JJC *Jordan Journal of Chemistry* Vol. 10 No.2, 2015, pp. 87-97

Dissymmetric bis(indenyl) Zirconium Dichloride Complexes as Catalyst Precursors for Homogeneous Ethylene Polymerization

Khalil Ahmad, Helmut G. Alt*

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251, D-95440 Bayreuth, Germany

Received on Feb. 5, 2015 **Accepted on** March 5, 2015

Abstract

Six new dissymmetric bis(indenyl) zirconium dichloride complexes of the type $(C_9H_7)[C_9H_6\text{-}(CH_2)n\text{-}O\text{-}Ar]ZrCl_2$ (n = 3-5; Ar = aryl group) bearing an unsubstituted and an ω-aryloxyalkyl substituted indenyl ligand were synthesized, characterized, activated with methylalumoxane (MAO) and tested for ethylene polymerization. The activities of the catalysts depend very much on the steric bulk of the O-Ar group as well as on the CH_2- chain length between the aryloxy group and the indenyl ligand. The best activity (26233 kg PE/mol cat h) was obtained with catalyst precursor **4a** (n = 3; Ar = 2- biphenyl). Obviously the biphenyl group and the limited length of the CH_2-chain protect the oxygen atom very efficiently from coordination to an active site of the same or a neighboured molecule during the polymerization process.

Keywords: Dissymmetric metallocene complexes; Aryloxyalkyl substituent; Ethylene polymerization; Structure-property-relationship.

Introduction

In the past 25 years metallocene complexes of group 4 metals in combination with methylalumoxane (MAO) have been extensively studied for a wide variety of catalytic homo- and copolymerization reactions of α-olefins.[1-21] The reason is the fact that tiny differences in such molecules can have a drastic effect on the performance as catalysts. Therefore, the structure-property-relationship plays an essential role for the design of tailored catalysts especially because the catalyst structure can be easily modified by introducing various substituents at various positions of the ligand framework. In the past, many attempts have been made to predict the best catalyst by molecular modeling. The results were not satisfying because there are too many open parameters involved in the polymerization reaction that cannot be controlled properly: The degree of activation of the catalyst precursor, the interaction of the generated catalyst cation and the counter anion, the nature of MAO being a dynamic equilibrium of a variety of different alumoxanes and free trimethyl aluminum, as well as the solvent contribute to the performance of these catalysts. Because of this situation, an empirical

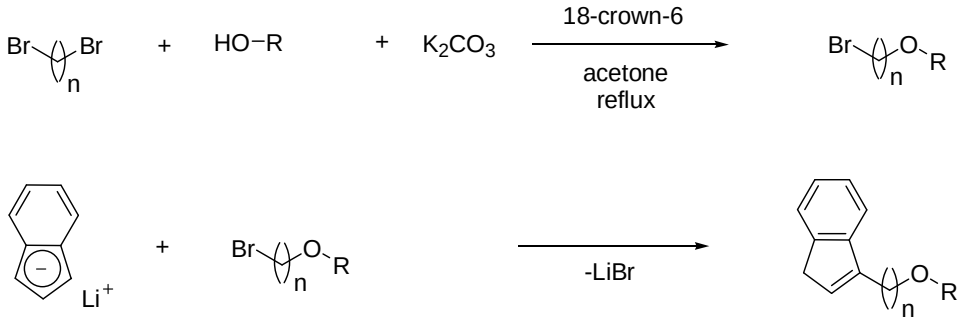
* Corresponding author: e-mail: helmut.alt@uni-bayreuth.de

approach is more realistic to design such catalysts. Alkyl substitution at the indenyl ligands generally enhances the polymerization activity. Functional groups can also alter the activity of a catalyst depending on their electron donating or withdrawing effects.[22-40] In this work we report six new dissymmetrical zirconocene dichloride complexes bearing an unsubstituted and an ω-aryloxyalkyl substituted indenyl ligand. A comparison with the unsubstituted parent complex, $(ind)_2ZrCl_2$, and symmetrically substituted bis(indenyl) complexes should reveal whether or not such substitutions improve the performance of these metallocene catalysts.

Results and Discussion

*Synthesis of the ω-phenoxyalkyl substituted indenyl compounds **1-6***

For the synthesis of the ω-phenoxyalkyl substituted indenyl compounds **1**-**6**, a substituted phenol was refluxed with an excess of an α,ω-dibromoalkane in the presence of potassium carbonate and catalytic amounts of a crown ether (18-crown-6) under reflux conditions to obtain the corresponding ω-bromo-1-phenoxyalkanes. The reaction of ω-bromo-1-phenoxyalkanes with indenyl lithium gave the desired ω-phenoxyalkyl substituted indenyl compounds (Scheme 1).



