Group (IV) Metallocene Complexes
with Bulky ω-aryloxy Alkyl-Substituted Indenyl Ligands
as Catalyst Precursors
for Homogeneous Ethylene Polymerization

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ABSTRACT: *A series of seven new complexes of zirconium and hafnium with bulky ω-aryloxyalkyl substituted indenyl ligands were synthesized and characterized by NMR spectroscopy and elemental analysis. These complexes were activated with methylaluminoxane and tested for homogeneous ethylene polymerization. The zirconium catalysts showed higher activities than their hafnium analogues. The effects of increasing separation between the indenyl and the aryloxy substituent and the introduction of an extra methyl group on the indenyl moiety were also investigated. Catalyst **6** bearing a spacer chain of three methylene groups between the indenyl and aryloxy substituents showed the highest activity (15500 kg PE/mol cat. h). The increase in the spacer chain length resulted in the decrease in catalyst activities.*

KEYWORDS: *Metallocene complexes; Bulky ω-aryloxyalkyl-substituted indenyl ligands; ethylene polymerization.*

INTRODUCTION

The synthesis of a huge number of metallocene catalysts during the past three decades can be justified with an excellent structure-property relationship of these catalysts. Tailoring can be achieved by varying a number of structural parameters at the ligands such as bridging, steric bulk and functional groups [1-8]. The introduction of bulky substituents at the indenyl ligands of non-bridged metallocene catalysts result in hindered rotation of the ligand moieties around the ligand-metal bond axis [9-25].

Such systems have been extensively studied for the synthesis of elastomeric polypropylene. Similarly the introduction of a heteroatom in the ligand structure of the catalyst can confer special properties to the produced polyolefin. Many research groups have introduced nitrogen, phosphorous, oxygen and sulphur bearing groups on cyclopentadienyl or indenyl ligands and investigated their effect on olefin polymerization properties of the resulting catalysts [26-41]. Here we are
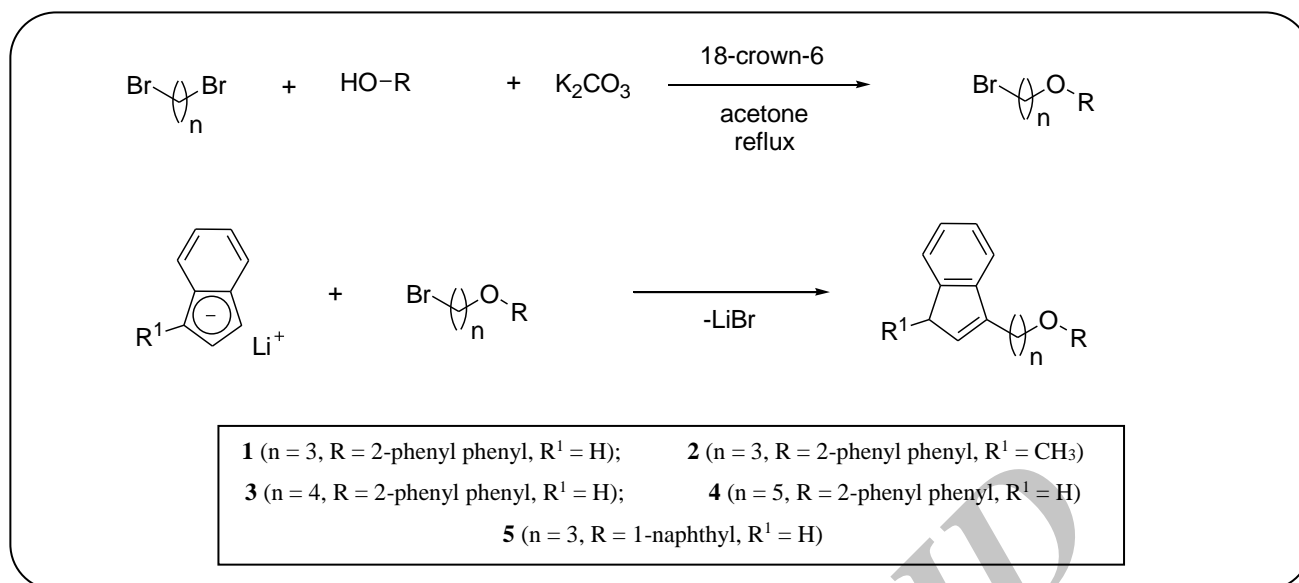
Scheme 1: Synthesis of compounds 1-5.

reporting the synthesis of zirconium and hafnium complexes with bulky ω-aryloxyalkyl-substituted indenyl ligands and their use as catalysts for homogeneous ethylene polymerization after activation with methylaluminoxane (MAO).

