

Unbridged cyclopentadienyl–fluorenyl complexes of zirconium as catalysts for homogeneous olefin polymerization [☆]

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Abstract

The reaction of various lithium fluorenyl compounds, $\text{Li}(\text{C}_{13}\text{H}_7\text{R}^1\text{R}^2)$ ($\text{R}^1, \text{R}^2 = \text{H}$, alkyl or aryl) (**1a–1n**), with $\text{C}_5\text{H}_5\text{ZrCl}_3$ leads to unbridged fluorenyl complexes of the type $(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_7\text{R}^1\text{R}^2)\text{ZrCl}_2$ (**2a–2n**) which can be converted to the corresponding metallocene dimethyl complexes (**3a–3e**). In combination with methylaluminoxane (MAO), **2a–2n** show a higher catalytic activity as homogeneous ethylene polymerization catalysts than $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$. Compound **2d** ($\text{R}^1 = 2\text{-Me}$; $\text{R}^2 = 7\text{-Me}$) was characterized by an X-ray structure analysis.

Keywords: Metallocene; Fluorenyl ligands; Olefin polymerization; Zirconium

1. Introduction

Unbridged metallocene dichloride complexes of the type $(\text{Cp})(\text{Cp}^*)\text{MCl}_2$ ($\text{Cp}^* =$ monosubstituted or multisubstituted cyclopentadienyl; $\text{M} = \text{Ti}$, Zr or Hf) have been known for a long time [1–5]. They are usually synthesized by reaction of the half-sandwich complex $\text{C}_5\text{H}_5\text{MCl}_3$ ($\text{M} = \text{Ti}$, Zr or Hf) with the lithium salt of the appropriate cyclopentadienyl anion. By contrast, the preparation of complexes that contain an η^5 -coordinated fluorenyl ligand is problematical. Apparently the fluorenyl ligand is substantially more weakly bound to the central atom, and in the presence of strong donor ligands or solvents it tends very slightly towards irreversible “ring-slippage” reactions [6,7].

2. Results and discussion

The reaction of fluorenyl anions with zirconium tetrachloride in tetrahydrofuran (THF) leads to the formation of bis(fluorenyl)zirconium dichloride complexes

which are stable for only a short time [8,9]. The instability is thought to be a result of the strong donor THF, inducing a change in hapticity in the fluorenyl ligand of $\eta^5 \rightarrow \eta^1$. The decreased bond strength of the ligand to the metal associated with this leads to elimination of the fluorenyl ligand and the subsequent formation of bisfluorenyl. This effect is not observed in solvents such as toluene, hexane, pentane or diethyl ether, which show no or only a slight tendency towards coordination.

2.1. Synthesis of metallocene dichloride complexes of the type $(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_7\text{-R}^1\text{R}^2)\text{ZrCl}_2$ (**2a–2n**) ($\text{R} = \text{H}$, alkyl or aryl)

Starting with this knowledge, the following process for preparation of unbridged fluorenyl complexes showed itself to be the best method of synthesis: the fluorene derivative **1a–1n** is dissolved in diethyl ether and transformed into the corresponding fluorenyl anion with BuLi , and this is subsequently reacted with $\text{C}_5\text{H}_5\text{ZrCl}_3$ to give the respective metallocene dichloride complexes **2a–2n** (Scheme 1).

Complex **2a** has already been described by another group [10]. However, the reaction product obtained in the reaction of $\text{Ti}(\text{C}_{13}\text{H}_9)$ with $\text{C}_5\text{H}_5\text{ZrCl}_3$ in the solvent THF and postulated as **2a** does not agree in its analytical data (^1H NMR spectrum, melting point and

