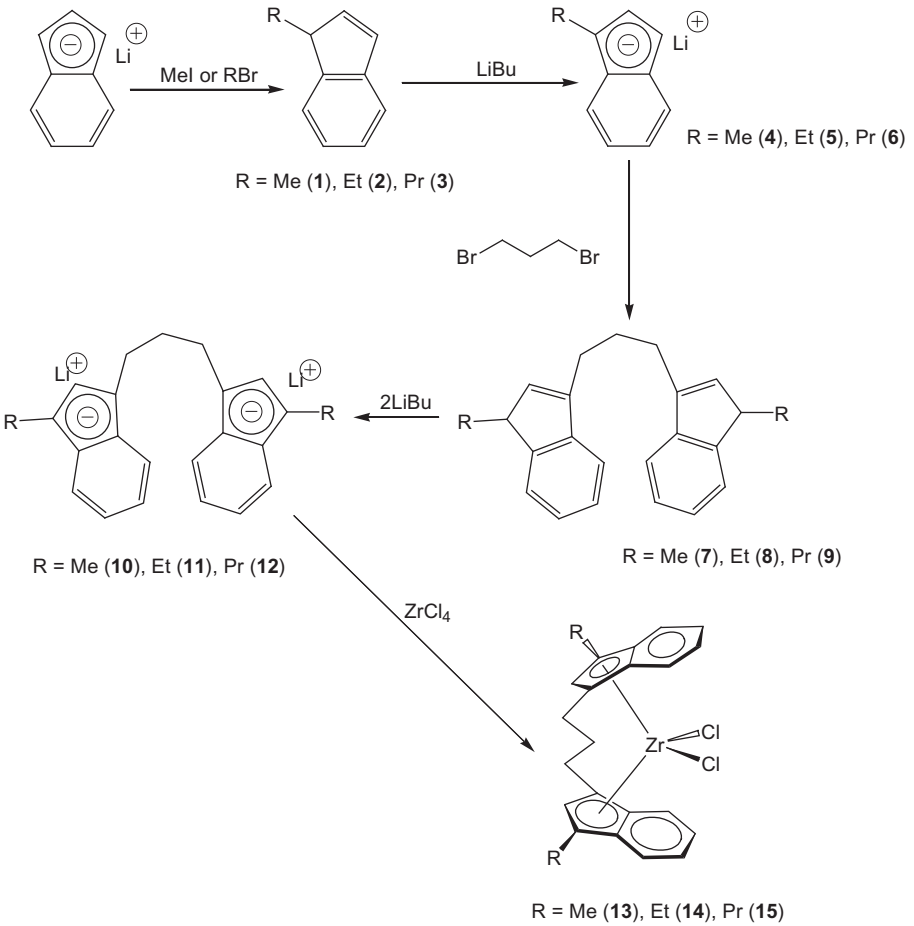
(200 mL) were mixed together for 15 min. The N_2 pressure inside the autoclave was reduced by applying vacuum. Ethylene pressure of 2 bar was then applied and maintained to the autoclave and stirring of the mixture commenced (1000 rpm). After exactly 15 min, stirring was halted and the ethylene pressure released. Excess MAO was then destroyed by adding cautiously a mixture of methanol/HCl (9:1). The polymer was isolated by filtration and washed with ethanol and dried under vacuum at 90 °C for 16 h.

3. Results and discussion

3.1. Synthesis and characterization of ansa-zirconocene complexes

Compounds **1**–**15** were prepared as indicated in Scheme 1. The alkyl substituted indene compounds, C_9H_7R-1 (R = Me (**1**), Et (**2**), Pr (**3**)) were prepared via the reaction of the corresponding iodo or bromo-alkyl with indene. The lithium derivatives, Li(C_9H_6R-1) (R = Me (**4**), Et (**5**), Pr (**6**)), were obtained, in the traditional manner by the reaction of **1**–**3** with butyl lithium (Scheme 1). Compounds **4**–**6** were isolated as highly moisture and oxygen sensitive white solids and characterized by elemental analysis (see Section 2.2.).

