

***ansa Metallocene complexes of zirconium and hafnium with
–SiMe₂-1,2-C₆H₄-CH₂- bridged indenyl ligands as catalyst
precursors for homogeneous ethylene polymerization***

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Abstract

Three new ansa metallocene dichloride complexes of zirconium and hafnium with a 1-methylene-2-dimethylsilylene phenylene bridge connecting two indenyl groups either in the 1,1' or 1,2' positions were synthesized and characterized. These complexes were tested for homogeneous ethylene polymerization after activation with methylaluminoxane (MAO). Zirconium catalysts with 1,2'-bridged bis-indenyl ligands showed higher activities (27100 kg PE/mol_{cat}.h) than 1,1'-bridged catalysts (21700 kg PE/mol_{cat}.h). The analogous hafnium catalyst with a 1,2'-bridged bis-indenyl ligand showed a much lower performance (1500 kg PE/mol_{cat}.h).

Keywords: *ansa Zirconocene and hafnocene complexes; Indenyl ligands; 1-Methylene-2-dimethylsilylene phenylene bridge; Catalytic ethylene polymerization.*

Introduction

ansa Metallocene complexes of group IV metals have been extensively studied as catalysts for the homo- and copolymerization of α -olefins because of their remarkably high activities and stereoselectivities.^[1-40] Factors such as the nature of the complexed transition metal, electron donating or withdrawing effects as well as the steric bulkiness of substituents on the ligands, the rigidity and the length of the bridging unit at the ligand can also play a substantial role in olefin polymerization reactions catalyzed by ansa metallocene complexes.^[1-14] The introduction of a bridge induces a fixed symmetry in metallocene complexes by preventing the rotation of the rings around the ligand-metal bond axis and it provides a wider dihedral angle that favors the coordination of olefins and the growth of the polymer chain with a tacticity controlled by the fixed symmetry.^[15-18] Since the use of chiral ethanediyl-bridged bis(indenyl)titanium and bis(indenyl)zirconium complexes along with methylaluminoxane (MAO) as catalysts for isotactic olefin polymerization,^[13, 14] complexes with alkylenes (up to 12 carbon atoms), silylenes, disilylenes, 1,2-

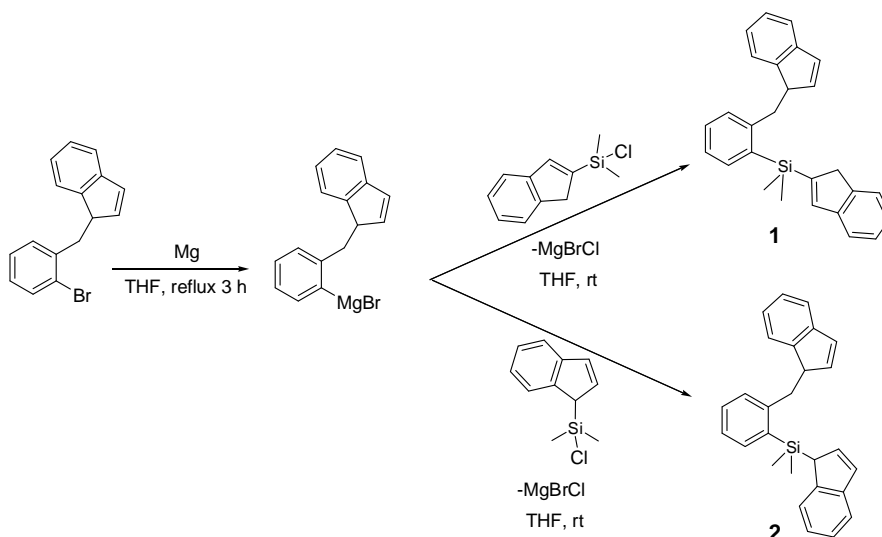
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cycloalkylenes, *o*-phenylene, *o*-phenylenedimethylene and 1,2-naphthylidene bridged bis-indenyl ligands have been studied as catalysts for olefin polymerization.^[15-37] Among different types of bridges, the silylene bridged catalysts show higher activities and provide higher degrees of stereoselectivity than the catalysts bridged with two-atom or longer chains because of their wider dihedral angle and greater stereorigidity of the ligand framework.^[5,15-18] Herein we report the synthesis and characterization of three new ansa metallocene complexes of zirconium and hafnium with a 1-methylene-2-dimethylsilylene phenylene bridge connecting two indenyl ligands either in the 1,1' or 1,2' positions and their ethylene polymerization activities after activation with MAO.