EXPERIMENTAL SECTION
General aspects

All reactions were routinely carried out using Schlenk line technique. Argon was used as an inert gas. Diethyl ether, n-pentane and toluene were purified by distillation over Na/K alloy. Deuterated solvents ($CDCl_3$ and C_6D_6) were purchased from Eurisotop and stored over molecular sieves (3Å). Argon (5.0) and ethylene (3.5) were purchased from Rieβner Company and purified prior to their use. Methylaluminoxane (10% in toluene) was purchased from Chemtura Europe Limited. All other starting materials were commercially available and used as received. NMR spectra were recorded with a Varian Inova (400 MHz) spectrometer at 298K. GC/MS spectra were recorded with a FOCUS Thermo gas chromatograph combined with a DSQ mass detector. Elemental analyses were performed with a Vario EL III CHN instrument. DSC analyses of the polymer samples were performed on a Mettler Toledo DSC/SDTA 821e instrument.

General description of the ethylene polymerization experiments

Complexes **6-12** were activated with a 2000-molar excess of methylaluminoxane (MAO) in 10 ml toluene.

The activated complexes were suspended in 250 mL n-pentane and transferred to a 1 liter Büchi autoclave under inert atmosphere of argon. The temperature of the system was maintained at 65 °C and an ethylene pressure of 10 bar was applied. After one hour the ethylene flow was disconnected and the system was cooled to room temperature. The pressure was released and the obtained polymer was filtered over a frit, washed with dilute hydrochloric acid, water and finally with acetone and dried under vacuum.

General procedure for the synthesis of ω-aryloxyalkyl-substituted indenyl compounds (1-5)

ω-Aryloxyalkyl-substituted indenyl compounds were synthesized via a two step reaction. In the first step ω-bromo-1-aryloxyalkanes were synthesized by refluxing a mixture of 10 mmol of an appropriate phenol or naphthol, 10 mmol of potassium carbonate, an excess of dibromoalkane and catalytic amounts of a crown ether (18-crown-6) in acetone for 12-24 hours. Acetone was removed, 200 ml diethyl ether was added and the mixture was washed with distilled water (200 ml) and dried over sodium sulphate. The solvent was removed and the residue was distilled to obtain the desired ω-bromo-1-aryloxyalkane compounds in 60-70% yield. In the second step an amount of 5 mmol of n-butyllithium (1.6 M in hexanes) was added to 5 mmol of indene dissolved in 100 mL diethyl ether at -78 °C. After warming up to room temperature and stirring for further 3 hours, the solution was cooled to -78 °C and an amount of 5 mmol

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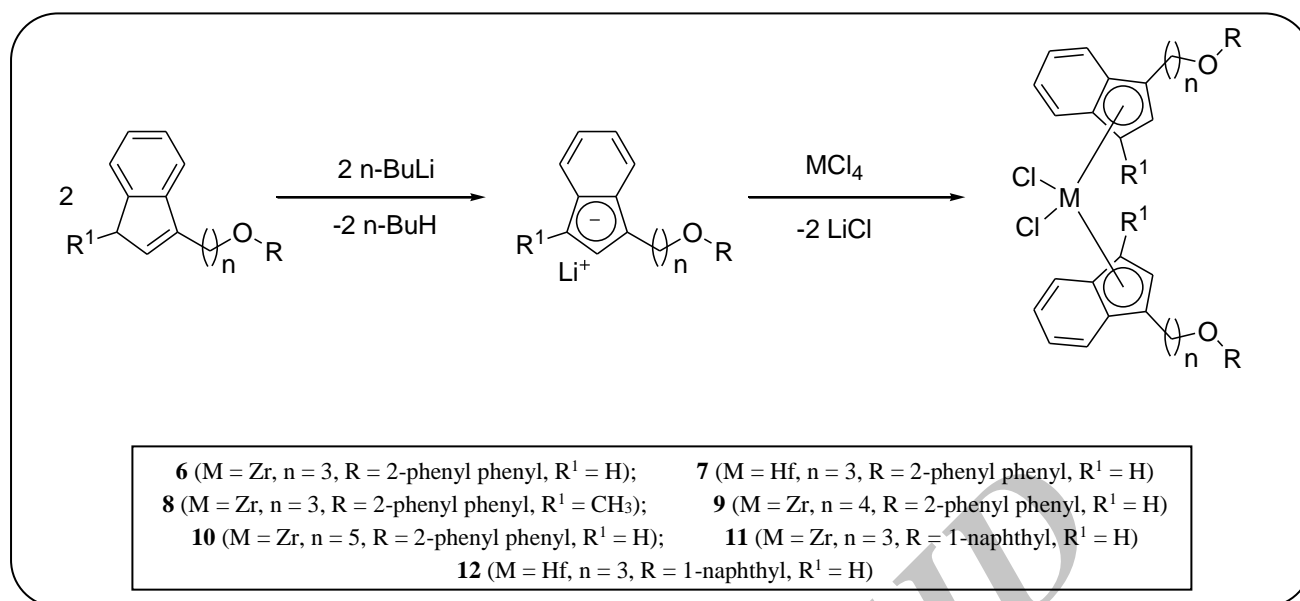
Scheme 2: Synthesis of complexes 6-12