The preparation of the *ansa* ligand precursors, $CH_2CH_2CH_2(C_9H_6R)_2$ (R = Me (**7**), Et (**8**), Pr (**9**)), was achieved by the reaction of two molar equivalents of **4**–**6** with one equivalent of 1,3-dibromopropane. The dilithium derivatives, $Li_2\{CH_2CH_2CH_2(C_9H_5R\text{-}3)_2\}$ (R = Me (**10**), Et (**11**), Pr (**12**)), were obtained by the reaction of **7**–**9** with two molar equivalents of butyl lithium and isolated as highly moisture and oxygen sensitive white solids and characterized by elemental analysis (see Section 2.2.).



Scheme 1. Synthesis of **1**–**15**.

The reaction of the dilithium derivatives **10**–**12** with $ZrCl_4$, gave the corresponding *ansa*-metallocene dichloride complexes [Zr{$CH_2CH_2CH_2(\eta^5$-C_9H_5R-3)$_2$}Cl_2] (R = Me (**13**), Et (**14**), Pr (**15**)) (Scheme 1), which were isolated as yellow crystalline solids and characterized spectroscopically.

The ^{1}H NMR spectra of **13**–**15** show multiplets for the protons of the indenyl moiety (between 6.0 and 7.5 ppm). Two multiplet signals corresponding to the $CH_2CH_2CH_2$ bridging unit (between 1.8 and 2.8 ppm) were also observed. For **13** the signal corresponding to the methyl substituent was recorded at 3.28 ppm. The ethyl substituent in **14** gave two multiplets at 0.91 and 3.05 ppm and the propyl group in **15** three multiplets at 0.83, 1.36 and 3.00 ppm. In **13**–**15** the NMR spectra indicated the predominance (>95%) of the *rac* isomer (as confirmed by their single crystal X-ray structures, see Section 3.2.).

3.2. Structural study. Single crystal X-ray structures of *14* and *15*

Compounds [Zr{$CH_2CH_2CH_2(\eta^5$-C_9H_5Et-3)$_2$}Cl_2] (**14**) and [Zr{$CH_2CH_2CH_2(\eta^5$-C_9H_5Pr-3)$_2$}Cl_2] (**15**) crystallize in the monoclinic *P*2(1)/*c* space group with four molecules in the unit cell. The structures of **14** (Fig. 1) and **15** (Fig. 2) show the typical bent metallocene conformation observed in other zirconocene dichloride complexes. The *ansa*-indenyl ligand chelates the zirconium atom with cyclopentadienyl rings of the indenyl ligand bound to the metal in an η^5 manner.

The Cent(1)–Zr(1)–Cent(2) angle of 130.12° and 129.66° for **14** and **15** is similar to those reported for other *ansa*-zirconocene complexes [9] (see Table 2). The Cl(1)–Zr(1)–Cl(2) angles of 95.427(18)° and 93.80(6)° for **14** and **15**, respectively, are similar to those recorded for related *ansa*-zirconocene complexes and the distances, Zr–Cl ca. 2.45 Å are also in the expected range.

The ethyl and propyl substituents in **14** and **15**, respectively, are nearly blocking both chlorine atoms (Cl(1) and Cl(2)) as can be deduced from the dihedral angles θ Cl(2)–Zr(1)–C(12)–C(24) = 25.78° and Cl(1)–Zr(1)–C(3)–C(22) = −50.12° in **14** and θ Cl(2)–Zr(1)–C(12)–C(25) = −51.58° and Cl(1)–Zr(1)–C(3)–C(22) = 32.98° in **15**. These angles show that the position of the alkyl substituent should therefore be influential in the coordination behavior of the olefin monomer at this site during polymerization and may reduce the polymerization activity of these compounds.

Interestingly, in the structure of **14** a six-membered ring in a chair conformation is formed by Zr(1)–C(1)–C(19)–C(20)–C(21)–C(10) (Fig. 3) in which C(20) and Zr(1) are located 0.701 Å (above) and 0.595 Å (below) out of the mean plane formed by C(1)–C(19)–C(20)–C(21), while in the case of structure **15** the six-membered ring formed by Zr(1)–C(1)–C(19)–C(20)–C(21)–C(10) is in a boat conformation (Fig. 3) with C(20) and Zr(1) located 0.714 and 0.635 Å, respectively, out of the mean plane formed by C(1)–C(19)–C(20)–C(21).

