

Unbridged 9-Substituted Bis(silylfluorenyl) Complexes of Zirconium and Hafnium

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Abstract

Two silyl substituted unbridged bis(fluorenyl) complexes of zirconium and hafnium were prepared and characterized. The influence of the tolyldimethylsilyl substituent in the 9-position of the fluorenyl ring did not support the catalytic activity of these complexes for ethylene polymerization after activation with methylaluminoxane (MAO). Obviously, the monomer ethylene induces the ring slippage behaviour of these ligands from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ decomposing the catalyst.

Keywords: *Bis(fluorenyl) complexes; Tolyldimethylsilyl substituent; Zirconium and hafnium complexes.*

Introduction

Bridged fluorenyl complexes of zirconium and hafnium are known to be highly active catalyst precursors in olefin polymerization and copolymerization^[1-16] and are known as the record holders in this field. However, unbridged bis(fluorenyl) complexes^[17-21] and the mixed fluorenyl and cyclopentadienyl complexes^[22-24] are far less active towards olefin polymerization than their analogous bridged bis(fluorenyl) complexes due to the ring slippage phenomenon^[3]. To date, symmetrical unbridged 9-silyl-substituted fluorenyl dichloride metallocene complexes still have not been reported. Herein, the synthesis of the zirconium and hafnium complexes of 9-(4-tolyldimethylsilyl) fluorenyl and their behavior in ethylene polymerization are reported.

Materials and Methods

General

All reactions were carried out under an inert gas atmosphere of pure oxygen-free argon using standard Schlenk techniques. n-Pentane, n-hexane, diethyl ether, toluene, and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether

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was additionally distilled over lithium aluminum hydride. Toluene was additionally distilled over phosphorus pentoxide. Methylene chloride and carbon tetrachloride were dried over phosphorus pentoxide. Deuterated organic solvent (CDCl_3) for NMR spectroscopy was purchased from Euriso-Top and stored over molecular sieves (3 Å). Argon (5.0) and ethylene (3.5) were purchased from Rießner Company. Methylaluminoxane (10% in toluene) was purchased from Chemtura Europe Limited (Bergkamen). All other starting materials were commercially available and used without further purification.

NMR spectroscopy

NMR spectra were recorded with Bruker ARX (250 MHz), Varian Inova (300 MHz) or Varian Inova (400 MHz) spectrometers. All spectra were recorded at 298 K. In the ^1H -NMR spectra, the chemical shift of the residual proton signal of the solvent was used as a reference ($\delta = 7.24$ ppm for chloroform). In the ^{13}C -NMR spectra, the chemical shift of the solvent was used as a reference ($\delta = 77.0$ ppm for chloroform- d_1).

GC/MS

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

Elemental analysis

Elemental analyses were performed with a Vario EL III CHN instrument. Therefore, 4-6 mg of the complex were weighed into a standard tin pan. The tin pan was carefully closed and introduced into the auto sampler of the instrument. The values of C, H and N were calibrated using acetamide as a standard.

Synthesis of 9-tolyldimethylsilylfluorene 2

n-Butyllithium (12 mmol, 1.6 M in hexanes) was added to 12 mmol of fluorene dissolved in 100 ml of diethyl ether at -78 °C. The solution was stirred for 12 hours at room temperature and then cooled to 0 °C. Tolychlorodimethylsilane **1** (12 mmol) in 50 ml of diethyl ether was added slowly. The resulting solution was stirred overnight at room temperature and then hydrolyzed by the addition of 100 ml of distilled water. The organic phase was separated and dried by passing through a sodium sulphate column. The solution was reduced in volume and kept at -24 °C for 72 hours to give **2** as yellow crystals in 85% yield.

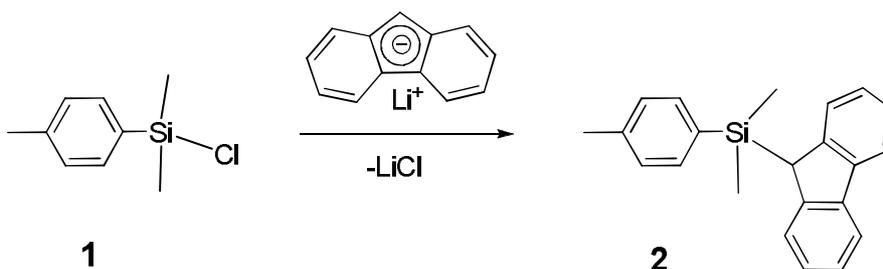
Synthesis of the transition metal complexes **3** and **4**

