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Preparation and crystal structures of the complexes $(\eta^5\text{-}C_5H_3Me\text{–}CMe_2\text{-}\eta^5\text{-}C_{13}H_8)MCl_2$ (M = Zr or Hf): mechanistic aspects of the catalytic formation of a syndiotactic–isotactic stereoblock-type polypropylene ☆

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Abstract

The reaction of MCl_4 (M = Zr or Hf) with the dilithium salt of 2-methyl-3-cyclopentadienyl-2-fluorenylpropane in pentane leads to the formation of the complexes $(\eta^5\text{-}C_5H_3Me)\text{-}CMe_2\text{-}\eta^5\text{-}C_{13}H_8)MCl_2$. NMR and X-ray diffraction data show that the fluorenyl groups are η^5 bonded in these complexes. When activated with methylaluminoxane or other appropriate ionizing agents, both complexes catalyze the polymerization of propylene in a di-stereospecific manner, to give syndiotactic–isotactic stereoblock polypropylene.

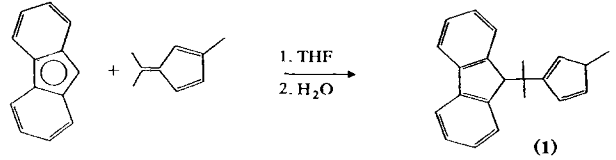
Keywords: Zirconium; Hafnium; NMR spectroscopy; Crystal structure

1. Introduction

The synthesis, structure and catalytic behavior of the complexes $(\eta^5\text{-}C_5H_4CR_2\text{–}\eta^5\text{-}C_{13}H_8)MCl_2$ (R = Me or Ph; M = Zr or Hf) have attracted considerable interest since our initial reports [1,2]. The η^5-bonded character of the fluorenyl group to a central transition metal had been established for the first time in these complexes without any ambiguity at least in the solid state [3]. Furthermore it was demonstrated that the bilateral symmetry of the ligand and the balanced non-bonding interaction of its substituents with the remaining terminal σ ligands attached to the transition metal are the prerequisites for the syndiotactic specific behavior of these metallocenes as prospective α-olefin polymerization catalysts. In this paper we describe the synthesis, the characterization and the catalytic behavior of the related compounds $(\eta^5\text{-}C_5H_3Me)\text{–}CMe_2\text{–}\eta^5\text{-}C_{13}H_8)MCl_2$ (M = Zr or Hf). The X-ray diffraction data and the polymerization results reveal that the simple substitution of a methyl group in one of the distal positions of the cyclopentadienyl moiety of the ligand provokes profound changes in the secondary structural features of the metallocene molecule, such as elimination of the bilateral symmetry and prochirality. These symmetry modifications have, in turn, dramatic consequences for the stereospecificity of the final activated catalyst. The increased M–C bond distances for the distal carbon atoms and the oblique posture of the methylcyclopentadienyl part of the ligand, revealed by single-crystal X-ray structure analysis, could be regarded as a pre-eminent sign for the observed modified catalytic performance and be used as a valuable tool for designing metallocene molecules with predictable catalytic properties.

2. Results and discussion

The bridged 2-(methylcyclopentadienyl)-2-(fluorenyl)propane (**1**) is produced by the following reaction:



(1)

☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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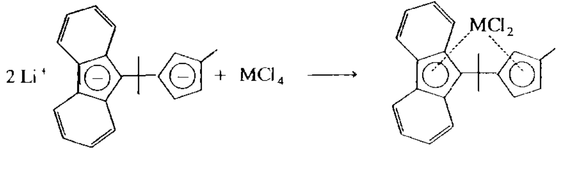
Double deprotonation of **1** with two equivalents of methyllithium in tetrahydrofuran (THF) solution gives the corresponding dianion **2**. The reaction of **2** with one equivalent of MCl_4 in pentane yields the red zirconium complex **3** and the yellow hafnium complex **4**:



(2)

(M = Zr(3), Hf(4))

Complexes **3** and **4** have been identified by their ^1H NMR spectra and X-ray structures. The ^1H NMR spectra of **3** and **4** in CD_2Cl_2 are almost identical. Therefore only the ^1H NMR of **3** (Fig. 1) is discussed. The proton signal assignments have been made following a procedure using a ^1H and ^{13}C NMR correlated spectroscopy. As a result of the methyl substitution of the cyclopentadienyl ring the local symmetry of the organic ligand is lost and the proton chemical shifts are all different [1]. In the fluorenyl aromatic region, protons 7 and 8 and protons 4 and 11 give rise to two sets of two nearly overlapping doublets at $\delta = 8.14$ and 8.12 ppm and $\delta = 7.88$ and 7.85 ppm respectively. The signals related to protons in the positions 6 and 9 and positions 5 and 10 appear as two sets of multiplets centered at $\delta = 7.55$ and 7.28 ppm. The cyclopentadienyl protons in positions 2 and 3 appear at $\delta = 5.95$ and 5.43 ppm. The signal at $\delta = 5.66$ ppm belongs to the proton in position 1. The three methyl substituents produce three signals in the alkyl region. The bridge methyl protons in the positions 12 and 13 give rise to signals at $\delta = 2.36$ and 2.35 ppm, and the methyl group in the position 14 produce the signal at $\delta = 2.02$ ppm.