The C–C bond distances of the propylene bridges as well as the alkyl substituents (ethyl or propyl groups) in complexes **14** and **15** are all of them between ca. 1.49 and 1.51 Å which are in the expected range for single bonds.

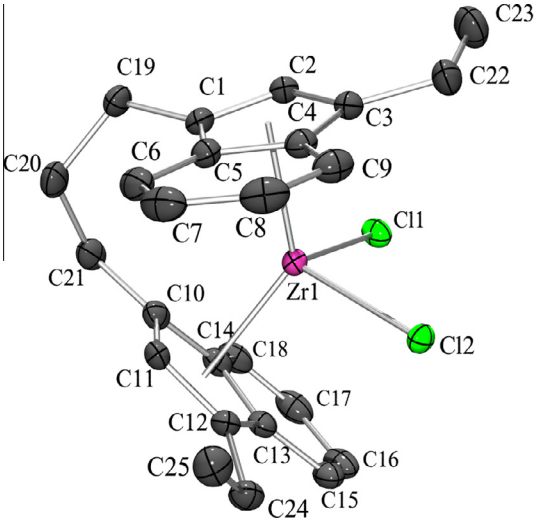


Fig. 1. Molecular structure of **14** with thermal ellipsoids at 30% probability. H atoms have been omitted for clarity.

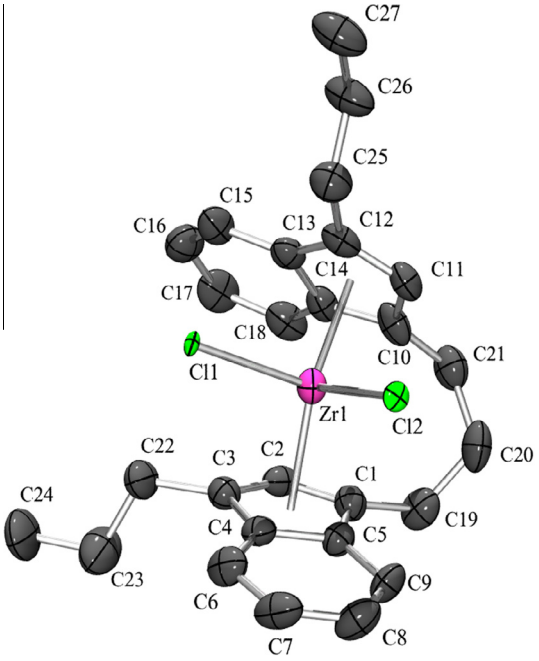


Fig. 2. Molecular structure of **15** with thermal ellipsoids at 30% probability. H atoms have been omitted for clarity.

3.3. Ethylene polymerization

The polymerization of ethylene, using the *ansa*-zirconocene complexes **13**–**15**, as catalyst has been carried out. The polymerization experiments were conducted with a MAO-metal catalyst ratio of 1000:1, at 60 °C and at olefin pressure of 2 bar during 15 min. Polymerization was also carried out with the reference compound [Zr(η^5-C_5H_5)$_2$$Cl_2$], under the same experimental conditions. The catalytic activities and polymer molecular weight and distribution values are given in Table 3.

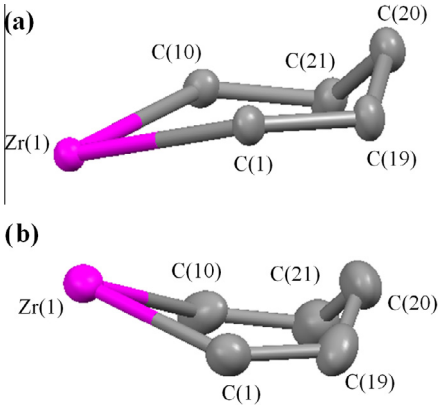


Fig. 3. Detail of the six-membered ring formed by Zr(1)–C(1)–C(19)–C(20)–C(21)–C(10) in (a) **14** (chair conformation) and (b) **15** (boat conformation).

Table 2
Selected bond lengths (Å), angles (°) and dihedral angles (°) for **14** and **15**.