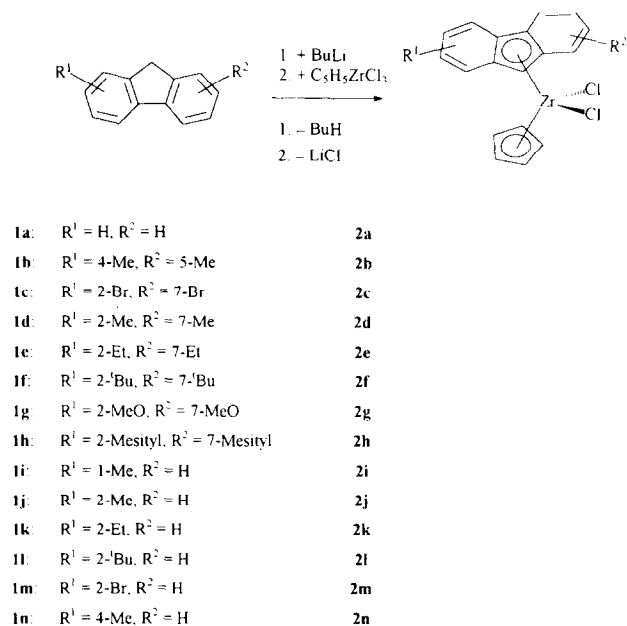
[☆] Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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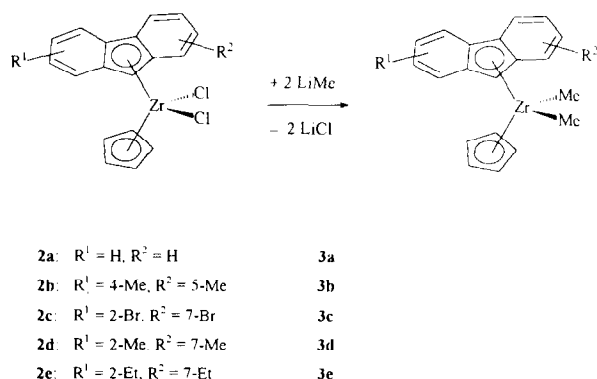
color) with the values determined within the framework of the present study.

2.2. Synthesis of metallocene dimethyl complexes of the type $(C_5H_5)(C_{13}H_7R^1R^2)ZrMe_2$ (**3a–3e**) ($R = H$, alkyl or aryl)

Unbridged metallocene dialkyl complexes with η^5 -coordinated fluorenyl ligands such as $(C_5H_5)(C_{13}H_7R^1R^2)ZrMe_2$ (**3a**) ($R^1 = R^2 = H$) are obtained by reaction of the corresponding metallocene dichloride compound with two equivalents of MeLi in diethyl ether (Scheme 2).



Scheme 1.



Scheme 2.

2.3. NMR spectroscopic characterization of **2a–2n** and **3a–3e**

The 1H and ^{13}C NMR data of **2a–2n** and **3a–3e** are given in Tables 1–4. The multiplicity of signals that is

observed for symmetrically substituted fluorenyl ligands (**2a–2h** and **3a–3e**) suggests the presence of C_s symmetry in the respective molecules in solution.

2.4. Molecular structure of the metallocene dichloride complex **2d**

The molecular structures of **2d**^{a,b} can be seen in Fig. 1. Selected bond distances and angles are given in Table 5.

The $Zr(1)-Cp(1)_C$ distance is 219.8 pm and thus corresponds exactly to the value that was determined for $(C_5H_5)_2ZrCl_2$ [12]. By comparison with this, the center of the five-membered ring of the fluorenyl ligand is displaced from the metal center by almost 10 pm. Moreover, the fluorenyl ligand is not perpendicular to the $Zr(1)-Flu'(1)_C$ bond axis; thus carbon atom C(9) at 240.0(3) pm is more than 32 pm closer to the metal center than are atoms C(11) or C(12).

An attempt to postulate the presence of η^3 coordination and thus a 14-electron complex, as was done by Wailes and coworkers [13] for $(C_{13}H_9)_2ZrCl_2$ on the basis of these bonding relationships stands in contradiction to the stability of these compounds. However, the bond strength, which is without doubt decreased compared with cyclopentadienyl or indenyl ligands [2,14], explains the lower stability of dissolved, η^5 -coordinated fluorenyl complexes in the presence of strong π donors.