n-Butyllithium (4 mmol, 1.6 M in hexanes) was added to 4 mmol of compound **2** dissolved in 50 ml of diethyl ether at -78 °C. This solution was allowed to warm up to room temperature and it was stirred overnight. The mixture was transferred to a suspension of either zirconium(IV) chloride (2 mmol) or hafnium(IV) chloride (2 mmol) in 50 ml of 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 in vacuo and toluene (100 ml) was added. The toluene suspension was filtered, the volume of the filtrate was reduced, and the complexes were precipitated by the addition of n-pentane. After filtration, the precipitate was washed several times with n-pentane and dried in vacuo to obtain the desired complexes **3** and **4** as yellow powders in 70-75% yields.

Results and discussion

Synthesis of the ligand precursor **2**

The 9-substituted silylfluorenyl compound **2** was obtained by the reaction of fluorenyllithium, prepared separately by the deprotonation of fluorene with n-BuLi, and an equivalent amount of p-tolylchlorodimethylsilane (**1**) in diethyl ether (Scheme 1).



Scheme 1: Preparation of compound **2**.

Characterization of compound **2**

The ¹H NMR spectrum of compound **2** (Figure 1) shows a doublet at $\delta = 7.76$ ppm (d, ³J = 7.4 Hz, 2H) which can be assigned to the aromatic protons H6 belonging to the silyl phenyl ring while the protons H7 and H1 produce the overlapping multiplet at $\delta = 7.29$ -7.24 ppm (4H). The other aromatic protons belonging to the fluorenyl moiety (H2, H3, and H4) give rise to the multiplet which appears at $\delta = 7.17$ -7.09 ppm (m, 6H). The singlet at $\delta = 4.00$ ppm (1H) is assigned to the proton H5 while the singlet at $\delta = 2.33$ ppm (s, 3H) is characteristic for the tolyl methyl protons H8. The singlet appearing further upfield at $\delta = 0.01$ ppm (s, 6H) corresponds to the equivalent methyl group protons (H9) attached to the silicon atom.

The ¹³C NMR spectrum of compound **2** (Figure 2) reveals thirteen signals which can be explained as follows: four signals at $\delta = 145.1$, 140.5, 139.2, and 133.5 ppm belong to the quaternary carbon atoms C11, C12, C5, and C6. Six equally intensive signals appear at $\delta = 134.2$, 128.6, 125.8, 125.2, 124.3, and 119.8 ppm and represent the CH-type carbon atoms C8, C9, C1, C2, C3, and C4. The signal at $\delta = 41.9$ ppm is

generated by C7 at the 9-position of the fluorenyl moiety whereas the signals at $\delta = 21.5$ and -4.9 ppm can be assigned to the methyl group carbon atoms C10 and C13.

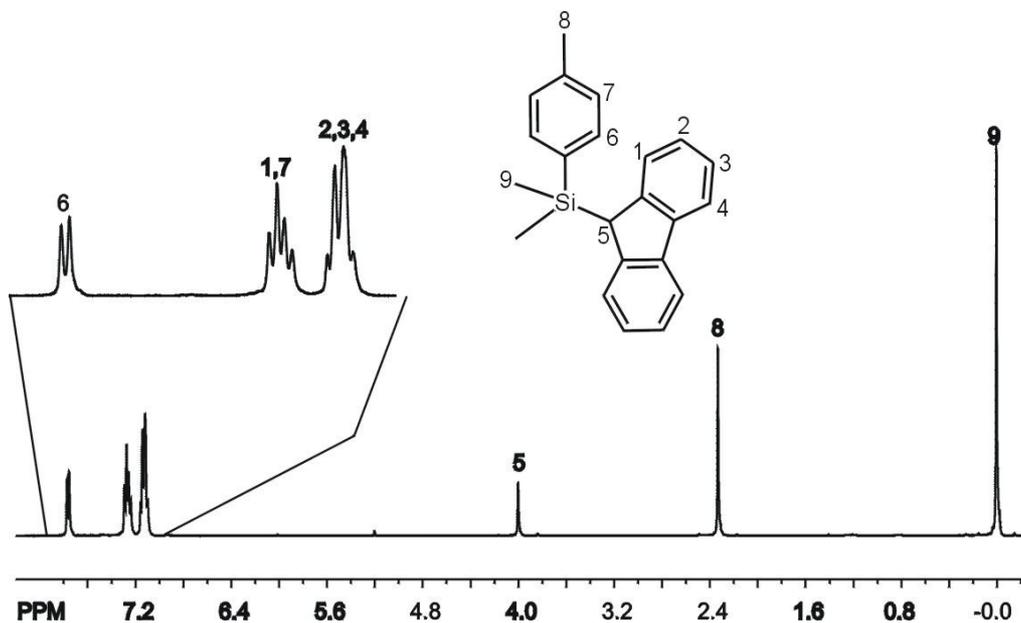


Figure 1: ¹H NMR spectrum of compound 2.

