

# The preparation and characterization of 9-substituted bis(flourenyl) zirconium dichloride complexes <sup>☆</sup>

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## Abstract

The preparation of new zirconocene dichloride complexes containing 9-substituted fluorenyl ligands is reported. The complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Keywords:** Bis(flourenyl)complexes of zirconium; Multinuclear NMR spectroscopy

## 1. Introduction

Metallocene dichloride complexes (especially ansa-metallocenes) have been established as catalyst precursors in the polymerization of olefins [1–10]. The first fluorenyl zirconium complex, (C<sub>13</sub>H<sub>9</sub>)<sub>2</sub>ZrCl<sub>2</sub>, was synthesized by Samuel and Setton [11] in 1965. In the following years, only very few examples of bis(flourenyl) complexes of zirconium were described [12–15]. Of these (1-CH<sub>3</sub>C<sub>13</sub>H<sub>8</sub>)<sub>2</sub>ZrCl<sub>2</sub> [13,15] and [(1-CH<sub>3</sub>C<sub>13</sub>H<sub>7</sub>)<sub>2</sub>ER<sub>2</sub>]ZrCl<sub>2</sub> (E = Si or Sn; R = Me or Ph) [14] can be used in combination with methyl alumoxane (MAO) to polymerization propylene to give isotactic polypropylene.

The ansa-bis(flourenyl) complexes (C<sub>13</sub>H<sub>8</sub>-C<sub>2</sub>H<sub>4</sub>-C<sub>13</sub>H<sub>8</sub>)MCl<sub>2</sub> (M = Zr or Hf) can be activated with MAO and prove as excellent catalysts for the polymerization of ethylene [16]. Obviously the bulky fluorenyl ligands are responsible for the high catalytic activity of these complexes. In order to investigate the catalytic potential of fluorenyl complexes metallocenes containing 9-substituted fluorenyl ligands were synthesized.

## 2. Results and discussion

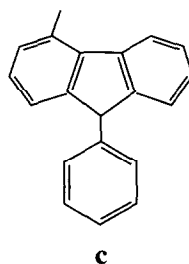
### 2.1. Synthesis of ligand precursors

Scheme 1 illustrates the syntheses of 9-cyclohexyl (a) and 9-phenylfluorene (b) and the corresponding complexes respectively.

The reaction of fluorenyl lithium with bromocyclohexane yields the corresponding cyclohexylfluorene (a). Dehydrogenation with Pd-C (10% Pd) at 300°C results in the formation of 9-phenylfluorene (b).

The <sup>1</sup>H, <sup>13</sup>C NMR and melting point data are collected in Tables 1 and 2.

Starting with 4-methylfluorene, 4-methyl-9-phenylfluorene (c) was prepared in a similar manner.



### 2.2. Preparation and characterization of the bis(flourenyl) complexes 1a–1c

Scheme 2 illustrates the general procedure used for the preparation of the metallocene dichloride complexes 1a–1c and the dimethyl complexes 2a–2c.

<sup>☆</sup> Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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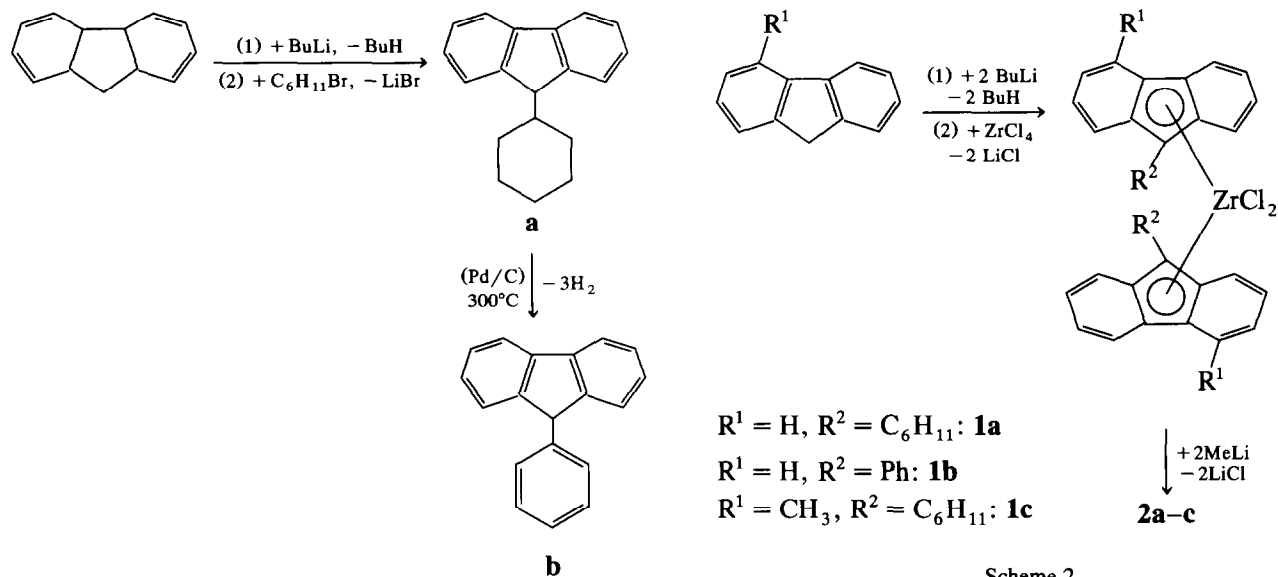