Results and Discussion

Synthesis of bis-indenyl compounds **1** and **2**

The reaction of the Grignard reagent of 2-bromo-1-(1-indenylmethyl)benzene with 2-indenyldimethylchlorosilane or 1-indenyl-dimethylchlorosilane in tetrahydrofuran yields 1-(1-indenylmethyl)-2-(2-indenyldimethylsilyl)benzene (compound **1**) and 1-(1-indenyl-methyl)-2-(1-indenyldimethylsilyl)benzene (compound **2**), respectively (Scheme 1).



Scheme 1: Synthesis of compounds **1** and **2**.

Compounds **1** and **2** were characterized by ¹H, ¹³C and ²⁹Si NMR spectroscopy as well as by EI mass spectrometry. Compound **1** exists in the form of two isomers depending on whether the CH₂ group of the bridge is bonded to C1 or C3 of the indenyl group. The 1-indenyl isomer is the major isomer. In the ¹H NMR spectrum of the 1-indenyl isomer (Figure 1), the signals at δ = 7.39-6.99 ppm (m, 14H) belong to the protons H₂₄, H₂₃, H₂₂, H₂₁, H₂₀, H₁₃, H₁₂, H₁₁, H₁₀, H₇, H₆, H₅, H₄ and H₃. The signal at δ = 6.92 ppm (br, 1H) is due to the indenyl proton H₂. The signal at δ = 3.81 ppm (br, 2H) belongs to the indenyl protons H₁₉ while the signal for the indenyl proton H₁₉ appears at δ = 3.42 ppm (br, 1H). The doublets at δ = 3.04 and 2.81 ppm (d,

10 Hz, 2H) derive from the diastereotopic CH₂ protons of H8. The signals for the Si-CH₃ groups, H16 and H17, arise at δ = 0.12 (s, 3H) and 0.06 ppm (s, 3H).

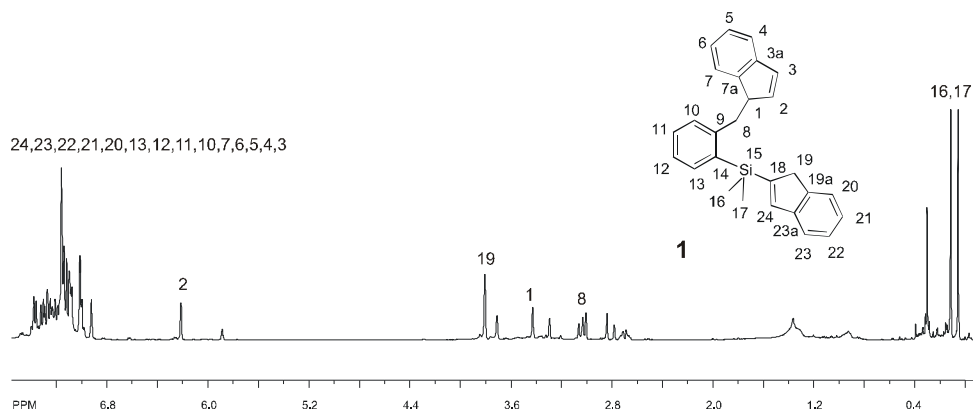


Figure 1: ¹H NMR spectrum of compound 1 in benzene-d₆.

The ¹³C NMR spectrum of 1 (Figure 2) is very indicative because every carbon atom shows, due to the asymmetry of the molecule, its own chemical shift. The signals for the quaternary carbon atoms C23a, C19a, C18, C14, C9, C7a and C3a arise at δ = 147.2, 146.2, 145.6, 144.7, 141.3 and 140.1 ppm. The signals at δ = 142.9, 132.1, 129.0, 128.6, 126.6, 126.3, 125.4, 125.3, 124.3, 124.0, 123.3, 121.4 and 120.2 ppm belong to the C23, C22, C21, C20, C24, C13, C12, C11, C10, C7, C6, C5, C4, C3 and C2 CH groups. The signal for the indenyl CH group (C1) can be observed at δ = 44.3 ppm while the signal at δ = 42.8 ppm belongs to the indenyl CH₂ group (C19). The signal for the C8 CH₂ group appears at δ = 34.8 ppm while the signals for the two magnetically non equivalent C16 and C17 CH₃ groups arise at δ = -3.1 and -3.7 ppm.