2.5. Olefin polymerization

The metallocene dichloride complexes **2a–2n** constitute catalyst precursors for homogeneous polymerization of α -olefins and can be converted to the catalytically active metallocene methyl cations $(C_5H_5)(C_{13}H_7R^1R^2)ZrMe^+$ with methylaluminoxane (MAO).

From the results of the polymerization of ethylene

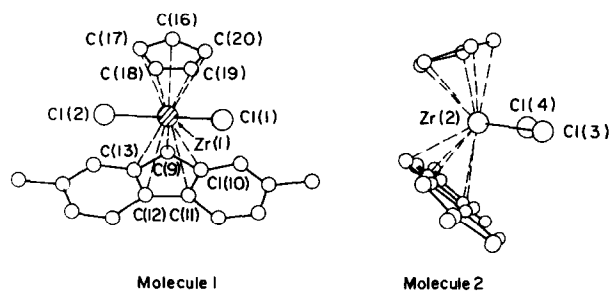


Fig. 1. Molecular structures of **2d**. The unit cell contains two independent molecules with different bond distances and angles. Owing to extensive agreement, the discussion is based on only molecule 1. For clarity, numbering of the atoms in molecule 2 has been omitted. Complex **2d** has C_s symmetry only at first glance. However, in actuality, the two ligand planes are rotated with respect to each other by approximately 4° . The angle that includes the metal center with the two centers of the ring $Cp(1)_C$ and $Flu'(1)_C$ is 131.2° ; it is thus only approximately 3° greater than the value determined for the bridged [(cyclopentadienyl)(9-fluorenyl)dimethylsilane]zirconium dichloride compound [11].