Fig. 1: ¹H-NMR spectrum of compound 1.
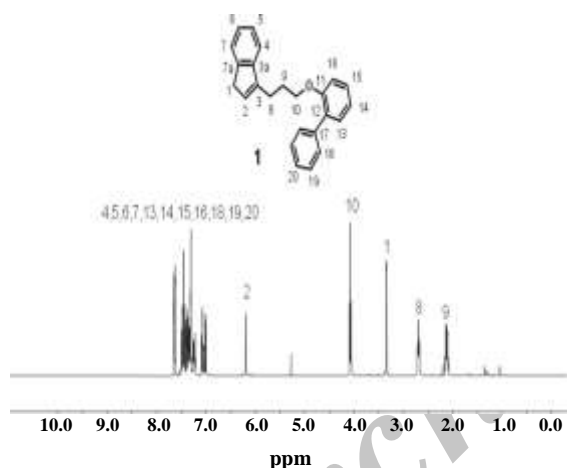
Fig. 2: ¹H-NMR spectrum of compound 2.

of the ω-bromo-1-aryloxyalkane was added. The solution was allowed to warm up to room temperature and stirred for a further 12 hours. The solution was washed with distilled water and dried over sodium sulphate. Removal of the solvent provided the desired a ω-aryloxyalkyl-substituted indenyl compound in almost quantitative yield.

1: ¹H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.65-7.62 (2H, m), 7.50-7.43 (3H, m), 7.41-7.30 (5H, m), 7.26-7.22 (1H, m), 7.09-7.05 (1H, m), 7.02-6.99 (1H, m), 6.20 (1H, br, Ind-H2), 4.08 (2H, t, *J* 6.1 Hz, OCH$_2$), 3.34 (2H, br,
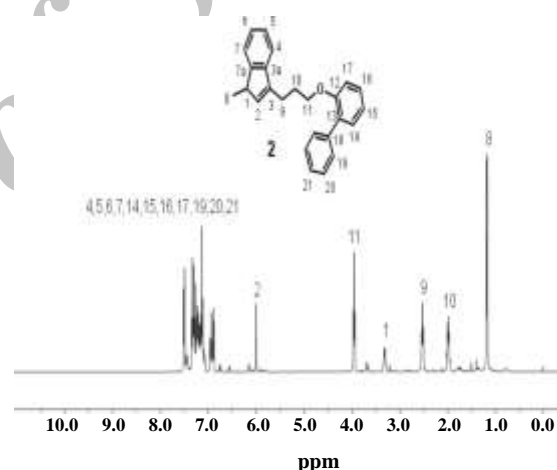
Ind-H1), 2.70 (2H, t, *J* 7.6 Hz, CH$_2$), 2.12 (2H, dt, CH$_2$) ppm.

¹³C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 155.9, 145.2, 144.4, 143.6, 138.6, 131.0 (C$_q$), 129.9, 129.6, 128.5, 128.2, 127.8, 126.7, 126.0, 124.5, 123.7, 120.8, 118.9, 112.4 (CH), 67.7 (OCH$_2$), 37.7 (CH$_2$-Ind), 27.8, 24.2 (CH$_2$) ppm.

MS: 326 (M$^+$, 6), 196 (100), 141 (53), 128 (96), 115 (76)

2: ¹H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.52-7.48 (2H, m), 7.35-7.10 (9H, m), 6.97-6.92 (1H, m), 6.90-6.87 (1H, m), 6.00 (1H, br, Ind-H2), 3.95 (2H, t, *J* 6.0 Hz, OCH$_2$), 3.35-3.28 (1H, m, Ind-H1), 2.53 (2H, t, *J* 7.6 Hz,