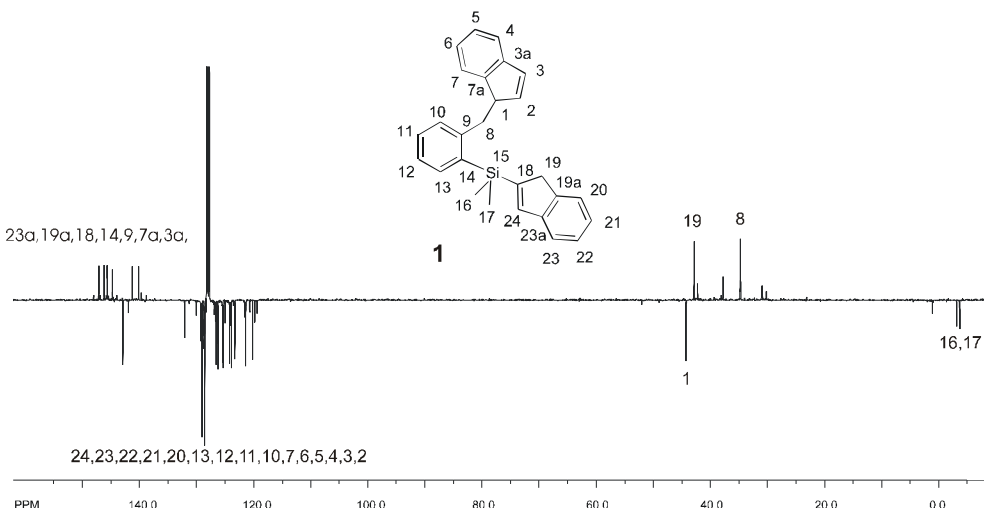


Figure 2: ¹³C NMR spectrum of compound 1 in benzene-d₆.

The mass spectrum of compound 1 (Figure 3) shows the molecular ion peak at m/z = 378. The loss of a methyl group followed by the loss of a hydrogen atom leads to a fragment at m/z = 362. The indenyldimethylsilyl fragment at m/z = 173 appears as base peak.

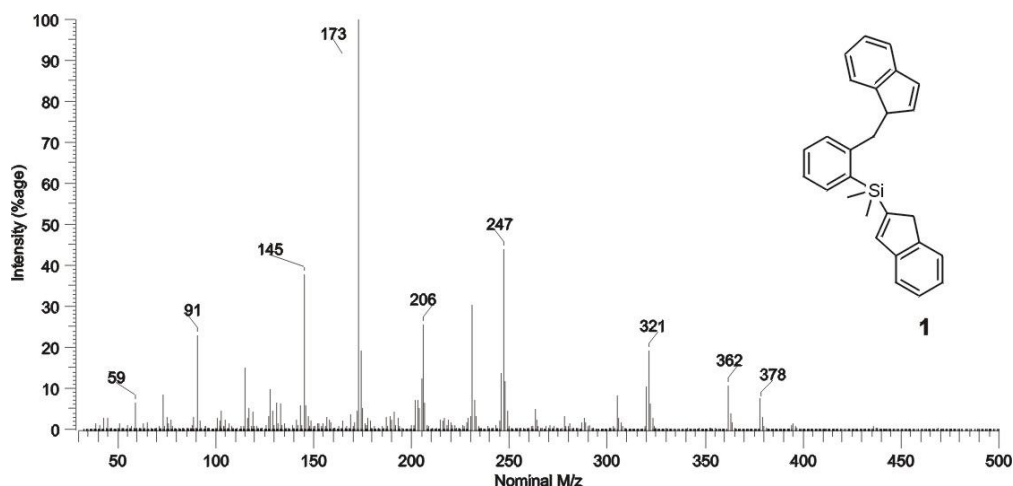
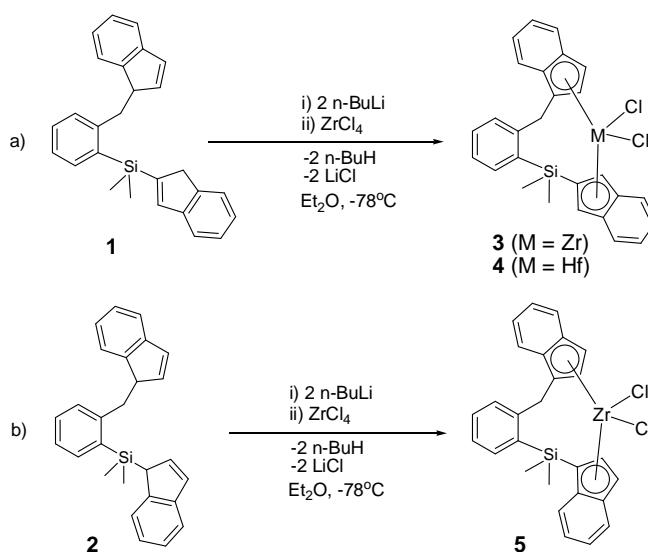