Table 1
¹H NMR spectroscopic characterization ^a of **2a–2n**

Complex	δ(aromatic H) (ppm)	δ(H) Cp ligand (ppm)	δ(H) in position 9 (ppm)	δ(H) R ¹ /R ²
2a	8.13 (d, 2, <i>J</i> (H,H) = 8.1 Hz) 7.57 (m,2) 7.38–7.48 (m,4)	6.08 (s,5)	6.53 (t,1), <i>J</i> (H,H) = 0.7 Hz	—
2b	7.39 (d, 2, <i>J</i> (H,H) = 8.2 Hz) 7.23 (m,4)	6.09 (s,5)	6.58 (s,1)	2.96 (s,6)
2c	7.95 (dt, 2, <i>J</i> (H,H) = 8.9, 0.7 Hz) 7.70 (dd, 2, <i>J</i> (H,H) = 1.7, 0.7 Hz) 7.53 (dd, 2, <i>J</i> (H,H) = 8.9, 1.7 Hz)	6.19 (s,5)	6.44 (t,1), <i>J</i> (H,H) = 0.7 Hz	— —
2d	7.95 (d, 2, <i>J</i> (H,H) = 8.5 Hz) 7.28 (m,2) 7.24 (d, 2, <i>J</i> (H,H) = 8.5 Hz)	6.05 (s,5)	6.31 (s,1)	2.46 (s,6)
2e	8.00 (d, 2, <i>J</i> (H,H) = 8.5 Hz) 7.31 (m,2) 7.27 (dd, 2, <i>J</i> (H,H) = 8.5, 1.3 Hz)	6.03 (s,5)	6.34 (t,1), <i>J</i> (H,H) = 0.6 Hz	2.72 (q, 4, <i>J</i> (H,H) = 7.7 Hz) 1.27 (t, 6, <i>J</i> (H,H) = 7.7 Hz)
2f	8.01 (d, 2, <i>J</i> (H,H) = 8.7 Hz) 7.47 (m,4)	5.99 (s,5)	6.37 (t,1, <i>J</i> (H,H) = 0.8 Hz)	1.38 (s,18)
2g	7.90 (d, 2, <i>J</i> (H,H) = 9.1 Hz) 7.02 (dd, <i>J</i> (H,H) = 9.1; 2.2 Hz) 6.78 (d, 2, <i>J</i> (H,H) = 2.2 Hz)	6.02 (s,5)	6.24 (t,1), <i>J</i> (H,H) = 0.6 Hz	3.87 (s,6)
2h	8.18 (d, 2, <i>J</i> (H,H) = 8.7 Hz) 7.31–7.38 (m,4) 6.99 (s,2) 6.90 (s,2)	6.24 (s,5)	6.67 (s,1)	2.35 (s,6) 2.16 (s,6) 1.99 (s,6)
2i	8.12 (m,1), 8.00 (d, 1, <i>J</i> (H,H) = 8.5 Hz) 7.68 (m,1), 7.10–7.45 (m,4 Hz)	6.02 (s,5)	6.48 (s,1)	2.45 (s,3)
2j	8.08 (m,1), 7.99 (d, 1, <i>J</i> (H,H) = 8.5 Hz) 7.57 (m,1), 7.20–7.45 (m,4)	6.07 (s,5)	6.43 (t,1, <i>J</i> (H,H) = 0.8 Hz)	2.48 (s,3)
2k	8.08 (m,1), 8.02 (d, 1, <i>J</i> (H,H) = 8.6 Hz) 7.54 (m,1), 7.27–7.45 (m,4)	6.06 (s,5)	6.43 (t, 1, <i>J</i> (H,H) = 0.7 Hz)	2.78 (q, 4, <i>J</i> (H,H) = 7.6 Hz) 1.29 (t, 6, <i>J</i> (H,H) = 7.6 Hz)
2l	8.09 (m,1), 8.04 (d, 1, <i>J</i> (H,H) = 8.9 Hz) 7.45–7.58 (m,2), 7.37–7.42 (m,2)	6.03 (s,5)	6.45 (t, 1, <i>J</i> (H,H) = 0.7 Hz)	1.38 (s,9)
2m	8.10 (m,1), 7.98 (d, 1, <i>J</i> (H,H) = 8.9 Hz) 7.71 (m,1), 7.38–7.58 (m,4)	6.13 (s,5)	6.49 (s,1)	—
2n	8.28 (m,1), 7.18–7.57 (m,6)	6.12 (s,5)	6.54 (d, 1, <i>J</i> (H,H) = 0.8 Hz) ^b	2.89 (s,3)

^a In chloroform-*d*₁, at 20 °C (300 MHz): δ relative to CHCl₃ (7.24) * s, singlet; d, doublet; dd, doublet of a doublet; dt, doublet of a triplet; m, multiplet; q, quartet; t, triplet.

^b The fact that the signal of the proton on carbon atom (9) in **2n** appears as a doublet provides proof that, during coupling, ⁵*J*(H,H) coupling of proton H(9) with the proton on carbon C(5) is involved. If the fluorenyl ligand on carbon atom C(4) has no substituent, a triplet signal is observed in most cases.