Fig. 3: ^{1}H-NMR spectrum of complex 6
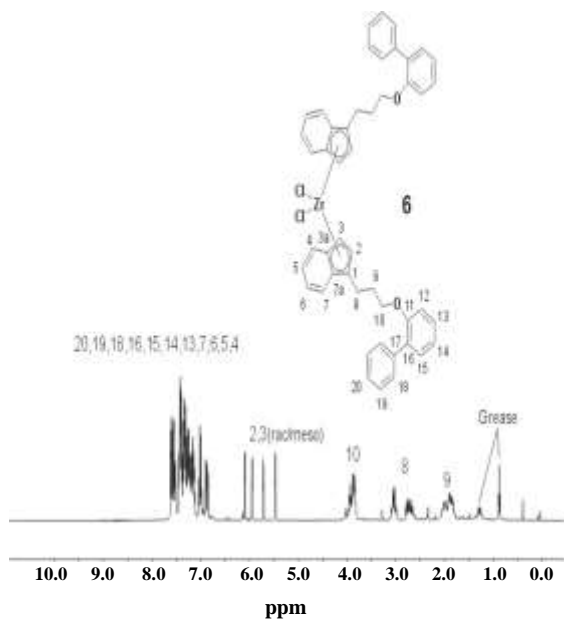
Fig. 4: ^{1}H NMR spectrum of complex 8.

CH$_2$), 2.03-1.94 (2H, m, CH$_2$), 1.18 (3H, d, *J* 7.3 Hz, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 155.9, 149.9, 144.2, 141.8, 138.7, 131.0 (C$_q$), 135.5, 130.9, 129.6, 128.6, 127.9, 126.8, 126.2, 124.8, 122.6, 120.8, 119.0, 112.5 (CH), 67.7 (OCH$_2$), 43.6 (CH-Ind), 27.8, 24.1 (CH$_2$), 16.3 (CH$_3$) ppm

MS: 340 (M$^+$, 6), 196 (35), 171 (100), 129 (95), 115 (32).

3: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.57-7.54 (2H, m), 7.46-7.43 (1H, m), 7.39-7.26 (7H, m), 7.21-7.17 (1H, m), 7.03-6.99 (1H, m), 6.97-6.94 (1H, m), 6.14 (1H, br, Ind-H2), 3.99 (2H, t, CH$_2$), 3.30 (2H, br, Ind-CH$_2$), 2.57-2.51 (2H, m, CH$_2$), 1.84-1.78 (4H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 155.9, 145.4, 144.4, 144.1, 138.6, 130.9 (C$_q$), 130.8, 129.5, 128.5, 127.8, 126.7, 125.9, 124.4, 123.6, 120.8, 118.9, 112.4 (CH), 68.1 (OCH$_2$), 37.6 (CH$_2$-Ind), 29.1, 27.3, 24.5 (CH$_2$) ppm.

MS: 340 (M$^+$, 3), 171 (100), 129 (84), 115 (44).

4: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.60-7.49 (2H, m), 7.47-7.14 (9H, m), 7.05-6.88 (2H, m), 6.14 (1H, br, Ind-H2), 3.93 (2H, t, OCH$_2$), 3.29 (2H, br, Ind-CH$_2$), 2.57-2.45 (2H, m, CH$_2$), 1.80-1.61 (4H, m, CH$_2$), 1.56-1.42 (2H, m, CH$_2$) ppm.
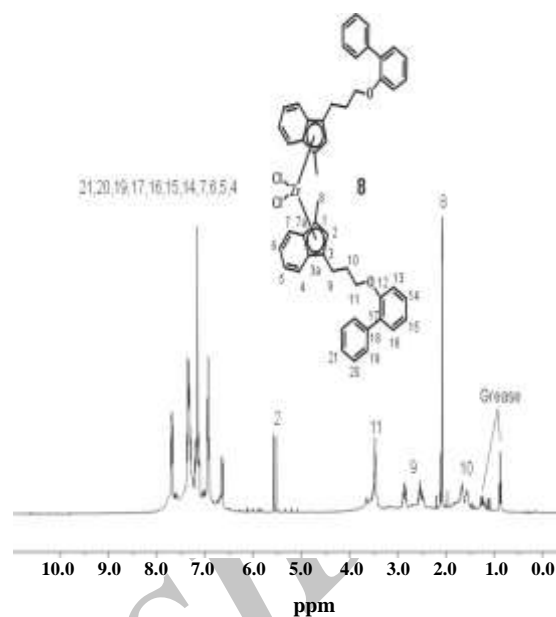
^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 155.9, 145.4, 144.4, 144.3, 138.6, 130.9 (C$_q$), 130.8, 129.5, 128.4, 127.7, 127.6, 126.6, 125.9, 124.4, 123.6, 120.7, 118.8, 112.4 (CH), 68.2 (OCH$_2$), 37.6 (CH$_2$-Ind), 29.0, 27.6, 27.5, 26.0 (CH$_2$).

MS: 354 (M$^+$, 1), 224 (8), 185 (100), 128 (76), 117 (54), 115 (42).