Figure 3: Mass spectrum of compound 1

Syntheses of compounds 3-5

The reaction of the lithium salts of compounds 1 and 2 with zirconium tetrachloride or hafnium tetrachloride in diethyl ether yields the desired metallocene complexes 3-5 (Scheme 2). The synthesized complexes were characterized by ^1H , ^{13}C and ^{29}Si NMR spectroscopy as well as EI mass spectrometry (see experimental part).



Scheme 2: Synthesis of complexes 3-5.

In the ^1H -NMR spectrum of complex 4 (Figure 4), the signals at $\delta = 7.50$ -7.43 (m, 2H), 7.33-7.28 (m, 1H) and 7.20-6.92 ppm (m, 9H) derive from the aryl protons H4, H5, H6, H7, H10, H11, H12, H13, H20, H20', H21 and H21'. The signals at $\delta = 5.85$ (d, $J=2.2$ Hz, 1H) and 5.79 ppm (d, $J=2.2$ Hz, 1H) are assigned to the cyclopentadienyl ring protons of the 1-indenyl group, the signal at $\delta = 5.75$ ppm (s, 2H) belongs to H19 and H19'. The signal for the diastereotopic CH₂ protons (H8) appear as an AB pattern

at $\delta = 4.10$ and 4.01 ppm (d, 16.0 Hz, 2H) while the signals for the two magnetically non-equivalent methyl groups arise at $\delta = 0.92$ (s, 3H) and 0.68 ppm (s, 3H).

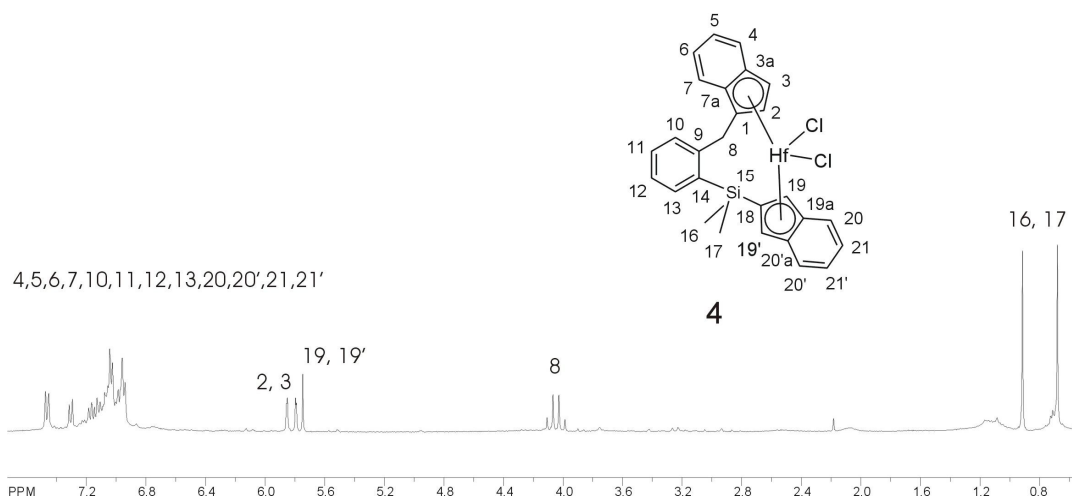


Figure 4: ^1H NMR Spectrum of complex **4** in chloroform- d .