	14	15
Zr–Cent(1)	2.227	2.220
Zr–Cent(2)	2.241	2.212
Zr–Cl(1)	2.4336(5)	2.5233(17)
Zr–Cl(2)	2.490(2)	2.4895(17)
C(1)–C(19)	1.504(3)	1.512(12)
C(10)–C(21)	1.506(3)	1.518(12)
C(19)–C(20)	1.523(3)	1.497(13)
C(20)–C(21)	1.519(3)	1.533(13)
C(3)–C(22)	1.503(3)	1.523(12)
C(22)–C(23)	1.503(3)	1.499(13)
C(12)–C(24)	1.503(3)	
C(24)–C(25)	1.514(3)	
C(12)–C(25)		1.506(12)
C(25)–C(26)		1.480(13)
Cent(1)–Zr–Cent(2)	130.12	129.66
Cl(1)–Zr(1)–Cent(1)	107.78	106.27
Cl(2)–Zr(1)–Cent(1)	105.71	107.61
Cl(1)–Zr(1)–Cent(2)	106.14	107.03
Cl(2)–Zr(1)–Cent(2)	106.28	106.66
Cl(1)–Zr(1)–Cl(2)	95.427(18)	93.80(6)
C(1)–C(19)–C(20)	117.42(18)	117.5(8)
C(10)–C(21)–C(20)	115.62(19)	116.2(8)
C(19)–C(20)–C(21)	114.21(19)	113.4(7)
C(3)–C(22)–C(23)	114.3(2)	115.0(8)
C(12)–C(24)–C(25)	114.32(18)	
C(12)–C(25)–C(26)		111.9(8)
Cl(2)–Zr(1)–C(12)–C(24)	25.78	
Cl(1)–Zr(1)–C(3)–C(22)	−50.12	32.98
Cl(2)–Zr(1)–C(12)–C(25)		−51.58

Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(10)–C(14), respectively.

Table 3
Ethylene polymerization results for **13**–**15** and $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$.[a,b]

Catalyst	Activity[b]	M_w (g mol^{-1})	M_w/M_n
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	12716	73 182	2.9
$[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5Me\text{-}3)_2\}Cl_2]$ (**13**)	1540	535 320	3.3
$[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5Et\text{-}3)_2\}Cl_2]$ (**14**)	1315	514 760	3.1
$[Zr\{CH_2CH_2CH_2(\eta^5\text{-}C_9H_5Pr\text{-}3)_2\}Cl_2]$ (**15**)	850	573 480	3.5

[a] At 60 °C, 2 bar monomer pressure, 200 mL toluene, [Al] = 3×10^{-2} mol L^{-1}, [Zr] = 3×10^{-5} mol L^{-1}, t_{Pol} = 15 min.
[b] In kg Pol (mol Zr h bar)$^{-1}$.

The *ansa*-zirconocene complexes **13**–**15** were all active as catalysts in the polymerization of ethylene with activities increasing in this order: **15** < **14** < **13**. The decrease in activity corresponds directly to the increase in size of the alkyl substituent. The single crystal X-ray structures show that the ethyl and propyl substituents in **14** and **15** are close to the chlorine atoms. Hence, the steric impositions of the alkyl substituent can be considered to be influential in the coordination behavior of the olefin monomer at zirconium during polymerization, with the larger substituents giving lower catalytic activity. On comparison with the reference catalyst $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$, activities recorded for **13**–**15** were around 10 times lower but in the same order to that previously reported by us for bis(indenyl)zirconium dichloride [10].

High molecular weight polyethylene (ca. 500 000) was produced with catalysts **13**–**15**. Polydispersity values of about 3, typical for single-site metallocene catalyst, were obtained for the polymers produced with **13**–**15**.

4. Conclusions

In this paper we have reported the synthesis of new three carbon atom bridged *ansa*-bis(indenyl)zirconocene complexes The structural characterization of these complexes is also described. These compounds have been shown to act as catalysts in the polymerization of ethylene with the catalytic activity decreasing with the increase in size of the alkyl substituent.

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Appendix A.

CCDC 978936 (**14**) and 978937 (**15**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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