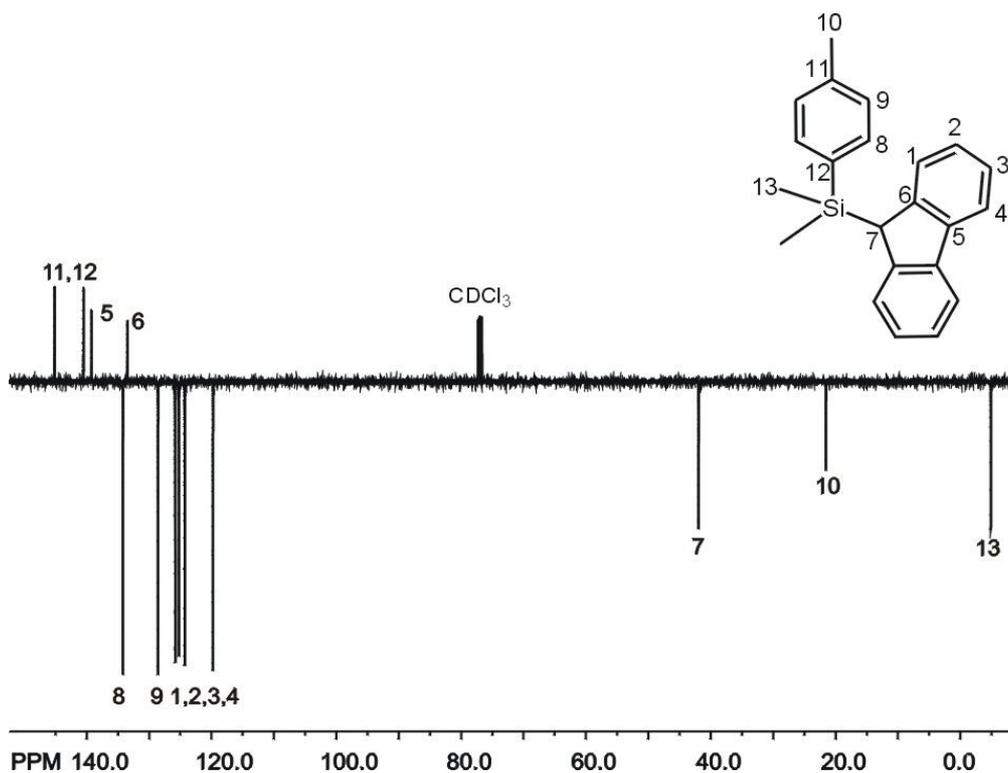


Figure 2: ¹³C NMR spectrum of compound 2.

The mass spectrum of compound 2 (Figure 3) shows the molecular ion peak at $m/z = 314$ with 6% intensity relative to the base peak. The fragmentation of the compound through the silicon fluorene bond results in two smaller fragments: The

fluorene fragment produces the peak at $m/z = 165$ with 94% intensity, and the tolyldimethylsilyl fragment generates the base peak at $m/z = 149$.