1 (n = 3; R = C_6H_4-4-t-Bu) **4** (n = 3; R = 2-Ph-Ph)
2 (n = 4; R = C_6H_4-4-t-Bu) **5** (n = 5; R = 2-Ph-Ph)
3 (n = 5; R = C_6H_4-4-t-Bu) **6** (n = 3; R = 1- Naphthyl)

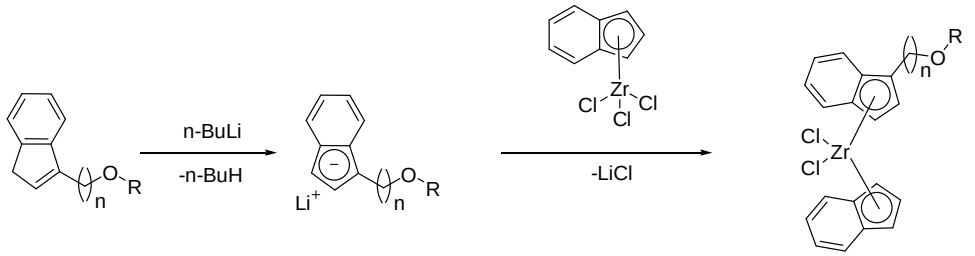
Scheme 1: Synthesis of the ligand precursors **1-6**.

*Synthesis of the dissymmetric bis(indenyl)zirconium dichloride complexes **1a-6a***

Dissymmetric zirconocene dichloride complexes can be prepared by the reaction of indenyl zirconium trichloride and the lithium salt of the desired ω-aryloxyalkyl substituted indenyl derivative (Scheme 2).

Complexes **1a**-**6a** were characterized by NMR spectroscopy and elemental analysis (see experimental section). At room temperature the signals of all complexes are comparatively broad and not resolved because of the existence of two rotamers and their dynamic behaviour in the NMR time scale. The rac and the meso isomers have very similar spectra and the signals are often superimposed. As a typical example, the ^{1}H NMR spectrum of **3a** is discussed: The three protons of the 5-membered ring of the unsubstituted indenyl ligand appear as two doublets at δ = 6.20 and 6.00 ppm (^{3}J(H,H) = 3,1 Hz) and as a triplet at δ = 6,43 ppm (^{3}J(H,H) = 3,1 Hz).

The two protons of the 5-membered ring of the substituted indenyl ligand give an AB spin coupling pattern at δ = 6,23 and 5,64 ppm (^{3}J(H,H) = 3,1 Hz). The phenyl protons of the three 6-membered rings appear as unresolved multiplets in the range of δ = 6,77 –7,67 ppm. The five methylene groups of the phenoxyalkyl substituent give signals at δ = 3.91 (2H, t), 3.01 (1H, m), 2.73 (1H,m) and 1.83 – 1.37 (6H, m) ppm. The methyl groups of the t-butyl group appear at δ = 1.29 ppm.



1a (n = 3; R = C_6H_4-4-t-Bu)
2a (n = 4; R = C_6H_4-4-t-Bu)
3a (n = 5; R = C_6H_4-4-t-Bu)
4a (n = 3; R = 2-Ph-Ph)
5a (n = 5; R = 2-Ph-Ph)
6a (n = 3; R = 1-Naphthyl)

Scheme 2: Synthesis of the dissymmetric zirconocene dichloride complexes **1a-6a.**

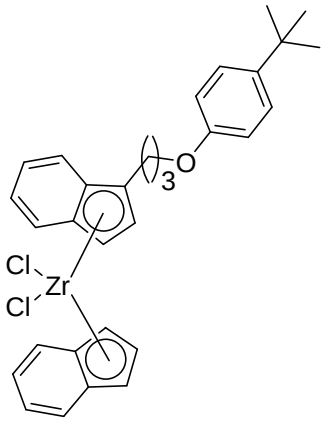
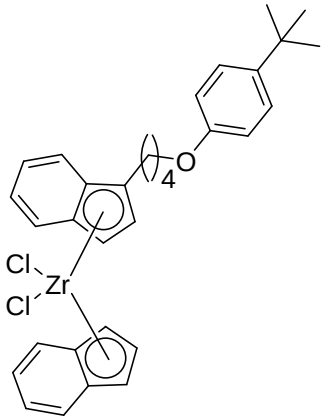
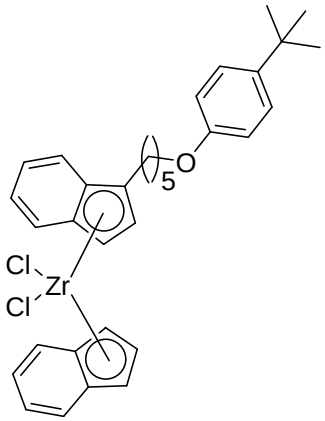
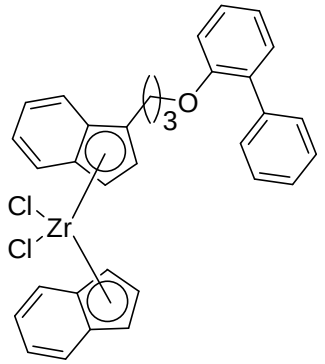
In the ^{13}C NMR spectrum, 29 signals are observed (see experimental section). Because of symmetry reasons, only 25 are expected for each species. The explanation for this discrepancy lies in the existence of rac and meso rotamers. Unsubstituted bis(indenyl) complexes often show only the spectrum of one species because the rotation of the aromatic ligands around the metal bond axis is fast enough in the NMR time scale. In the case of substituted indenyl ligands, however, the rotation is slowed down and two rotamers can be detected at room temperature.