Table 1

<sup>1</sup>H NMR data, MS and melting points (mps) of a–c

Compound	<sup>1</sup> H NMR <sup>a</sup>	<sup>1</sup> H NMR <sup>a</sup>	<sup>1</sup> H NMR <sup>a</sup>	<sup>1</sup> H NMR <sup>a</sup>	MS (M <sup>+</sup> )	M.p. (°C)
	$\delta(\text{CH}(\text{Ar}))^b$ (ppm)	$\delta(\text{C}(\text{9})\text{H})$ (ppm)	$\delta(\text{H}(\text{C}_6\text{H}_{11}))$ (ppm)	$\delta(\text{CH}_3)$ (ppm)		
<b>a</b>	7.89 (d, 2, $J(\text{H,H}) = 7.1$ Hz), 7.70 (d, 2, $J(\text{H,H}) = 7.3$ Hz), 7.42–7.53 (m,4)	4.04 (d, 1, $J(\text{H,H}) = 2.9$ Hz)	2.34 (m,1), 1.81 (m,3), 1.65 (m,2), 1.32 (m,5)	—	248	110
<b>b</b>	7.87 (d, 2, $J(\text{H,H}) = 7.6$ Hz), 7.44 (t, 2, $J(\text{H,H}) = 8.2$ Hz), 7.29–7.40 (m,7)	5.11 (s,1), 7.17 (dd, 2, $J(\text{H,H}) = 7.8$ and 1.9 Hz)	—	—	—	139
<b>c</b>	7.99 (d, 1, $J(\text{H,H}) = 7.7$ Hz), 7.44 (t, 1, $J(\text{H,H}) = 7.7$ Hz), 7.26–7.37 (m,5), 7.12 (m,2)	5.06 (s,1), 7.20 (s,3)	—	2.81 (s,3)	256	94

<sup>a</sup> In CDCl<sub>3</sub>, at 25°C,  $\delta$  relative to CHCl<sub>3</sub> ( $\delta = 7.24$ ) (ppm).<sup>b</sup> For **b** and **c** the values for the fluorenyl and phenyl groups are summarized.

Table 2

<sup>13</sup>C NMR data of a–c

Compound	<sup>13</sup> C NMR <sup>a</sup>	<sup>13</sup> C NMR <sup>a</sup>	<sup>13</sup> C NMR <sup>a</sup>	<sup>13</sup> C NMR <sup>a</sup>	<sup>13</sup> C NMR <sup>a</sup>
	$\delta(\text{C}_q(\text{Ar}))^b$ (ppm)	$\delta(\text{CH}(\text{Ar}))^b$ (ppm)	$\delta(\text{C}_9)$ (ppm)	$\delta(\text{C}_6\text{H}_{11})$ (ppm)	$\delta(\text{CH}_3)$ (ppm)
<b>a</b>	146.4, 141.6	126.7, 126.5, 124.8, 119.5	53.5	43.1, 29.6, 26.9, 26.4	—
<b>b</b>	147.9, 141.6, 141.0	128.6, 128.3, 127.3, 126.8, 125.3, 119.8	54.4	—	—
<b>c</b>	148.3, 148.3, 142.0, 141.9, 139.0, 132.9	129.5, 128.6, 128.4, 127.2, 126.9, 126.7, 126.6, 125.2, 123.0, 122.8	54.4	—	21.1

<sup>a</sup> In CDCl<sub>3</sub>, at 25°C,  $\delta$  relative to CDCl<sub>3</sub> ( $\delta = 77$  ppm).<sup>b</sup> For **b** and **c** the values for the fluorenyl and phenyl groups are summarized.