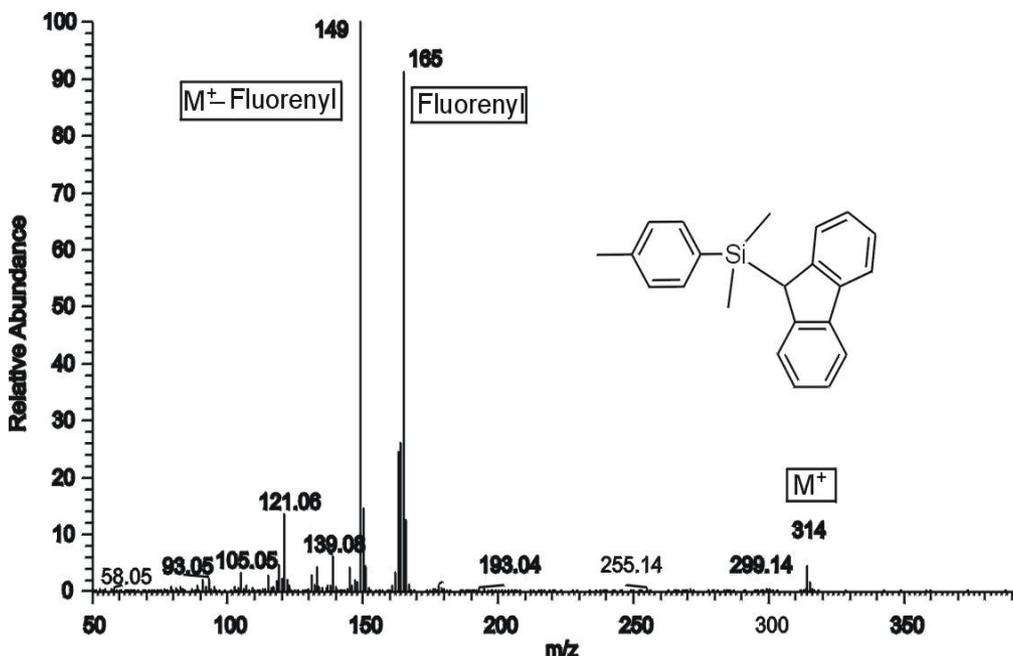
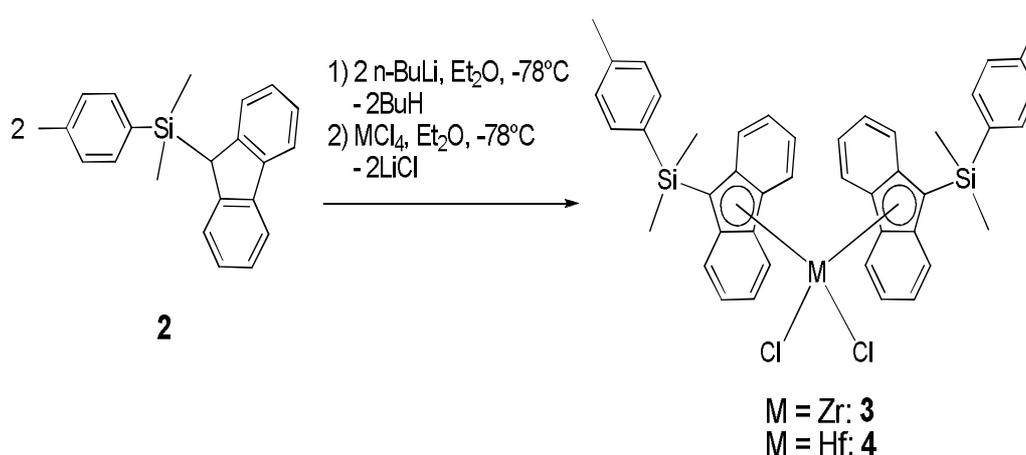


Figure 3: Mass spectrum of compound 2.

Synthesis of complexes 3 and 4

The conversion of the ligand precursor **2** to the corresponding lithium salt was accomplished via deprotonation by a stoichiometric amount of *n*-butyllithium in diethyl ether. A subsequent metallation of the lithiated fluorenyl derivative with 0.5 equivalents of zirconium(IV) chloride or hafnium(IV) chloride in diethyl ether afforded the desired complexes **3** and **4** in 60-70% yield (Scheme 2).



Scheme 2: Synthesis of complexes **3** and **4**.

Characterization of complexes 3 and 4

Complexes **3** and **4** were characterized by elemental analysis (Experimental part) and NMR spectroscopy (Table 1). The deviations of the C,H values relative to the

calculated values could be referred to partial decompositions of these complexes during the preparation steps of the probes. The mass spectrometric characterization of complexes **3** and **4** using a direct inlet mass spectrometer (EI, 70 eV) was not successful. Molecular peaks could not be detected, only fragments. This is another indication for the easy decomposition of these complexes triggered by the ring-slippage behavior of the fluorenyl ligands.