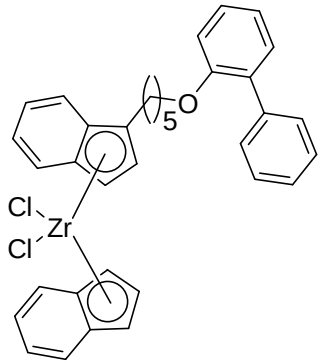
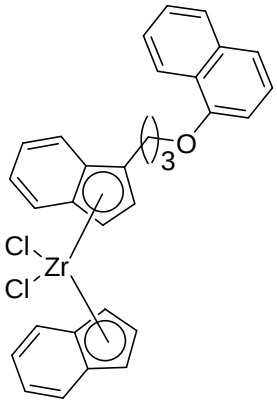
Ethylene polymerization

The dissymmetric zirconocene dichloride complexes **1a-6a** proved to be suitable catalyst precursors for ethylene polymerization. They were activated with a 2000-fold molar excess of MAO. The activated complexes were suspended in 250 ml of n-pentane and the suspension was transferred to a 1 litre Büchi reactor. The polymerization of ethylene was performed at 65°C under 10 bar ethylene pressure. The ethylene polymerization activities and the thermal analysis results of the selected polymer samples are listed in Table 1.

The ethylene polymerization activities of complexes **1a-6a** depend strongly on the bulk at the phenoxy substituent as well as on the length of the spacer chain separating the aryloxy group from the indenyl ligand. In the series **1a-3a**, with the same tert. butyl substituent in para position, complex **4a** with a chain length of three CH_2 groups shows the highest activity (26233 kg PE/mol_{cat}.h). Obviously this is the best CH_2- chain length and the bulkiest group in this series to protect the oxygen atom from intra- or intermolecular interactions with oxophilic zirconium atoms. Simultaneously the -I effect of oxygen decreases the electron density at the active centre and hence increases the activity of the catalyst. An additional increase of activity can

Table 1: Polymerization and polymer data.

No.	Complex	Activity[a] (kg PE/mol$_{cat}$.h)	ΔH_m (J/mol)	T_m (°C)	Crystallinity (α)
1a		7800	137.3	135.7	0.47
2a		11666	145.8	138.8	0.50
3a		3600	155.3	137.2	0.54
4a		26233	116.7	127.2	0.40

5a		1400	150.7	139.0	0.52
6a		5333	-	-	-

a) Polymerization conditions: M: Al = 1:2000; 250 mL n-pentane; 65°C, 10 bar ethylene, 1 h.

be reached when both indenyl ligands are substituted with bulky ω-aryloxyalkyl groups.[41] Simultaneously, deactivation reaction pathways are minimized. A comparison of catalyst activities with that of unsubstituted $(ind)_2ZrCl_2$ (3200 kg PE/mol_{cat} h) shows that the catalyst activity can be increased via this strategy. Very similar results are reported in the literature.[5] Compared to **4a**, catalyst **6a** shows a much lower activity. This could be due to the stronger intermolecular interactions of the 2-naphthyloxy group with the catalyst centre favoured by a longer CH_2-chain. The DSC results reveal that these catalysts produce polyethylenes with high heats of fusion, melting points and crystallinities and the values of these parameters grow by increasing the length of the spacer chain between the aryloxy moieties and the indenyl ligand.

Experimental

General aspects

All reactions were carried out under inert atmosphere using Schlenk technique. Argon was purified before its use as an inert gas. Methylene chloride was distilled over phosphorus pentoxide. Toluene, tetrahydrofuran, diethyl ether and n-pentane 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 (3 Å). Argon (5.0) and ethylene (3.5) were purchased from Rieβner Company. Methylalumoxane (10% in

toluene) was purchased from Chemtura Europe Limited. All other starting materials were commercially available and used without further purification.

NMR spectroscopy

A Varian Inova (400 MHz) spectrometer was available for recording the NMR spectra at 298 K. In the ^{1}H NMR spectra the chemical shift of the residual proton signal of the solvent was used as a reference (δ = 7.24 ppm for chloroform and δ = 7.16 ppm for benzene), while in the ^{13}C NMR spectra the chemical shift of the solvent was used as a reference (δ = 77.0 ppm for chloroform-d_1 and δ = 128.0 ppm for benzene-d_6).