5: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 8.46-8.40 (1H, m), 7.92-7.84 (1H, m), 7.60-7.54 (3H, m), 7.52-7.49 (2H, m), 7.46-7.37 (2H, m), 7.34-7.28 (1H, m), 6.88-6.83 (1H, m), 6.34 (1H, br, Ind-H2), 4.26 (2H, t, OCH$_2$), 3.41 (2H, br, Ind-CH$_2$), 2.98-2.90 (2H, m, CH$_2$), 2.43-2.35 (2H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 154.7, 145.3, 144.5, 143.6, 134.5, 125.7 (C$_q$), 128.3, 127.4, 126.3, 126.0, 125.9, 125.1, 124.6, 123.8, 122.0, 120.0, 118.9, 104.5 (CH), 67.4 (OCH$_2$), 37.7 (CH$_2$-Ind), 27.7, 24.4 (CH$_2$) ppm.

MS: 300 (M$^+$, 88), 170 (100), 129 (88), 115 (78).

General procedure for the synthesis of the metallocene dichloride complexes 6-12

n-Butyllithium (2 mmol, 1.6 M in hexanes) was added to 2 mmol of the appropriate substituted indenyl compound dissolved in 50 ml diethyl ether at -78 °C.

The solution was allowed to come to room temperature and stirring was continued for further 3-4 hours. Then the solution was transferred to a suspension of zirconium tetrachloride or hafnium tetrachloride (1 mmol) in 50 mL diethyl ether at -78 °C. The mixture was slowly allowed to come to room temperature and stirred for further 24 hours**.** Diethyl ether was removed followed by the addition of 100 mL toluene. The toluene suspension was filtered and the volume of the filtrate was reduced. The complexes were precipitated by adding n-pentane and filtered. The precipitate was washed several times with n-pentane and dried under vacuum to obtain the desired complexes as yellow powders in 50-60% yields.

6: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.62-7.51 (8H, m), 7.45-7.37 (12H, m), 7.36-7.11 (24H, m), 7.04-6.98 (4H, m), 6.91-6.85 (4H, m), 6.10 (2H, d, *J* 3.2 Hz, Ind-H), 5.95 (2H, d, *J* 3.2 Hz, Ind-H), 5.72 (2H, d, *J* 3.2 Hz, Ind-H), 5.47 (2H, d, *J* 3.2 Hz, Ind-H), 3.97-3.81 (8H, m, CH$_2$), 3.10-2.98 (4H, m, CH$_2$), 2.80-2.64 (4H, m, CH$_2$), 2.10-1.78 (8H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 155.6, 138.6, 130.8, 127.0, 126.0, 121.7 (C$_q$), 130.9, 129.6, 128.6, 128.0, 126.8, 126.1, 125.6, 125.4, 123.7, 121.8, 120.8, 112.2, 99.6 CH), 67.1 (OCH$_2$), 29.6, 24.6 (CH$_2$) ppm.

Elemental analysis: Found: C 71.52, H 5.91. Calc.: C 71.23, H 5.74 %.

7: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.61-7.47 (12H, m), 7.44-7.07 (32H, m), 7.03-6.97 (4H, m), 6.90-6.84 (4H, m), 6.04 (2H, d, *J* 3.2 Hz, Ind-H), 5.88 (2H, d, *J* 3.2 Hz, Ind-H), 5.56 (2H, d, *J* 3.2 Hz, Ind-H), 5.30 (2H, d, *J* 3.2 Hz, Ind-H), 3.96-3.80 (8H, m, CH$_2$), 3.12-3.00 (4H, m, CH$_2$), 2.80-2.62 (4H, m, CH$_2$), 2.07-1.76 (8H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 155.7, 138.6, 130.8, 125.8, 125.0, 118.9 (C$_q$), 130.9, 129.7, 128.6, 128.0, 126.8, 126.1, 125.5, 125.2, 123.7, 121.2, 120.9, 112.2, 96.6 (CH), 67.1 (OCH$_2$), 29.9, 24.5 (CH$_2$) ppm.

Elemental analysis: Found: C 64.15, H 5.62. Calc.: C 64.04, H 4.70%.

8: ^{1}H-NMR: (400 MHz, C$_6$D$_6$, 298 K): δ = 7.71-7.67 (8H, m), 7.38-7.29 (20H, m), 7.22-7.11 (8H, m), 6.97-6.91 (12H, m), 6.66-6.62 (4H, m), 5.58 (2H, s, Ind-H), 5.52 (2H, s, Ind-H), 3.53-3.43 (8H, m, CH$_2$), 2.91-2.81 (4H, m, CH$_2$), 2.58-2.46 (4H, m, CH$_2$), 1.72-1.62 (4H, m, CH$_2$), 1.60-1.51 (4H, m, CH$_2$), 2.08 (3H, s, CH$_3$), 2.07 (3H, s, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, C$_6$D$_6$, 298 K): δ = 156.2, 139.4, 129.0, 116.4, 116.1, 113.2, 113.0 (C$_q$), 131.3, 130.1, 128.9, 128.4, 127.2, 125.5, 125.4, 124.4, 124.3, 121.4, 121.3, 112.5 (CH), 66.9 (OCH$_2$), 31.1, 24.6 (CH$_2$), 13.0 (CH$_3$) ppm.