Table 2
¹³C NMR spectroscopic characterization ^a of **2a–2f** and **2h–2n** ^b

Complex	δ(C _{quart}) (ppm)	δ(aromatic C) (ppm)	δ(C) Cp-ligand (ppm)	δ(C) in position 9 (ppm)	δ(C) R ¹ /R ² (ppm)
2a	128.8, 122.8	128.4, 125.2, 125.0, 124.7	115.6	85.0	—
2b	137.4, 130.9, 121.3	128.1, 122.0, 120.7	115.3	86.5	27.1
2c	128.3, 126.1, 123.5	129.2, 126.3, 126.1	115.8	83.2	—
2d	138.6, 129.9, 120.6	126.6, 124.6, 123.3	115.4	84.3	22.2
2e	145.0, 129.9, 120.6	126.6, 124.7, 122.2	115.5	84.7	29.4, 15.9
2f	151.7, 130.0, 124.4	124.2, 119.9, 99.6	115.5	85.7	35.3, 31.2
2h	141.7, 138.1, 137.1, 136.3, 135.9, 127.8, 122.6	128.4, 128.3, 128.2, 124.7, 123.7	114.8	85.4	21.4, 21.0, 20.9
2i	134.5, 133.5, 129.0, 122.5, 121.3	128.2, 127.7, 125.5, 125.5, 124.9, 124.6, 121.9	116.6	84.7	19.6
2j	139.9, 130.0, 128.3, 122.9, 120.6	127.9, 127.7, 124.9, 124.8, 124.7, 124.6, 123.2	115.4	84.6	22.1
2k	145.5, 130.0, 128.6, 122.8, 120.6	127.9, 126.8, 124.9, 124.8, 124.7, 124.6, 122.1	115.5	84.8	29.4, 15.7
2l	152.3, 130.0, 128.9, 122.7, 120.0	127.9, 125.0, 124.9, 124.9, 124.5, 124.4, 119.7	115.6	85.4	35.3, 31.2
2m	127.5, 126.9, 123.3, 122.9, 120.7	128.8, 128.6, 126.3, 126.2, 125.6, 124.9, 124.4	115.7	102.0	—
2n	138.6, 128.8, 128.1, 124.2, 123.4	128.3, 128.0, 127.3, 125.9, 125.2, 124.3, 121.6	115.2	84.8	22.1

^a In chloroform-*d*₁, at 20 °C; δ relative to CDCl₃ (77.0).

^b No ¹³C NMR spectrum could be obtained for **2g** because of its sparing solubility.

(Table 6), it can be seen that the productivity of the complexes used appears to depend on the electron density at the central atom. The latter is in turn directly determined by the R^1 and R^2 substituents found in the fluorenyl ligand system; if the fluorenyl ligand has electron-attracting substituents in positions 2 and 7, ($R^1 = R^2 = \text{Br}$ (**2c**) or MeO (**2g**)), a decreased activity is observed compared with the unsubstituted complex **2a**; the presence of electron-donating substituents ($R^1 = R^2 = \text{Me}$ (**2d**), $t\text{Bu}$ (**2f**) or mesityl (**2h**)), by contrast, increases the activity [15]. Thus the initiator system

2h–MAO produces 30 t-polyethylene ($\text{mol Zr}^{-1} \text{ h}^{-1}$) at 30°C and an ethylene pressure of 10 bar and is therefore five times more active than the $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ –MAO system.

After activation with MAO, the catalyst precursors **2a**–**2n** are also suitable for polymerization of propylene. However, atactic polymers are formed. The formation of an atactic microstructure is believed to arise because the C_s symmetry of the catalyst necessary for syndiospecific polymerization is not present owing to the unhindered rotation of the two π ligands.

Table 3
 ^1H NMR spectroscopic characterization ^a of **3a**–**3e**

Complex	$\delta(\text{aromatic H})$ (ppm)	$\delta(\text{H})$ Cp ligand (ppm)	$\delta(\text{H})$ in position 9 (ppm)	$\delta(\text{Zr-Me})$ (ppm)	$\delta(\text{H})$ R^1/R^2 (ppm)
3a	8.13 (m,2) 7.21–7.36 (m,6)	5.81 (s,5)	6.04 (s,1)	–1.35 (s,6)	—
3b	7.04–7.20 (m,6)	5.80 (s,5)	6.11 (s,1)	–1.33 (s,6)	2.95 (s,6)
3c	7.95 (dt, 2, $J(\text{H,H}) = 8.9, 0.7 \text{ Hz}$) 7.50 (dd, 2, $J(\text{H,H}) = 1.7, 0.7 \text{ Hz}$) 7.41 (dd, 2, $J(\text{H,H}) = 8.9, 1.7 \text{ Hz}$)	5.86 (s,5)	5.91 (s, 1, $J(\text{H,H}) = 0.8 \text{ Hz}$)	–1.18 (s,6)	—
3d	7.96 (d, 2, $J(\text{H,H}) = 8.5 \text{ Hz}$) 7.14 (m,2) 7.06 (m,2)	5.78 (s,5)	5.84 (t, 1, $J(\text{H,H}) = 0.7 \text{ Hz}$)	–1.28 (s,6)	2.40 (s,6)
3f	8.00 (d, 2, $J(\text{H,H}) = 8.6 \text{ Hz}$) 7.18 (dd, 2, $J(\text{H,H}) = 8.6, 1.6 \text{ Hz}$) 7.15 (dd, 2, $J(\text{H,H}) = 1.6, 0.8 \text{ Hz}$)	5.78 (s,5)	5.89 (t, 1, $J(\text{H,H}) = 0.7 \text{ Hz}$)	–1.25 (s,6)	2.71 (q, 4, $J(\text{H,H}) = 7.6 \text{ Hz}$) 1.26 (t, 6, $J(\text{H,H}) = 7.6 \text{ Hz}$)