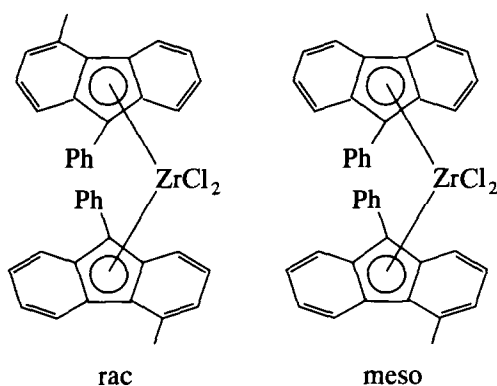
Table 3  
<sup>1</sup>H NMR data of **2a–2c**

Compound	<sup>1</sup> H NMR <sup>a</sup>			
	$\delta(\text{CH}(\text{Ar}))^b$ (ppm)	$\delta(\text{C}_6\text{H}_{11})$ (ppm)	$\delta(\text{CH}_3)$ (ppm)	$\delta(\text{Zr}-\text{CH}_3)$ (ppm)
<b>2a</b>	7.67 (d, 4, $J(\text{H,H}) = 8.6$ Hz), 7.47 (d, 4, $J(\text{H,H}) = 9.0$ Hz) 7.15–7.21 (m,4), 7.00–7.07 (m,4)	2.70–2.90 (m,2), 1.45–1.70 (m,10) 1.20–1.49 (m,10)	—	–1.10 (s,6)
<b>2b</b>	7.81–7.84 (m,4), 7.50–7.53 (m,4), 7.36–7.42 (m,2), 7.13–7.28 (m,8), 6.96–7.03 (m,8)	—	—	–1.14 (s,6)
<b>2c</b>	8.16–8.20 (m), 7.40–7.46 (m), 7.24–7.37 (m), 6.99–7.19 (m), 6.63–6.86 (m)	—	2.79 (s) 2.35 (s)	–1.07(s), –1.26 (s), –1.47 (s)

<sup>a</sup> In CDCl<sub>3</sub>, at 25°C,  $\delta$  is relative to CHCl<sub>3</sub> ( $\delta = 7.24$  ppm) (270 MHz).

<sup>b</sup> For **2b** and **2c** the values for the fluorenyl and phenyl groups are summarized.

For the methyl-substituted complexes **2a–2c**, *rac* and *meso* isomers are possible, e.g.



The reaction of the fluorene compounds **a–c** with butyllithium yields the corresponding lithium salts. Those react with ZrCl<sub>4</sub> to give **1a–1c**. Further treatment of the metallocene dichloride complexes with two equivalents of methyl lithium yields the metallocene dimethyl complexes **2a–2c**. The dichloride complexes **1a–1c** have a very low solubility in common solvents,

making it difficult to do spectroscopic identification. However, the corresponding methyl derivatives **2a–2c** are much more soluble and can be identified spectroscopically.

Identification of the methyl derivatives was therefore used to provide evidence and proof for the identity of **1a–1c**.

The <sup>1</sup>H and <sup>13</sup>C NMR data are collected in Tables 3 and 4.

While (1-CH<sub>3</sub>C<sub>13</sub>H<sub>8</sub>)<sub>2</sub>ZrCl [13,15] activated with MAO polymerizes propylene to give isotactic polypropylene, complex **1c** with MAO as cocatalyst shows no activity for the polymerization of propylene under the reaction conditions used for this study. The same behaviour was observed for **1a** and **1b**. Further investigations using ethylene instead of propylene showed only a low polymerization activity. This could be due to the bulky 9-substituents. They block the growth of the polymer chain in the coordination sphere of the metal. In addition this effect could be enhanced by the possibility of an intramolecular rotation of the fluorenyl ligands around their bond axis to the metal. The situa-