In the ^{13}C NMR spectrum of complex **4** (Figure 5), the signals for the quaternary carbon atoms C20'a, C19a, C18, C14, C9, C7a, C3a and C1 arise at $\delta = 140.4$, 134.0, 133.3, 130.6, 127.9, 125.0, 112.1 and 89.1 ppm. The signals at $\delta = 128.5$, 128.4, 127.2, 126.4, 126.3, 126.2, 126.1, 125.3, 124.9 and 124.2 ppm are assigned to the C21', C21, C20', C20, C13, C12, C11, C10, C7, C6, C5 and C4 CH groups. The signals at $\delta = 118.4$, 104.2 and 100.6 ppm can be assigned to the C19', C19, C3 and C2 CH groups. The signal at $\delta = 34.2$ ppm belongs to the C8 carbon atom while the signals for C16 and C17 appear at $\delta = -2.3$ and -4.5 ppm.

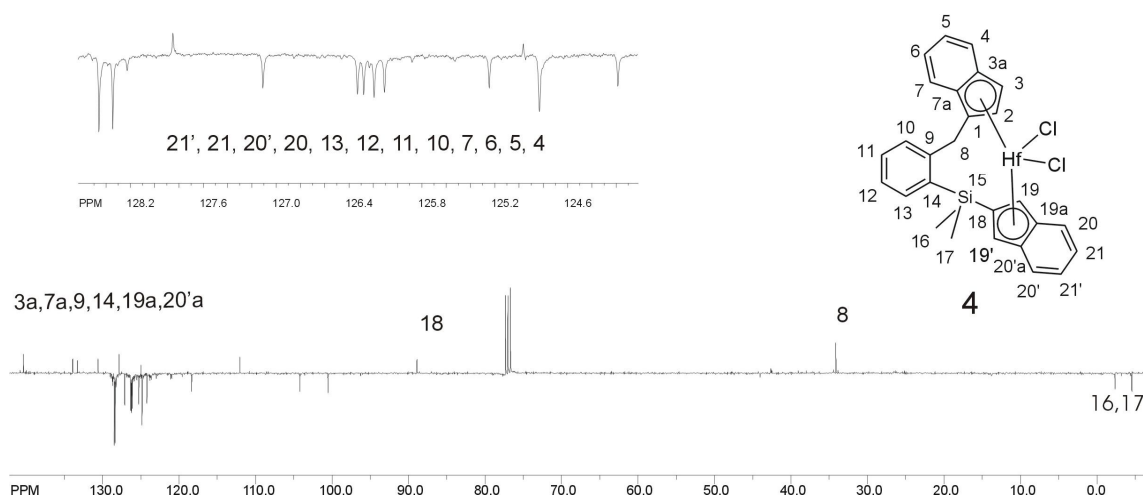


Figure 5: ^{13}C NMR spectrum of complex **4** in chloroform- d

In the mass spectrum of complex **3** (Figure 6), the peak for the molecular ion appears at $m/z = 536$ with 12% intensity relative to the base peak. The loss of a chloride fragment leads to a peak at $m/z = 501$. The peak at $m/z = 378$ corresponds to

the free ligand while the base peak at $m/z = 173$ corresponds to an indenyl dimethylsilyl fragment.