Elemental analysis: Found: C 70.93, H 6.18. Calc.: C 70.92, H 6.51%.

9: ^{1}H-NMR: (400 MHz, C$_6$D$_6$, 298 K): δ = 7.33-7.27 (8H, m), 7.15-7.10 (2H, m), 7.06-6.93 (14H, m), 6.91-6.81 (12H, m), 6.73-6.59 (12H, m), 6.43-6.36 (4H, m), 5.76 (2H, d, *J* 3.2 Hz, Ind-H), 5.58 (2H, d, *J* 3.2 Hz, Ind-H), 5.20 (2H, d, *J* 3.2 Hz, Ind-H), 5.07 (2H, d, *J* 3.2 Hz, Ind-H), 3.28-3.16 (8H, m, CH$_2$), 2.62-2.50 (4H, m, CH$_2$), 2.46-2.36 (4H, m, CH$_2$), 1.35-1.05 (16H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, C$_6$D$_6$, 298 K): δ = 156.5, 139.4, 131.5, 127.5, 126.6, 123.3 (C$_q$), 131.3, 130.1, 128.8, 128.2, 127.0, 126.4, 125.8, 125.5, 124.3, 122.4, 121.2, 112.9, 99.0 (CH), 68.0 (OCH$_2$), 29.3, 28.2, 26.8 (CH$_2$) ppm.

Elemental analysis: Found: C 71.90, H 5.50. Calc.: C 71.40, H 5.51%.

10: ^{1}H-NMR: (400 MHz, C$_6$D$_6$, 298 K): δ = 7.35-7.28 (8H, m), 7.20-7.16 (2H, m), 7.10-6.83 (28H, m), 6.75-6.60 (10H, m), 6.47-6.39 (4H, m), 5.81 (2H, d, *J* 3.2 Hz, Ind-H), 5.61 (2H, d, *J* 3.2 Hz, Ind-H), 5.24 (2H, d, *J* 3.2 Hz, Ind-H), 5.13 (2H, d, *J* 3.2 Hz, Ind-H), 3.33-3.21 (8H, m, CH$_2$), 2.67-2.55 (4H, m, CH$_2$), 2.50-2.41 (4H, m, CH$_2$), 1.23-0.81 (24H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, C$_6$D$_6$, 298 K): δ = 156.5, 139.3, 131.5, 127.4, 126.6, 123.4 (C$_q$), 131.2, 130.0, 128.8, 128.1, 127.0, 126.3, 125.8, 125.5, 124.3, 122.4, 121.2, 112.9, 99.0 (CH), 68.2 (OCH$_2$), 29.8, 29.2, 28.5, 26.2 (CH$_2$) ppm.

Elemental analysis: Found: C 71.42, H 6.49. Calc.: C 71.86, H 5.80%.

11: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 8.28-8.18 (4H, m), 7.78-7.73 (4H, m), 7.59-7.50 (4H, m), 7.47-7.09 (28H, m), 6.69-6.62 (4H, m), 6.25 (2H, d, *J* 3.2 Hz, Ind-H), 5.99 (2H, d, *J* 3.2 Hz, Ind-H), 5.80 (2H, d, *J* 3.2 Hz, Ind-H), 5.58 (2H, d, *J* 3.2 Hz, Ind-H), 4.12-3.93 (8H, m, CH$_2$), 3.28-3.14 (4H, m, CH$_2$), 3.08-2.90 (4H, m, CH$_2$), 2.29-2.04 (8H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 154.5, 134.5, 127.4, 126.2, 125.9, 122.2 (C$_q$), 127.5, 127.4, 126.4, 126.3, 125.9, 125.6, 125.2, 123.8, 122.2, 122.0, 120.2, 104.6, 99.3 (CH), 66.9 (OCH$_2$), 29.3, 24.8 (CH$_2$) ppm.

12: ^{1}H-NMR: (400 MHz, C$_6$D$_6$, 298 K): δ = 8.52-8.38 (4H, m), 7.99-7.91 (4H, m), 7.74-7.26 (32H, m), 6.91-6.76 (4H, m), 6.39 (2H, d, *J* 3.2 Hz, Ind-H), 6.13 (2H, d, *J* 3.2 Hz, Ind-H), 5.84 (2H, d, *J* 3.2 Hz, Ind-H), 5.60 (2H, d, *J* 3.2 Hz, Ind-H), 4.28-4.11 (8H, m, CH$_2$), 3.48-3.12 (8H, m, CH$_2$), 2.46-2.00 (8H, m, CH$_2$) ppm.