Table 4  
<sup>13</sup>C NMR data of **2a–2c**

Compound	<sup>13</sup> C NMR <sup>a</sup>				
	$\delta(\text{C}_q(\text{Ar}))^b$ (ppm)	$\delta(\text{CH}(\text{Ar}))^b$ (ppm)	$\delta(\text{C}_6\text{H}_{11})$ (ppm)	$\delta(\text{CH}_3)$ (ppm)	$\delta(\text{Zr}-\text{CH}_3)$ (ppm)
<b>2a</b>	128.2, 115.4, 108.7	125.4, 124.2, 123.5, 120.6	37.6, 32.6, 27.5, 26.5	—	44.7
<b>2b</b>	134.7, 131.2, 119.3, 103.8	128.6, 128.4, 127.1, 124.0, 122.8, 122.5, 116.7	—	—	45.7
<b>2c</b>	136.8, 136.6, 134.6, 129.0 119.4, 118.5, 102.7	128.6, 128.6, 128.3, 126.6, 126.3, 126.1, 125.7, 124.2, 123.9, 122.9, 120.8, 128.0, 126.4, 122.7	—	22.7 22.6	44.9

<sup>a</sup> In CDCl<sub>3</sub>, at 25°C,  $\delta$  is relative to CDCl<sub>3</sub> ( $\delta = 77.0$  ppm) (67.9 MHz).

<sup>b</sup> For **2b** and **2c** the values for the fluorenyl and phenyl groups are summarized.

tion is different with ansa bis(fluorenyl) complexes containing a C<sub>2</sub> bridge; such complexes show excellent activity [16].

### 3. Experimental details

All operations were carried out with Schlenk technique under argon. Pentane, hexane, ether and tetrahydrofuran (THF) were dried and distilled over Na–K alloy. Methylene chloride was treated with P<sub>2</sub>O<sub>5</sub> and CaH<sub>2</sub>.

NMR spectra were performed on a JEOL EX 270 instrument using anhydrous CDCl<sub>3</sub> as a solvent: 4-methylfluorene was prepared according to literature procedures [13].

#### 3.1. Preparation of the 9-substituted fluorene compounds a–c

##### 3.1.1. 9-(cyclohexyl)fluorene (a)

A solution of 20 g (0.12 mol) of fluorene in 150 ml of THF was reacted dropwise with 76 ml of butyllithium (1.6 M in hexane) at room temperature. The mixture was stirred for an additional hour and then cooled to –78°C. After this, 22 g (0.14 mol) of bromocyclohexane were added and the mixture was allowed to warm to room temperature. The solution was stirred for an additional 4 h and then it was hydrolyzed with a saturated solution of NH<sub>4</sub>Cl in water. The organic layer was separated and washed with water. After the solution was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was dissolved in 100 ml of pentane and the solution was crystallized at –30°C to yield colorless needles (yield; 90%).

##### 3.1.2. 9-(phenyl)fluorene (b)

15 g (0.06 mol) of 9-(cyclohexyl)fluorene (a) and 2 g of Pd–C (10% Pd) were heated to 300°C and held at this temperature for 24 h. The residue was extracted with THF, and then the mixture was filtered over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent the residue was dissolved in 100 ml of pentane and the solution was crystallized at –30°C to yield a yellow powder (yield, 95%).

##### 3.1.3. 4-(methyl)-9-(phenyl)fluorene (c)

The procedure used was analogous to that given in Sections 3.1.2 and 3.1.3 (yield, 90%).

#### 3.2. Preparation of the metallocene dichloride complexes 1a–1c

For the preparation of the complexes the following general procedure was used: 8 mmol of the corresponding ligand precursor a–c was dissolved in 250 ml of

ether and reacted with 8 mmol of butyllithium. After gas evolution ceased, 1 g (4 mmol) of ZrCl<sub>4</sub> was added and the reaction mixture was stirred for 1 h. After evaporation of the solvent the crude product was extracted with ether in a Soxhlet apparatus to remove lithium chloride and starting material (yield, 85–85%).

#### 3.3. Preparation of the metallocene dimethyl complexes 2a–2c

For the preparation of the dimethyl complexes 2a–2c the following general procedure was used. 2 mmol of the metallocene dichloride complex was suspended in 50 ml of toluene and reacted with 4 mmol of methyl-lithium. The mixture was stirred for 1–2 h and then filtered over Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, the residue was crystallized from hexane at –30°C to yield yellow to orange powders (yield, 80–90%).

#### 3.4. Polymerization conditions

For all polymerization reactions a 1 l Büchi steel autoclave was used. The metallocene complexes were activated with a 500-fold molar excess of MAO (Witco: 30% in toluene). Ethylene was polymerized in a pentane solution at 60°C with an ethylene pressure of 10 bar. Propylene was polymerized without a solvent as a liquid at 60°C.

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