GC/MS

GC/MS spectra were recorded with a FOCUS Thermo gas chromatograph combined with a DSQ mass detector. A 30m HP-5 fused silica column (internal diameter 0.32 mm, film thickness 0.25 µm and carrier flow 1mL/min) was used with helium (4.6) applied as a carrier gas. The measurements were recorded using the following temperature program: Starting temperature: 50°C, duration: 2 minutes; Heating rate: 20°C/minute, duration: 12 minutes; Final temperature: 290°C, duration: 27 minutes.

Elemental analysis

Elemental analyses were performed with a Vario EL III CHN instrument. The values of C, H and N were calibrated using acetamide as standard.

DSC analysis

DSC analyses were performed on a Mettler Toledo DSC/SDTA 821e instrument. The polymer samples (4-6 mg) were enclosed in standard aluminum pans and introduced into the auto sampler of the instrument. The measurements were recorded using the following temperature program: First heating phase: from 50 to 160°C (10°C/minute); Cooling phase: 160 to 50°C (10°C/minute); Second heating phase: from 50 to 160°C (10°C/minute). Nitrogen was used as a cooling medium. Melting enthalpies and melting points were taken from the second heating phase. The values were calibrated using indium as a standard (m.p. 429.78 K, H_m = 28.45 J/g). Crystallinities were calculated using the extrapolated value of 290 J/g for 100% crystalline polyethylene.

General description of ethylene polymerization experiments

For the homogeneous polymerization of ethylene, a few milligrams of the complex is dissolved in toluene (5-10 mL) and activated with methylalumoxane (MAO). The activated complex is suspended in pentane (250 mL) and transferred to a 1 litre Büchi autoclave under inert atmosphere. The temperature of the thermostat was adjusted to the desired value and a slurry polymerization of ethylene was carried out under 10 bar ethylene pressure for one hour. After cooling the system, the pressure

was released, the obtained polymer was filtered over a glass frit, washed with dilute hydrochloric acid, water and finally with acetone and then it was dried under vacuum.

*General synthesis procedure for the ω-aryloxyalkyl substituted indenyl complexes **1-6***

An amount of 10 mmol of the appropriate phenol, 10 mmol of potassium carbonate, 30 mmol of the desired α,ω-dibromoalkane and catalytic amounts of 18-crown-6 were refluxed in acetone for 24-72 hours. The reaction mixture was cooled, the solvent removed followed by the addition of distilled water and extraction with diethyl ether (2×100 mL). After passing the solution over sodium sulphate and removing the solvent, the residue was distilled to obtain the corresponding ω-bromo-1-aryloxyalkane compound in 80% yield. An amount of 5 mmol of n-butyllithium (1.6 M in n-hexane) was added to 5 mmol of indene dissolved in 100 mL of 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 of the ω-bromo-1-aryloxyalkane was added. The solution was allowed to warm up to room temperature and stirred for further 12 hours. The solution was washed with distilled water and dried over sodium sulphate. Removal of the solvent gave the desired ω-aryloxyalkyl substituted indene compound in almost quantitative yield. The synthesized compounds were characterized by GC/MS and NMR spectroscopy.

C_9H_6-[$(CH_2)_3$-O-C_6H_4-tBu] (1): ^{1}H NMR: (400 MHz, $CDCl_3$, 298K): δ = 7.47-7.43 (m, 1H), 7.39-7.35 (m, 1H), 7.32-7.25 (m, 3H), 7.22-7.16 (m, 1H), 6.87-6.82 (m, 2H), 6.23 (br, 1H, Ind-H2), 4.02 t (2H, OCH_2), 3.31 (br, 2H, Ind-H1), 2.77-2.69 (m, 2H, CH_2), 2.21-2.11 (m, 2H, CH_2), 1.29 s (9H, CH_3).

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): δ = 156.8, 145.3, 144.5, 143.7, 143.2 (C_q), 128.2, 128.1, 126.2, 126.0, 124.6, 123.8, 119.0, 114.0 (CH), 67.3 (OCH_2), 37.8 (CH_2-Ind), 34.0 (C_q), 31.5 (CH_3), 27.7, 24.2 (CH_2).

MS: 306 (M^+, 8); 176 (78); 161 (81); 129 (100); 115 (56).

C_9H_6-[$(CH_2)_4$-O-C_6H_4-tBu] (2): ^{1}H : (400 MHz, $CDCl_3$, 298K): δ = 7.45-7.42 (m, 1H), 7.36-7.33 (m, 1H), 7.29-7.24 (m, 3H), 7.20-7.15 (m, 1H), 6.83-6.79 (m, 2H), 6.20 (br, 1H, Ind-H2), 3.96 (t, 2H, OCH_2), 3.30 (br, 2H, Ind-H1), 2.63-2.57 (m, 2H, CH_2), 1.88-1.83 (m, 4H, CH_2), 1.27 (s, 9H, CH_3).