^{13}C-NMR: (100 MHz, C$_6$D$_6$, 298 K): δ = 155.1, 135.2, 127.5, 126.4, 125.4, 119.6 (C$_q$), 128.3, 126.8, 126.5, 126.2, 125.7, 125.6, 125.4, 124.2, 122.6, 121.6, 120.5, 105.1, 96.2 (CH), 66.9 (OCH$_2$), 29.6, 25.0 (CH$_2$) ppm.

Elemental analysis: Found: C 62.87, H 4.96. Calc.: C 62.31, H 4.52%.

RESULTS AND DISCUSSION
Synthesis and characterization of ω-aryloxyalkyl-substituted indenyl compounds

ω-Aryloxyalkyl-substituted indenyl compounds were synthesized via a two-step reaction. In the first step, ω-bromo-1-aryloxyalkanes were synthesized by refluxing a mixture of an appropriate phenol or naphthol with an excess of α,ω-dibromoalkane in the presence of potassium carbonate and catalytic amounts of a crown ether (18-crown-6) in acetone. The reaction of ω-bromo-1-aryloxyalkanes with indenyl lithium provided ω-aryloxyalkyl-substituted indenyl compounds (Scheme 1).

Compounds 1-5 were characterized by ^{1}H- and ^{13}C-NMR spectroscopy and GC/MS (see experimental section). In the ^{1}H-NMR spectrum of compound 1 (Fig. 1), the signals at δ = 7.65-7.62 (2H, m), 7.50-7.43 (3H, m), 7.41-7.30 (5H, m), 7.26-7.22 (1H, m), 7.09-7.05 (1H, m), and 7.02-6.99 (1H, m) ppm belong to the aryl protons H20, H19, H18, H16, H15, H14, H13, H7, H6, H5 and H4. The signal at δ = 6.20 (1H, br) ppm is an unresolved triplet which derives from the indenyl proton H2. The signal for the OCH$_2$ protons H10 can be located at δ = 4.08 (2H, t, ^3J(H,H) 6.1 Hz) ppm while the indenyl CH$_2$ protons H1 show an unresolved doublet at δ = 3.34 ppm (2H, br). The CH$_2$ protons H8 give a triplet at δ = 2.70 ppm (^3J(H,H) = 7.6 Hz) while the CH$_2$ group H9

appears as a doublet of triplets at δ = 2.12 ppm.

The ^{1}H-NMR of compound 2 shows signals for aryl protons H20, H19, H18, H16, H15, H14, H13, H7, H6, H5 and H4 at δ = 7.52-7.48 (2H, m), 7.35-7.10 (9H, m), 6.97-6-92 (1H, m) and 6.90-6.87 (1H, m) ppm. The unresolved doublet at δ = 6.00 (1H, br) ppm derives from the indenyl proton H2. The signal at δ = 3.95 (2H, t, *J* 6.0 Hz) ppm belongs to the OCH$_2$ protons H11 while the signal for the indenyl CH proton H1 appears at δ = 3.35-3.28 (1H, m) ppm. The signals at δ = 2.53 (2H, t, ^{3}J(H,H) 7.6 Hz) and 2.03-1.94 (2H, m) ppm are assigned to the CH$_2$ protons H9 and H10. The signals for the methyl protons H8 can be located at δ = 1.18 (3H, d, *J* 7.3 Hz) ppm.

Synthesis and characterization of the complexes

The metallocene dichloride complexes 6-12 were synthesized by the reaction of the lithium salts of the indenyl compounds with the corresponding metal tetrachlorides in diethyl ether (Scheme 2).

Complexes 6-12 were characterized by ^{1}H- and ^{13}C-NMR spectroscopy and elemental analysis (see Experimental Section).

The ^{1}H-NMR spectrum of complex 6 (Fig. 3) shows signals for both rac and meso isomers. The signals for the aryl protons H20, H19, H18, H16, H15, H14, H13, H7, H6, H5 and H4 appear at δ = 7.62-7.51 (8H, m), 7.45-7.37 (12H, m), 7.36-7.11 (24H, m), 7.04-6.98 (4H, m) and 6.91-6.85 (4H, m) ppm. The signals at δ = 6.10 (2H, d, *J* 3.2 Hz,), 5.95 (2H, d, *J* 3.2 Hz), 5.72 d (2H, *J* 3.2 Hz) and 5.47 (2H, d, *J* 3.2 Hz) ppm are assigned to the indenyl protons H2 and H3. The signals for the methylene group attached to oxygen atom appear at δ = 3.97-3.81 (8H, m) ppm. At δ = 3.10-2.98 (4H, m) and 2.80-2.64 (4H, m) ppm the signals for the methylene protons H8 can be located while the signals for the methylene protons H9 can be found at δ = 2.10-1.78 (8H, m) ppm.