^a In chloroform- d_1 , at 20 °C (300 MHz): δ relative to CHCl_3 (7.24) s, singlet; d, doublet; dd, doublet of a doublet; dt, doublet of a triplet; m, multiplet; q, quartet; t, triplet.

Table 4
 ^{13}C NMR spectroscopic characterization ^a of **3a**–**3e**

Complex	$\delta(\text{C}_{\text{quan}})$ (ppm)	$\delta(\text{aromatic C})$ (ppm)	$\delta(\text{C})$ Cp ligand (ppm)	$\delta(\text{C})$ in position 9 (ppm)	$\delta(\text{Zr-Me})$ (ppm)	$\delta(\text{C})$ R^1/R^2 (ppm)
3a	123.9, 119.3	126.4, 126.3, 123.4, 122.3	110.0	80.2	35.2	—
3b	135.7, 127.7, 120.2	126.1, 125.2, 120.7	110.0	82.9	34.5	27.5
3c	128.3, 121.2, 117.3	126.2, 125.3, 125.2	110.5	79.7	36.2	—
3d	136.1, 127.2, 117.4	124.7, 123.6, 122.0	110.0	79.6	34.6	22.0
3e	142.6, 127.2, 117.6	126.2, 123.7, 125.2	110.0	80.0	34.8	29.4, 15.9

^a In chloroform- d_1 , at 20 °C; δ relative to CDCl_3 (77.0).

Table 5
Selected bond distances (pm) and angles (°) for **2d** (molecule 1)

Bond distances					
Zr(1)–C(9)	240.0(3)	Zr(1)–C(16)	248.0(4)	Zr(1)–Cl(1)	243.5(1)
Zr(1)–C(10)	255.0(3)	Zr(1)–C(17)	248.2(4)	Zr(1)–Cl(2)	243.7(1)
Zr(1)–C(11)	272.0(2)	Zr(1)–C(18)	247.3(4)	Zr(1)–Cp(1) _C	219.8
Zr(1)–C(12)	273.7(3)	Zr(1)–C(19)	247.7(4)	Zr(1)–Flu'(1) _C	229.4
Zr(1)–C(13)	257.2(3)	Zr(1)–C(20)	249.1(5)		
Bond angles					
Cl(1)–Zr–Cl(2)	95.3(1)	Cp(1) _C –Zr–Flu'(1) _C	131.2	Cp(1) _E –Flu'(1) _E	58.4

Cp(1)_C, center of the Cp ligand (1); Flu'(1)_C, center of the five-membered ring in the fluorenyl ligand (1); Cp(1)_E, Cp(1) ligand plane; Flu'_E, fluorenyl(1) ligand plane.