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): δ = 156.8, 145.5, 144.6, 144.2, 143.1 (C_q), 128.0, 126.2, 126.0, 124.5, 123.8, 119.0, 114.0 (CH), 67.7 (OCH_2), 37.7 (CH_2-Ind), 34.0 (C_q), 31.5 (CH_3), 29.2, 27.4, 24.5 (CH_2).

MS: 320 (M^+, 6); 171 (100); 129 (78); 115 (22).

C_9H_6-[$(CH_2)_5$-O-C_6H_4-tBu] (3): ^{1}H NMR: (400 MHz, $CDCl_3$, 298K): δ = 7.46-7.43 (m, 1H), 7.37-7.34 (m, 1H), 7.30-7.26 (m, 3H), 7.21-7.16 (m, 1H) 6.84-6.81 (m, 2H), 6.19 (br, 1H, Ind-H2), 3.94 (t, 2H, OCH_2), 3.31 (br, 2H, Ind-H1), 2.60-2.54 (m, 2H, CH_2), 1.86-1.71 (m, 4H, CH_2), 1.61-1.52 (m, 2H, CH_2), 1.29 (s 9H, CH_3).

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): δ = 156.8, 145.5, 144.5, 144.4, 143.1 (C_q), 127.8, 126.1, 125.9, 124.4, 123.7, 118.9, 113.9 (CH), 67.8 (OCH_2), 37.7 (CH_2-Ind), 34.0 (C_q), 31.5 (CH_3), 29.2, 27.8, 27.7, 26.1 (CH_2).

MS: 334 (M^+, 3); 204 (6); 185 (100); 135 (74); 117 (65); 115 (23).

C_9H_6-[$(CH_2)_3$-O-2-(Ph-Ph)] (4): ^{1}H NMR: (400 MHz, $CDCl_3$, 298K): δ = 7.65-7.62 (m, 2H), 7.50-7.43 (m, 3H), 7.41-7.30 (m, 5H), 7.26-7.22 (m, 1H), 7.09-7.05 (m, 1H), 7.02-6.99 (m, 1H), 6.20 (br, 1H, Ind-H2), 4.08 (t, 2H, OCH_2), 3.34 (br, 2H, Ind-H1), 2.72-2.66 (m, 2H, CH_2), 2.16-2.08 (m, 2H, CH_2).

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): 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).

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

C_9H_6-[$(CH_2)_5$-O-2-(Ph-Ph)] (5): ^{1}H NMR: (400 MHz, $CDCl_3$, 298K): δ = 7.60-7.49 (m, 2H), 7.47-7.14 (m, 9H), 7.05-6.88 (m, 2H), 6.14 (br, 1H, Ind-H2), 3.93 (t, 2H, OCH_2), 3.29 (br, 2H, Ind-CH_2), 2.57-2.45 (m, 2H, CH_2), 1.80-1.61 (m, 4H, CH_2), 1.56-1.42 (m, 2H, CH_2).

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): 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).

C_9H_6-[$(CH_2)_3$-O-1-Naphthyl] (6): ^{1}H NMR: (400 MHz, $CDCl_3$, 298K): δ = 8.46-8.40 (m, 1H), 7.92-7.84 (m, 1H), 7.60-7.54 (m, 3H), 7.52-7.49 (m, 2H), 7.46-7.37 (m, 2H), 7.34-7.28 (m, 1H), 6.88-6.83 (m, 1H), 6.34 (br, 1H, Ind-H2), 4.26 (t, 2H, OCH_2), 3.41 (br, 2H,Ind-CH_2), 2.98-2.90 (m, 2H, CH_2), 2.43-2.35 (m, 2H, CH_2)

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): 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).

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

General synthesis procedure for the dissymmetric bis(indenyl)zirconium dichloride complexes 1a-6a.

An amount of 1 mmol of n-butyllithium (1.6 M in hexane) was added to 1 mmol of the substituted indene compound dissolved in 50 mL of toluene at -78°C. The solution was allowed to come to room temperature and it was stirred for further 3 hours. This solution was then transferred to a suspension of indenyl zirconium trichloride (1 mmol) in 50 mL toluene at -78°C. The reaction mixture was allowed to come to room temperature and stirred for further two days. The mixture was filtered, the volume of the filtrate was reduced and pentane was added to precipitate the complex. After filtration, the residue was washed several times with pentane and dried under vacuum to obtain the desired complex as yellow powder in 40% yield. The

synthesized complexes were characterized by NMR spectroscopy and elemental analysis.