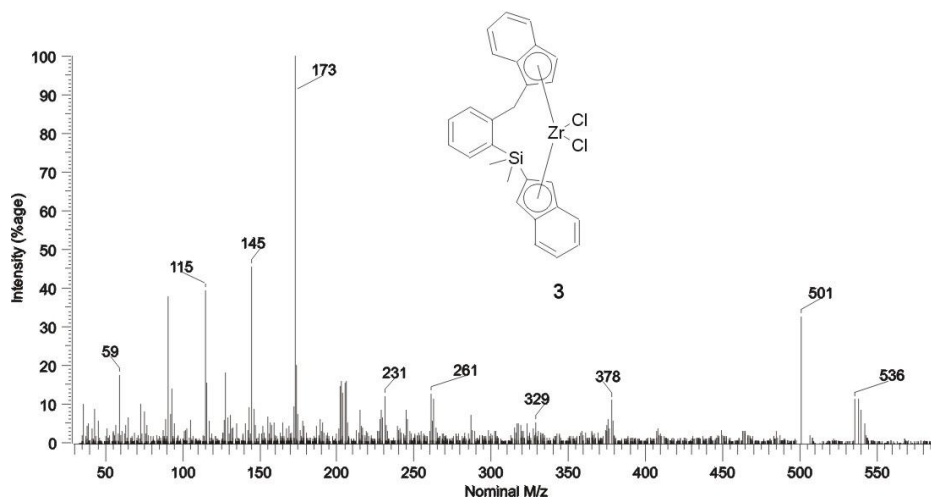


Figure 6: Mass spectrum of complex **3**

Ethylene polymerization

The metallocene complexes **3-5** were activated with a 2000 molar excess of methylaluminoxane (MAO) and applied to homogeneous ethylene polymerization. Their ethylene polymerization activities are listed in Table 1.

Table 1: Ethylene polymerization activities of complexes **3-5**.

Complex	Temperature (°C)	Activity (kg PE/mol _{cat} ·h)
3	65	27100
3	85	61900
4	65	1500
5	65	21700

Polymerization conditions: M : Al = 1: 2000, 250 mL n-pentane, 10 bar ethylene, 1h.

Among complexes **3-5**, the zirconium complex **3** with a 1,2'-bridged bis-indenyl ligand shows the highest activity for ethylene polymerization (27100 kg PE/mol_{cat}·h) after activation with MAO. When the polymerization temperature was increased to 85 °C, the activity was more than doubled (61900 kg PE/mol_{cat}·h) indicating a high thermal stability of the catalyst. Zirconium complex **5** with a 1,1'-bridged bis-indenyl ligand shows 20% lower activity (21700 kg PE/mol_{cat}·h) than complex **3**. The only difference of the catalysts is the 1,1'-connection instead of the 1,2'-connection of the two indenyl ligands. All the other parameters were the same. Ethylene polymerization activities of both catalysts **3** and **5** are much higher than the productivities of the non-bridged bis-indenyl zirconium dichloride/MAO catalyst (3200 kg PE/mol_{cat}·h) and the methylene-bridged bis-indenyl zirconium dichloride/MAO catalyst (1200 kg PE/mol_{cat}·h).^[39] Their activities are also much higher than those of ansa-dichloro[o-phenylenedimethylenebis(η⁵-1-indenyl)]zirconium (2400 kg PE/mol_{cat}·h).^[28] The only structural

difference between them is that in the case of complexes **3** and **5** one methylene group of the *o*-phenylenedimethylene bridge is replaced by a dimethylsilyl group. The hafnium catalyst **4** shows a considerable lower activity (1500 kg PE/mol_{cat}·h) than the analogous zirconium catalyst **3**. The reason seems to be the thermodynamically stronger metal carbon bonds in case of the hafnium complex slowing down the kinetics of the various polymerization steps.^[16,19] In *rac*-Et[IndH₄]₂HfC1₂, the Hf-ring centroid distance and Hf-C1 lengths are 0.02 and 0.04 Å, shorter, respectively, than the corresponding distances in *rac*-Et[IndH₄]₂ZrC1₂^[40] confirming thus these results.

Experimental

General aspects

All reactions were carried out under an inert atmosphere of argon using Schlenk line technique. Diethyl ether, *n*-pentane, tetrahydrofuran and toluene were purified by distillation over Na/K alloy. Deuterated solvents (CDCl₃ and C₆D₆) were purchased from Eurisotop and stored over molecular sieves (3Å). Argon (5.0) and ethylene (3.5) were purchased from Rießner Company. Methylaluminoxane (MAO) (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 298 K. The chemical shift of the residual proton signal of the solvent was used as a reference (δ = 7.24 ppm for chloroform and δ = 7.15 ppm for benzene) for the ¹H NMR spectra, while the chemical shift of the solvent was used as a reference (δ = 77.0 ppm for chloroform-*d* and δ = 128.0 ppm for benzene-*d*₆) for the ¹³C-NMR spectra.