Table 6
Polymerization results ($T_p = 30^\circ\text{C}$; $p(\text{C}_2\text{H}_4) = 10\text{ bar}$)

Complex	$m(\text{complex})$ (mg)	$m(\text{poly-ethylene})$ (g)	Activity (t polyethylene (mol Zr) $^{-1}$ h $^{-1}$)
$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$	2.0	40	5.8
2a	2.0	82	16.1
2c	1.5	15	5.5
2d	1.5	75	21.3
2f	1.5	65	21.9
2g	1.9	16	4.0
2h	2.0	97	30.2

3. Experimental section

All work was routinely done under an argon atmosphere and with freshly distilled anhydrous solvents. For NMR spectroscopic characterization, a Bruker AC 300 instrument was used.

2,7-Dibromofluorene (**1c**) [16], 2,7-dimethylfluorene (**1d**) [17], 2,7-di-*tert*-butylfluorene (**1f**) [18], 2,7-dimethoxyfluorene (**1g**) [17], 2,7-dimesitylfluorene (**1h**) [17], 1-methylfluorene (**1i**) [19], 2-methylfluorene (**1j**) [19], 2-ethylfluorene (**1k**) [19], 2-*tert*-butylfluorene (**1l**) [19], 4-methylfluorene (**1n**) [19] and CpZrCl_3 [20] were prepared according to literature procedures. All other reagents were commercial products and were used without further purification.

3.1. Preparation of **1b**

300 g of polyphosphoric acid are heated to 140°C in a 1 l Erlenmeyer flask. Subsequently 27.0 g (100 mmol) 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid [21] are added in portions. After stirring for 2 h at 140°C , the brown reaction product is brought to room temperature and reacted carefully with 500 ml of ice-water. The precipitated yellowish-brown 4,5-dimethylfluorenone is filtered, washed with much water, dried in a vacuum, dissolved in 100 ml of THF and hydrogenated on 1g Pd-C. After hydrogen uptake is complete, the Pd-C is filtered off, and the filtrate is dried. The light-yellow solid is extracted with pentane, and the solution is filtered through silica gel. After evaporation of the solvent, 12.2 g of **1b** remain as colorless flakes (yield for the two steps, 63%).

^1H NMR (CDCl_3): δ 7.42 (m, 2), 7.21–7.31 (m, 4), 3.93 (s, 2), 2.82 (s, 6) ppm. ^{13}C NMR (CDCl_3): δ 144.5, 141.5, 132.4, 130.5, 126.3, 122.2, 37.5, 25.4 ppm. Electron impact (EI) mass spectroscopy (MS): m/e (I_{rel}) 194 (M^+ 53%).

3.2. Preparation of **1e**

38 ml (400 mmol) of Ac_2O are dropped into a suspension of 108 g (800 mmol) of AlCl_3 in 300 ml of CH_2Cl_2 under ice cooling. Subsequently, 16.6 g (100

mmol) of fluorene are added in portions, and the reaction mixture is stirred for 2 h at room temperature. Thereafter the red solution is slowly poured into 500 ml of ice-cooled dilute hydrochloric acid. The light-yellow precipitate is filtered off, washed twice with 200 ml of pentane and dried. The quantitatively obtained 2,7-diacylfluorene and 1 g of palladium on activated carbon (10% Pd) are suspended in 300 ml of THF and hydrogenated to give 2,7-diethylfluorene (**1e**). The processing of the products is done analogously to the synthesis of **1b**. The yield of **1e** for both stages is 20.0 g (90%) as a colorless solid.

^1H NMR (CDCl_3): δ 7.66 (d, 2, $J(\text{H}, \text{H}) = 7.8\text{ Hz}$), 7.37 (s, 2), 7.20 (d, 2, $J(\text{H}, \text{H}) = 7.8\text{ Hz}$), 3.84 (s, 2), 2.73 (q, 4, $J(\text{H}, \text{H}) = 7.6\text{ Hz}$), 1.30 (t, 6, $J(\text{H}, \text{H}) = 7.6\text{ Hz}$) ppm. ^{13}C NMR (CDCl_3): δ 143.4, 142.6, 139.1, 126.4, 124.6, 119.3, 36, 7, 29.0, 15.9 ppm. EI MS: m/e (I_{rel}) 222 (M^+ 95%).