{C_9H_6-[$(CH_2)_3$-O-C_6H_4-tBu]}(C_9H_7)$ZrCl_2$ (1a): ^{1}H NMR: (400 MHz, C_6D_6, 298K): δ = 7.50-7.44 (m, 2H), 7.32-7.19 (m, 6H), 6.96-6.90 (m, 2H), 6.86-6.81 (m, 2H), 6.06 (dd, J = 3.3 Hz, 1H), 5.91 (d, J = 3.1 Hz, 1H), 5.86 (br, 1H), 5.72 (br, 1H), 5.46 (d, J = 3.1 Hz, 1H), 3.61 (t, 2H), 3.19-3.2.94 (m, 2H), 1.92-1.79 (m, 2H), 1.25 (s, 9H).

^{13}C NMR: (100 MHz, C_6D_6, 298 K): δ = 157.4, 143.3, 127.4, 126.7, 126.1, 122.2, 122.1(C_q), 126.5, 126.4, 126.3, 126.2, 125.8, 125.7, 125.6, 125.5, 124.2, 124.1, 122.3, 121.5, 114.4, 104.0, 99.1 (CH), 66.8 (OCH_2), 34.1 (C_q), 31.7 (CH_3), 29.7, 24.8 (CH_2).

Elemental analysis. (Found: C, 63.65; H, 6.01. Calculated C, 63.90; H, 5.54%).

{C_9H_6-[$(CH_2)_4$-O-C_6H_4-tBu]}(C_9H_7)$ZrCl_2$ (2a): ^{1}H NMR: (400 MHz, C_6D_6, 298K): δ = 7.50-7.42 (m, 2H), 7.36-7.29 (m, 2H), 7.25-7.20 (m, 4H), 6.97-6.92 (m, 2H), 6.89-6.84 (m, 2H), 6.10 (dd, J = 3.3 Hz, 1H), 6.05 (br, 1H), 5.91 (br, 1H), 5.74 (br, 1H), 5.45 (br, 1H), 3.64 (t, 2H), 3.02-2.77 (m, 2H), 1.69-1.54 (m, 4H), 1.25 (s, 9H).

^{13}C NMR: (100 MHz, C_6D_6, 298K): δ = 156.8, 143.4, 127.4, 126.6, 126.3, 123.3, 123.1 (C_q), 126.5, 126.4, 126.1, 126.0, 125.9, 125.8, 125.6, 125.4, 124.0, 123.8, 122.0, 121.8, 113.9, 104.2, 99.3 (CH), 67.6 (OCH_2), 34.1(C_q), 31.6 (CH_3), 29.2, 27.8, 26.6 (CH_2).

Elemental analysis. (Found: C, 64.51; H, 5.79. Calculated: C, 64.41; H, 5.74).

{C_9H_6-[$(CH_2)_5$-O-C_6H_4-tBu]}(C_9H_7)$ZrCl_2$ (3a): ^{1}H NMR: (400 MHz, $CDCl_3$, 298K): δ = 7.67-7.53 (m, 2H), 7.35-7.16 (m, 8H), 6.83-6.77 (m, 2H), 6.43 (t, J = 3.2 Hz, 1H), 6.23 (d, J = 3.1 Hz, 1H), 6.20 (br, 1H), 6.00 (br, 1H), 5.64 (d, J = 3.1 Hz, 1H), 3.91 (t, 2H), 3.01-2.73 (m, 2H), 1.83-1.37 (m, 6H), 1.29 s (9H).

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): δ = 156.8, 143.1, 127.3, 126.5, 125.9, 123.4, 123.2 (C_q), 126.4, 126.3, 126.2, 125.7, 125.6, 125.5, 125.4, 124.4, 123.8, 122.0, 121.6, 121.0, 113.9, 104.0, 99.2 (CH), 67.6 (OCH_2), 34.0 (C_q), 31.5 (CH_3), 29.7, 29.1, 27.7, 26.0 (CH_2).

Elemental analysis. (Found: C, 65.55; H, 6.09. Calculated: C, 65.89; H, 5.94).

{C_9H_6-[$(CH_2)_3$-O-2-(Ph-Ph)]}(C_9H_7)$ZrCl_2$ (4a): ^{1}H NMR: (400 MHz, C_6D_6, 298K): δ = 7.69-7.65 (m, 2H), 7.42-7.28 (m, 5H), 7.20-7.11 (m, 4H), 6.96-6.90 (m, 4H), 6.67-6.61 (m, 2H), 6.04 (dd, J = 3.3 Hz, 1H), 6.00 (d, J = 3.1 Hz, 1H), 5.87 (br, 1H), 5.83 (d, J = 3.1 Hz, 1H), 5.71 (br, 1H), 3.48 (t, 2H), 3.09-2.74 (m, 2H), 1.72-1.56 (m, 2H).