General description of ethylene polymerization experiments

Complexes **3-5** were activated with MAO (M : Al = 1: 2000). The activated complexes were transferred to a 1 liter Büchi reactor as pentane suspension. A constant ethylene pressure of 10 bar was applied for 1 h. After disconnecting the ethylene flow and cooling the system to room temperature, the pressure was released. The obtained polymer was filtered over a frit, washed with dilute hydrochloric acid, water and finally with acetone and dried under vacuum.

Synthesis of the bis(indenyl) compounds 1 and 2.

An amount of 5 mmol (1.43 g) of 2-bromo-1-(1-indenylmethyl)benzene in 50 mL THF was added dropwise to a 20 mmol (0.50 g) suspension of magnesium powder in 50 mL THF at room temperature. The mixture was refluxed for 3 h, cooled to room temperature and filtered. The filtrate was added dropwise to 5 mmol (1.04 g) of 2-indenyldimethylchlorosilane or 1-indenyldimethyl-chlorosilane at room temperature and stirring was continued for 3 h. THF was removed, 100 mL *n*-pentane was added and the mixture was filtered. The filtrate was passed over a silica gel filled column, *n*-pentane was removed by evacuation and the obtained oily compound was washed

several times with little amounts of cold pentane to obtain the desired compound as pale yellow oil.

Compound 1:

¹H-NMR (400 MHz, C₆D₆, 298 K): 7.39-6.99 m (14H), 6.92 br (1H), 3.81 br (2H, Ind-CH₂), 3.42 br (1H, Ind-CH), 3.04, 2.81 (d, 10 Hz, 2H, CH₂), 0.12 s (3H, SiCH₃), 0.06 s (3H, SiCH₃).

¹³C-NMR (100 MHz, C₆D₆, 298 K): δ = 147.2, 146.2, 145.6, 145.6, 144.7, 141.3, 140.1 (Cq), 142.9, 132.1, 129.3, 129.0, 128.6, 126.6, 126.4, 126.3, 125.4, 125.3, 124.3, 124.0, 123.3, 121.4, 120.2, 44.3 (CH), 42.8 (Ind-CH₂), 34.8 (CH₂), -3.1 (SiCH₃), -3.7 (SiCH₃).

²⁹Si-NMR (79.4 MHz, C₆D₆, 298 K): δ = -6.2

MS: 378 (M⁺, 9), 362 (12), 321 (20), 247 (48), 173 (100).

Compound 2:

¹H-NMR (400 MHz, C₆D₆, 298 K): δ = 7.47-7.10 m (12H), 7.07 d (J=5.6Hz, 1H), 6.80 d (J=5.6Hz, 1H), 6.27 d (J=5.6Hz, 1H), 5.98 br (1H), 3.82 br (1H), 3.46 br (1H), 2.76-2.62 m (2H), -0.18 s (3H), -0.57 s (3H).

¹³C-NMR (100 MHz, C₆D₆, 298 K): δ = 145.9, 145.1, 144.8, 144.7, 141.7, 140.2 (Cq), 135.2, 131.4, 129.8, 129.7, 129.2, 129.1, 128.6, 126.4, 125.5, 125.4, 124.4, 124.3, 123.4, 123.3, 121.6, 120.2 (CH), 45.5, 43.6, 34.7 (CH₂), -4.8 (CH₃), -6.8 (CH₃).

Synthesis of complexes 3-5

An amount of 2 mmol of n-butyllithium (1.6 M in hexanes) was added to 1 mmol (0.38 g) of the ligand precursor dissolved in 50 mL diethyl ether at -78 °C. The solution was allowed to warm to room temperature and stirred for further 3 h. This solution was then transferred to a 1 mmol (0.23 g) suspension of zirconium tetrachloride in 50 mL diethyl ether at -78 °C. The solution was allowed to warm to room temperature and stirring was continued for 24 h. Diethyl ether was removed, an amount of 60 mL toluene was added and the suspension was filtered. The volume of the filtrate was reduced, the complex was precipitated by addition of pentane and filtered. The precipitate was washed several times with pentane and dried in vacuo to obtain the desired complex as yellow powder in 50% yield.