3.3. Preparation of **2a–2n**

The general procedure is as follows. 2.4 mmol of the respective fluorene derivatives **1a–1n** are dissolved in 50 ml of Et_2O and reacted with 1.5 ml of BuLi (1.6 M in hexane) at room temperature. After the evolution of gas is complete, an equimolar amount of $\text{C}_5\text{H}_5\text{ZrCl}_3$ is added, and the mixture is stirred for 1 h. Subsequently, the solvent is removed in a diaphragm pump vacuum. The remaining residue is extracted with toluene, and the suspension is filtered through sodium sulfate. The filtrate is partly evaporated and crystallized at -78°C (yield, 50–70%).

3.4. Preparation of **3a–3e**

The general procedure is as follows. 1.5 ml of BuLi (1.6 M in hexane) are added to a solution of 2.4 mmol of the respective fluorene derivative at room temperature and, after the evolution of gas is complete, an equimolar amount of $\text{C}_5\text{H}_5\text{ZrCl}_3$ is added. After 1 h, the mixture is reacted with 3.0 ml (4.8 mmol) of MeLi (1.6 M in Et_2O) and stirred for an additional 30 min. Subsequently, the solvent is removed. The residue obtained is taken up in pentane, and the suspension is filtered over sodium sulfate. After evaporation of the solution and crystallization at -78°C , fine crystalline needles are obtained (yield, 50–70%).

An elemental analysis of **3d** gave the following results. Found: C, 70.51, H, 6.83. $\text{C}_{24}\text{H}_{28}\text{Zr}$ (407.71), calc.: C, 70.70, H, 6.92%.

3.5. X-ray analysis of the crystal structure

$\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{Zr}$ (**2d**), orange plates of dimensions $0.20 \times 0.08 \times 0.50\text{ mm}$; triclinic; space group, $P\bar{1}$; $a = 7.999(2)\text{ \AA}$, $b = 12.652(3)\text{ \AA}$ and $c = 18.777(4)\text{ \AA}$;

$\alpha = 74.00(3)^\circ$, $\beta = 79.82(3)^\circ$ and $\gamma = 77.10(3)^\circ$; $V = 1767.1(7) \text{ \AA}^3$; $Z = 4$; Siemens P4 diffractometer (Mo K α ; $\lambda = 0.71073 \text{ \AA}$); graphite monochromator; measured reflections; 7690; independent and observed reflections ($F > 0.0\sigma(F)$), 6228 with $R_{\text{int}} = 0.85\%$; structure elucidation with Siemens SHELXTL PLUS (VMS); number of refined parameters, 416; $R = 3.71\%$ and $wR = 2.22\%$; C and Zr atoms, anisotropic; semiempirical absorption correction; maximum transmission factor, 0.4751; minimum transmission factor, 0.4477; maximum residual electron density, 0.58 electrons $\text{\AA}^{-3}$; minimum residual electron density, -0.41 electrons $\text{\AA}^{-3}$.

Additional details on the crystal structure studies can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, upon indication of the deposition number CSD-401848, the authors and the journal reference.

3.6. Polymerization reactions

3.6.1. Activation of the catalyst precursors

2 mg of the respective metallocene dichloride complex are dissolved in 5 ml of toluene and reacted with 2 ml of MAO solution (Witco; 30 wt% MAO in toluene; $M_w = 1100$). The formation of the polymerization-active metallocene methyl cation can be observed by the color change.

3.6.2. Polymerization of ethylene

500 ml of pentane are placed into a 1 l autoclave from b.a.r. Co. at an internal temperature of 20°C and reacted with 5 ml of catalyst solution. Thereafter, an ethylene pressure of 10 bar is applied, and the reaction mixture is stirred at 30°C for 1 h. The polymerization data are given in Table 6.

3.6.3. Polymerization of propylene

No solvent was used in the polymerization of propylene, liquid propylene was used. The polymerization temperature was 60°C .

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