^{13}C NMR: (100 MHz, C_6D_6, 298K): δ = 156.2, 139.3, 131.4, 127.4, 126.7, 126.6, 126.3, 122.0 (C_q), 131.3, 130.1, 128.8, 128.4, 127.1, 127.0, 126.6, 126.5, 126.2, 125.8, 125.6, 125.5, 124.2, 124.1, 122.4, 121.3, 121.2, 112.6, 104.1, 99.5 (CH), 67.1 (OCH_2), 29.9, 24.8 (CH_2).

Elemental analysis. (Found: C, 65.34; H, 4.86. Calculated: C, 65.76; H, 4.68).

{C_9H_6-[$(CH_2)_5$-O-(Ph-Ph)]}(C_9H_7)$ZrCl_2$ (5a): ^{1}H NMR: (400 MHz, $CDCl_3$, 298K): δ = 7.56-7.38 (m, 4H), 7.31-7.09 (m, 9H), 6.95-6.80 (m, 4H), 6.32 (dd, J = 3.3 Hz, 1H),

6.09 (d, J = 3.2 Hz, 1H), 6.06 (br, 1H), 5.88 (br, 1H), 5.70 (d, J = 3.2 Hz, 1H), 3.82 (t, 2H), 2.87-2.51 (m, 2H), 1.69-1.22 (m, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$, 298K): δ = 155.9, 138.5, 130.9, 127.2, 126.2, 126.0, 125.8, 123.2 (C_q), 130.8, 129.5, 128.5, 127.8, 126.7, 126.4, 126.2, 126.1, 125.9, 125.6, 125.5, 125.4, 125.3, 124.4, 123.8, 122.0, 120.8, 112.5, 104.0, 99.0 (CH), 68.1 (OCH_2), 28.9, 27.6, 27.5, 25.9 (CH_2).

Elemental analysis. (Found: C, 65.76; H, 4.95. Calculated: C, 66.65; H, 5.11).

{C_9H_6-[$(CH_2)_3$-O-1-Naphthyl]}(C_9H_7)$ZrCl_2$ (6a): ^{1}H NMR: (400 MHz, C_6D_6, 298K): δ = 8.57-8.51 (m, 1H), 7.70-7.65 (m, 1H), 7.48-7.44 (m, 1H), 7.40-7.20 (m, 9H), 6.97-6.86 (m, 2H), 6.48-6.41 (m, 1H), 6.08 (dd, J = 3.3 Hz, 1H), 6.00 (d, J = 3.1 Hz, 1H), 5.86 (br, 1H), 5.72 (br, 1H), 5.47 (d, J = 3.1 Hz, 1H), 3.61 (t, 2H), 3.22-3.15 (m, 1H), 3.10-2.98 (m, 1H), 1.98-1.84 (m, 2H).

^{13}C NMR: (100 MHz, C_6D_6, 298K): δ = 155.1, 135.2, 127.6, 126.6, 126.4, 126.3, 122.3, 122.2 (C_q), 126.8, 126.7, 126.5, 126.4, 126.3, 126.2 126.1, 125.8, 125.7, 125.6, 125.5, 125.5, 124.2, 122.6, 122.4, 120.6, 120.5, 105.0, 104.2, 98.9 (CH), 66.9 (OCH_2), 29.4, 24.9 (CH_2).

Conclusion

Dissymmetric mono aryloxy substituted bis(indenyl) zirconium dichloride complexes can be activated with MAO and be applied as efficient homogeneous catalysts for ethylene polymerization. The activities of the catalysts can vary in a wide range. Because of the high oxophilicity of zirconium, oxygen atoms are catalyst poisons blocking active sites in the polymerization process. However, when bulky protection groups in the right distance from the metal are applied, this negative effect can be efficiently compensated and the electron withdrawing effect of oxygen can be used to increase the catalyst activity.

Acknowledgements

We thank the Higher Education Commission of Pakistan (HEC Pakistan) and Deutscher Akademischer Austauschdienst (DAAD) for financial support.

References

[1] Baier, M. C.; Zuideveld, M. A.; Mecking, S., *Angew. Chem. Int. Ed.*, 2014, 53, 9722.
[2] Redshaw, C.; Tang, Y., *Chem. Soc. Rev.*, 2012, 41, 4484.
[3] Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M., *Angew. Chem. Int. Ed. Engl.,* 1995**,** *34, 1143*.
[4] Aulbach, M.; Küber, F., *Chemie in unserer Zeit,* 1994, *28*, 197.
[5] Alt, H. G.; Köppl, A., *Chem. Rev.* 2000, *100*, 1205.
[6] Möhring, P. C.; Coville, N. J., *J. Organomet. Chem.*, 1994, 479, 1.
[7] Bochmann, M. J., *J. Chem. Soc. Dalton Trans.*, 1996, 255.
[8] Alt, H. G.; Samuel, E., *Chem. Soc. Rev.*, 1998, 27, 323.
[9] Alt, H. G., *J. Chem. Soc. Dalton Trans.*, 1999, 1703.
[10] Hlatky, G. G., *Coord. Chem. Rev.*, 1999, 181, 243.