Compound 8 also exists as a mixture of rac and meso isomers, in the ^{1}H-NMR (Fig. 4) the signals at δ = 7.71-7.67 (8H, m), 7.38-7.29 (20H, m), 7.22-7.11 (8H, m), 6.97-6.91 (12H, m) and 6.66-6.62 (4H, m) ppm belong to the aryl protons H21, H20, H19, H17, H16, H15, H14, H7, H6, H5 and H4. The signals for the indenyl proton H2 for rac and meso isomers appear at δ = 5.58 (2H, s) and 5.52 (2H, s) ppm. The signals at δ = 3.53-3.43 (8H, m) belong to OCH$_2$ protons H11 while the signals at

Table 1: Polymerization and polymer data for complexes 6-12.

Complex	Activity (kg PE/mol cat. h)	ΔH_m [J/g]	T_m [°C]	Crystallinity (α)
6	15500	141.3	134.3	0.49
7	800	103.8	134.5	0.36
8	2400	142.3	134.0	0.49
9	9000	143.4	133.3	0.49
10	2200	118.1	134.8	0.41
11	3200	148.3	138.3	0.51
12	0	-	-	-

δ = 2.91-2.81 (4H, m) and 2.58-2.46 (4H, m) derive from CH₂ protons H9. The signals for the methyl group can be located at δ = 2.08 (6H, s) and 2.07 (6H, s) ppm while the signals at δ = 1.72-1.62 (4H, m) and 1.60-1.51 (4H, m) ppm belong to CH₂ protons H10.

Ethylene polymerization

After activation with a 2000-fold molar excess of methyl aluminoxane (MAO), complexes **6-12** were tested for homogeneous ethylene polymerization. The polymerization results and polymer analysis data of the selected polymer samples are given in Table 1.

Ethylene polymerization activities of the catalysts **6-12** depending on the length of the spacer chain between the indenyl moiety and the aryloxy substituent, the steric bulk on the aryloxy substituent, the number of groups attached to the indenyl moiety and the nature of the metal.

Length of the spacer chain bridging the indenyl moiety with aryloxy substituents has a substantial influence on the activity of the catalyst. Catalyst **6** with three methylene bridging units shows the highest activity for ethylene polymerization (15500 kg PE/mol cat. h). The activity decreases sharply by increasing the length of the spacer chain (9000 kg PE/mol cat. h for catalyst **9** and 2200 kg PE/mol cat. h for catalyst **10**).

Steric bulk on the ortho carbon of the phenoxy or naphthoxy group also has profound effects on the catalyst activity. Catalyst **11** bearing no substituent on the ortho carbon of the naphthoxy group shows very low activity (3200 kg PE/mol cat. h) as compared to catalyst **6**.

Another important factor is the number of substituents on the indenyl moiety. Increasing the number of substituents on the indenyl group results in a very sharp decrease in the catalytic activity. Compared to catalyst **6**,

catalyst **8** bearing a methyl substituent on position 1 of the indenyl moiety shows very low activity (2400 kg PE/mol cat. h). The reason for the low activity of catalyst **8** is probably the blocking of the active site of the catalyst by the methyl group. The hafnium catalyst **7** showed very low activity while **12** was inactive. The lower activity of hafnium complexes is due to the stronger metal-carbon bonds in the hafnium complexes [42] which result in slower kinetics in the various reaction steps of the catalysis reaction and the higher oxophilicity of hafnium as compared to zirconium [30, 43]. Hafnium catalyst **7** shows some activity due to the bulky phenyl group at the ortho position of the phenoxy group. The steric bulk of the phenyl group prevents coordination of oxygen atom with oxophilic hafnium atom, catalyst **12** is totally inactive due to the absence of steric bulk at this position.

CONCLUSIONS

Seven new complexes of zirconium and hafnium with indenyl ligands bearing bulky ω-aryloxy substituents were synthesized. These complexes were activated with methyl aluminoxane and tested for ethylene polymerization. Zirconium complex 6 bearing a spacer of three methylene groups between indenyl and the 2-phenylphenoxy group showed the highest activity. Activity decreases by increasing the length of the spacer. The introduction of a methyl group on the indenyl moiety (complex **8**) resulted in a substantial decrease in activity due to blocking of the catalyst centre. Complex **11** bearing a naphthoxy group instead of 2-phenylphenoxy group showed very low activity as compared to complex **6**. The hafnium complex **7** showed very low activity compared with complex **6** while the hafnium complex **12** was totally inactive

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