The ^1H and ^{13}C NMR spectra of complex **3** are discussed as examples. The ^1H NMR spectrum of complex **3** (Figure 4) exhibits seven resonance signals that can be interpreted as follows: The two doublets at $\delta = 7.78$ ppm ($^3J = 8.2$ Hz, 4H) and 7.33 ppm ($^3J = 8.2$ Hz, 4H) are assigned to the aromatic protons H6 and H5 belonging to silyl phenyl rings. The protons at the fluorenyl moieties (H1, H2, H3, and H4) produce the three signals at $\delta = 7.20$ -7.17 (t, 4H), 7.00-6.94 (m, 8H), and 6.87 (d, $^3J = 7.3$ Hz, 4H) ppm. The signal for the tolyl methyl protons (H7) appears at $\delta = 2.15$ ppm as a singlet with 6H intensity, while the signal associated to the silyl methyl groups (H8) appears as a singlet at $\delta = 0.70$ ppm.

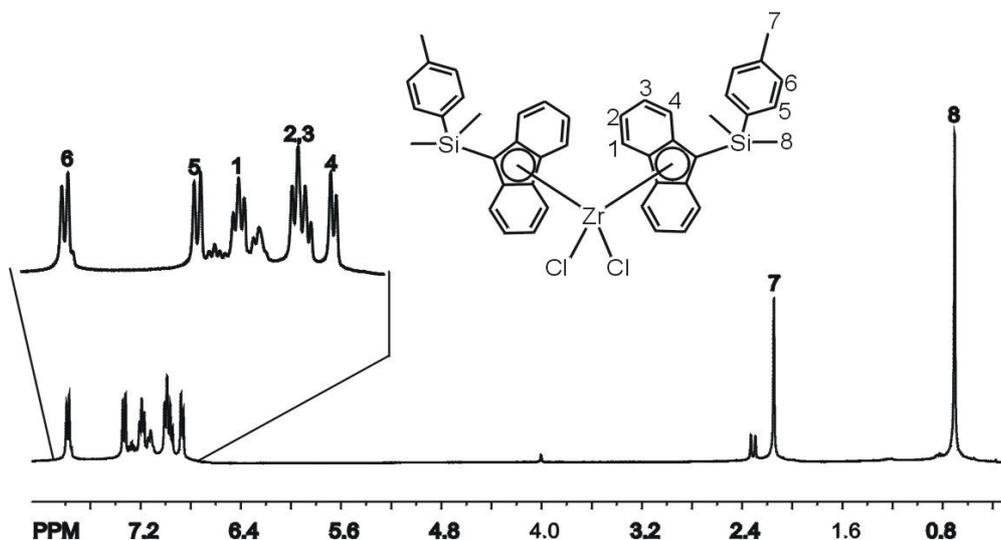


Figure 4: ^1H NMR spectrum of complex **3**.

The ^{13}C NMR spectrum of complex **3** (Figure 5) shows three signals at $\delta = 138.3$, 137.4 and 136.3 ppm representing the quaternary carbon atoms C11, C12, and C6. The CH-type carbon atoms of the silyl phenyl rings (C9 and C8) appear at $\delta = 134.0$ and 128.3 ppm while the CH-type carbon atoms at the fluorenyl moieties (C1, C2, C3, and C4) give rise to the signals at $\delta = 127.5$, 126.2, 124.0 and 123.3 ppm. The signal at $\delta = 120.4$ ppm is assigned to the quaternary carbon atom C5 while the signal at $\delta = 102.0$ ppm can be interpreted as the quaternary carbon atom C7 indicating a η^5 bonding mode^[25]. The methyl groups (C10 and C13) furnish the upfield shifted signals at $\delta = 21.3$ and 0.5 ppm.