[11] Hamielec, A. E.; Soares, J. B. P., *Progr. Polym. Sci.*, 1996, 21, 651.
[12] Zhang, J.; Wang, X.; Jin, G.-X., *Coord. Chem. Rev.*, 2006, 250, 95.
[13] Kristen, M. O., *Topics in Catalysis*, 1999, 7, 89.
[14] Alt, H. G.; Licht, E. H.; Licht, A. I.; Schneider, K. J., *Coord. Chem. Rev.,* 2006, *250*, 2.
[15] Dreier, T.; Unger, G.; Erker, G.; Wibbeling, B.; Fröhlich, R., *J. Organomet. Chem.* 2001, *622*, 143.
[16] Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D., *J. Am. Chem. Soc.*, 1988, 110, 6255.
[17] Razavi, A.; Peters, L.; Nafpliotis, L. V.; Den Dauw, D. K.; Atwood, J. L., *Macromol. Symp.*, 1995, 89, 345.
[18] Andresen, A.; Cordes, H.-G.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H.-J., *Angew. Chem. Int. Ed. Engl.*, 1976, 15, 630.
[19] Barron, A. R., *Macromol. Symp.*, 1995, 97, 15.
[20] Sinn, H., *Makromol. Chem. Macromol. Symp.*, 1995, 97, 27.
[21] Chen, E. Y.-C.; Marks, T. J., *Chem. Rev.*, 2000, 100, 1391.
[22] Luttikhedde, H. J. G.; Leino, R. P.; Wilén, C.-E.; Näsman, J. H.; Ahlgrén, M. J.; Pakkanen, T.J., *Organometallics,* 1996, *15,* 3092.
[23] Leino, R. P.; Luttikhedde, H. J. G.; Lehmus, P.; Wilen, C.-E.; Sjöholm, R.; Lehtonen, A.; Seppälä, J. V.; Näsman, J. H., *Makromol.*, 1997, 30, 3477.
[24] Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M., *Organometallics,* 1990**,** *9,* 1998.
[25] Jordan, R. F., *Adv. Organomet. Chem.,* 1991, *32*, 325.
[26] Burger, P.; Diebold, J.; Gutmann, S.; Hund, H.-U.; Brintzinger, H.-H., *Organometallics,* 1992, *11*, 1319.
[27] Marks, T. J., *Acc. Chem. Res.,* 1992, *25,* 57.
[28] Qian, C.; Zhu, D., *J. Chem. Soc. Dalton Trans.,* 1994, 1599.
[29] Plenio, H.; Burth, D., *J. Organomet. Chem.,* 1996, *519*, 269.
[30] Barsties, E.; Schaible, S.; Prosenc, M.-H.; Rief, U.; Röll, W.; Weyand, O.; Dorer, B.; Brintzinger, H.-H., *J. Organomet. Chem.,* 1996, *520*, 63.
[31] Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G., *Organometallics,* 1996, *15*, 4153.
[32] Ewen, J.A.; Jones, R. L.; Elder, M. J.; Rheingold, A. L.; Liable-Sands, L. M., *J. Am. Chem. Soc.,* 1998, *120*, 10786.
[33] Carter, C. A. G.; McDonald, R.; Stryker, J. M., *Organometallics,* 1999, *18*, 820.
[34] Witte, P.; Lal, T. K.; Waymouth, R. M., *Organometallics,* 1999, *18,* 4147.
[35] Knüppel, S.; Fauré, J.-L.; Erker, G.; Kehr, G.; Nissinen, M.; Fröhlich, R., *Organometallics,* 2000, *19,* 1262.
[36] Dreier, T.; Erker, G.; Fröhlich, R.; Wibbeling, B., *Organometallics* 2000, *19*, 4095.
[37] Dreier, T.; Unger, G.; Erker, G.; Wibbeling, B.; Fröhlich, R., *J. Organomet. Chem.,* 2001, *622*, 143.
[38] Alonso-Moreno, C.; Antiñolo, A.; Carrillo-Hermosilla, F.; Carrión, P.; López-Solera, I.; Otero, A.; Prashar, S.; Sancho, J. *Eur. J. Inorg. Chem.,* 2005, 2924.
[39] Nifant´ev, I. E.; Ivchenko, P. V.; Bagrov, V. V.; Churakov, A. V.; Mercandelli, P., *Organometallics*, 2012, 31, 4962.
[40] Kaminsky, W.; Fernandes, M., Polyolefins, 2015, 2, 1.
[41] Ahmad, K.; Alt, H. G., unpublished results.