Complex 3:

¹H-NMR (400 MHz, CDCl₃, 298 K): δ = 7.46-6.83 m (12H), 5.89 br (1H), 5.82 br (1H), 5.72 br (2H), 4.02, 3.92 (d, 16.0 Hz, 2H), 0.86 s (3H), 0.60 s (3H).

¹³C-NMR (100 MHz, CDCl₃, 298 K): δ = 140.1, 134.7, 133.6, 131.1, 130.5, 109.4, 89.0 (Cq), 128.5, 128.4, 127.2, 126.5, 126.3, 126.2, 125.3, 125.0, 124.8, 124.4, 119.9, 107.2, 103.5, 34.3 (CH₂), -2.2 (CH₃), -4.6 (CH₃).

²⁹Si-NMR: (79.4 MHz, CDCl₃, 298 K): δ = -2.6.

MS: 536 (M⁺, 58), 501 (30), 173 (100), 115 (40).

Complex 4:

¹H-NMR (400 MHz, CDCl₃, 298 K): δ = 7.50-7.43 m (2H), 7.33-7.28 m (1H), 7.20-6.92, m (9H), 5.85 d (J=2.2 Hz, 1H), 5.79 d (J=2.2 Hz 1H), 5.75 s (2H), 4.10, 4.01 (d, 16.0 Hz, 2H), 0.92 s (3H), 0.68 s (3H).

¹³C-NMR (100 MHz, CDCl₃, 298 K): δ = 140.4, 134.0, 133.3, 130.6, 127.9, 125.0, 112.1, 89.1 (Cq), 128.5, 128.4, 127.2, 126.4, 126.3, 126.2, 126.1, 125.3, 124.9, 124.2, 118.4, 104.2, 100.6 (CH), 34.2 (CH₂), -2.3 (CH₃), -4.5 (CH₃).

²⁹Si-NMR: (79.4 MHz, CDCl₃, 298 K): δ = -2.5.

MS: 626 (M⁺, 100), 591 (35), 173 (11).

Complex 5:

¹H-NMR (400 MHz, CDCl₃, 298 K): (major isomer) δ = 7.62-6.80 m (12H), 6.06 br (2H), 5.72 br (2H), 4.16, 4.07 (d, 15.5 Hz, 2H), 1.08 s (3H), 1.05 s (3H).

¹³C-NMR: (100 MHz, CDCl₃, 298 K): (major isomer) δ = 140.0, 134.1, 133.8, 132.6, 130.2, 125.8, 88.9, 86.4 (Cq), 128.4, 128.3, 127.3, 127.2, 126.8, 126.6, 126.1, 124.8, 124.3, 117.9, 117.6, 116.8 (CH), 34.2 (CH₂), -1.4 (CH₃), -1.7 (CH₃).

MS: 537 (M⁺, 70), 499 (90), 263 (60), 173(100), 115 (44).

Conclusions

Zirconium and hafnium complexes with a 1-methylene-2-dimethylsilylene phenylene bridge connecting two indenyl ligands either in the 1,1' or 1,2' positions were synthesized and tested for ethylene polymerization after activation with MAO. The zirconium catalyst with a 1,2'-bridge showed higher activity than the 1,1'-bridged catalyst. Both zirconium catalysts showed much higher activities than the known non-bridged bis(indenyl) zirconium dichloride, methylene-bridged bis(indenyl) zirconium dichloride and o-phenylenedimethylene-bridged bis(indenyl) zirconium dichloride catalysts. This is a convincing justification that small changes in a molecule can have strong effects in the performance of such catalysts. The hafnium catalyst with a 1,2'-bridged bis-indenyl ligand showed much lower activity than the analogous zirconium catalyst confirming that higher homologues slow down the kinetics in polymerization reactions due to stronger metal carbon bonds.

Acknowledgements

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