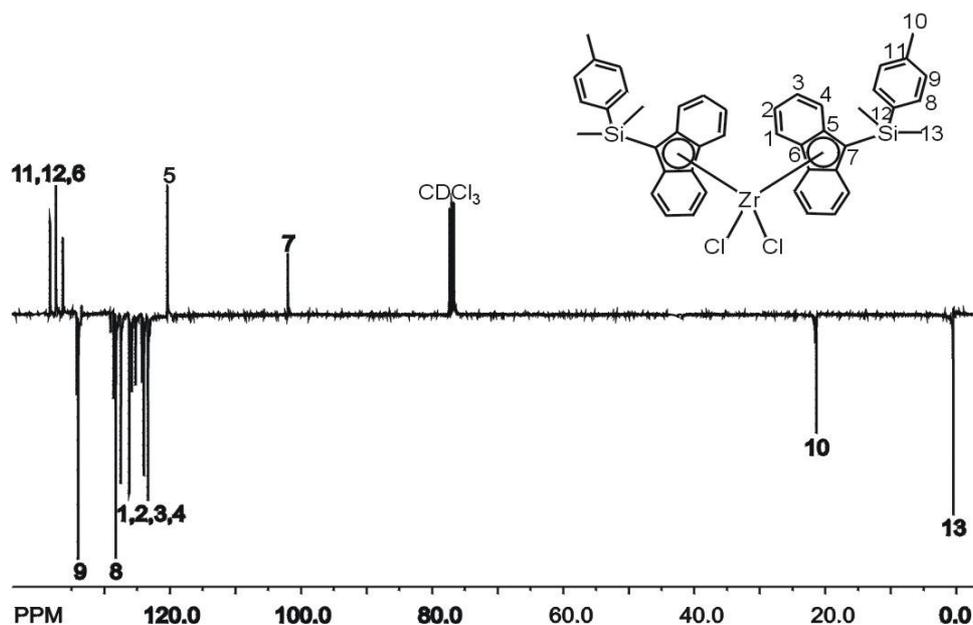


Figure 5: ^{13}C NMR spectrum of complex 3.

Table 1: ^1H and ^{13}C NMR^a spectra of complexes 3 and 4.

No.	^1H NMR	^{13}C NMR
3	7.78 d ($^3J = 8.2$ Hz, 4H, Ar-H)	138.3, 137.4, 136.3 (C_q)
	7.33 d ($^3J = 8.2$ Hz, 4H, Ar-H)	134.0, 128.3, 127.5, 126.2,
	7.20-7.17 t (4H)	124.0, 123.3 (CH)
	7.00-6.94 m (8H)	120.4, 102.0 (C_q)
	6.87 d ($^3J = 7.3$ Hz, 4H)	21.3, (CH_3)
	2.15 s (6H, Ar- CH_3)	0.5 ($\text{Si}(\text{CH}_3)_2$)
	0.70 s (12H, $\text{Si}(\text{CH}_3)_2$)	
4	7.81 d ($^3J = 9.1$ Hz, 4H, Ar-H)	139.7, 137.9, 136.1 (C_q)
	7.39 d ($^3J = 9.1$ Hz, 4H, Ar-H)	134.6, 128.4, 127.7, 126.5,
	7.21-7.12 t (4H)	124.2, 123.1 (CH)
	7.05-6.89 m (8H)	120.9, 103.1 (C_q)
	6.85 d ($^3J = 7.3$ Hz, 4H)	21.4, 0.5 (CH_3)
	2.15 s (6H, Ar- CH_3)	0.5 ($\text{Si}(\text{CH}_3)_2$)
	0.70 s (12H, $\text{Si}(\text{CH}_3)_2$)	

^a δ (ppm) rel. CDCl_3 (7.24 ppm, ^1H NMR and 77.0 ppm, ^{13}C NMR) at 298 K.

Table 2: The elemental analysis for complexes 3 and 4.

Complex No.	$\text{C}_{\text{exp}}\%$	$\text{C}_{\text{theor}}\%$	$\text{H}_{\text{exp}}\%$	$\text{H}_{\text{theor}}\%$
3	64.33	66.97	4.19	5.36
4	57.52	60.30	3.35	4.83

Ethylene polymerization experiments with complexes 3 and 4

Complexes **3** and **4** were tested for ethylene polymerization after activation with methylaluminumoxane (MAO) with an M : Al ratio of 1:2000. The experiments were conducted at 60°C and 10 bar ethylene pressure in 250 ml of pentane. These complexes were found to be inactive in polymerization reactions. The same result was reported using unbridged 9-substituted phenyl fluorenyl complexes for the polymerization of ethylene and propene^[3]. The inertness of the fluorenyl complexes **3** and **4** could be attributed to the thermal instability resulting from ethylene induced ring-slippage reactions changing the hapticity of the fluorenyl rings from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ ^[3]. The bulkiness of the substituents may also be a reason for the inactivities of **3** and **4**.

Conclusions

The negative charge of the ligand favours the coordination to the metal. This contribution underlines the fact that fluorenyl ligands cannot be considered as cyclopentadienyl or indenyl derivatives but rather as two tethered benzene rings forming a five-membered ring that is able to participate on their aromaticity. The inertness of the fluorenyl complexes **3** and **4** could be attributed to the thermal instability resulting from ring-slippage reactions changing the hapticity of the five membered fluorenyl rings from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ ^[2] induced by the coordination of the coordinated ethylene monomer. The bulkiness of the substituents may also be a reason for the inactivity of **3** and **4**.

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