3. X-ray structures of 3 and 4

The molecular structures of **3** and **4** are presented in Fig. 2. Important bond distances and bond angles are given in Table 1. Since both compounds have very similar structures only the molecular structure of **3** is discussed here. As in similar metallocene complexes having a $C_5H_4CR_2C_{13}H_8$ chelating ligand system [4], the least-squares planes defined by the two C(5) fragments in **3** are inclined towards the transition metal with respect to C(6)–C(5) and C(6)–C(7) vectors. The effect is more pronounced for the cyclopentadienyl ring than the fluorenyl group with inclination angles of 15° and 11° respectively. Similarly the angle formed by the two centroid zirconium connections, Flu–Zr–Cp, of 118.5° and the Cl–Zr–Cl angle of 99.1° are within the ex-

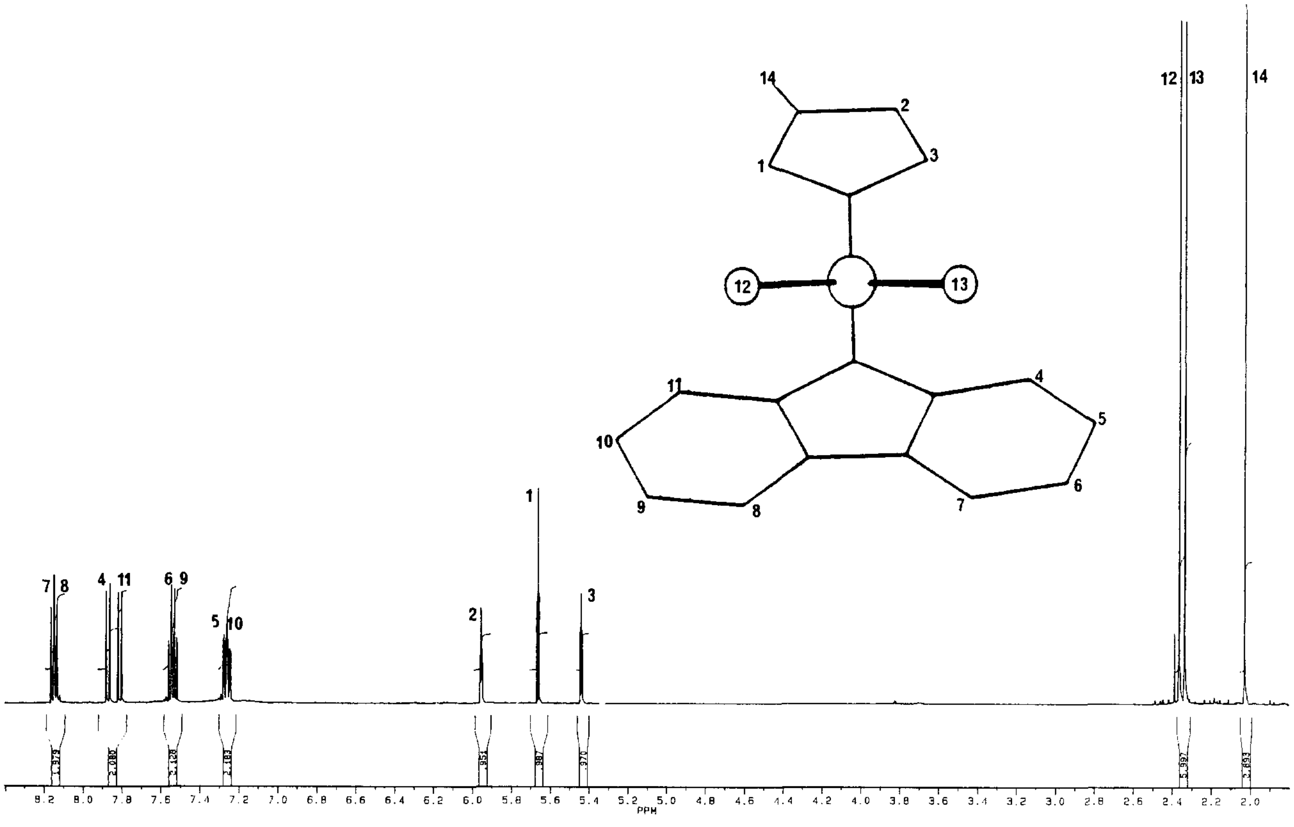


Fig. 1. ^1H NMR spectrum of **3** in CD_2Cl_2 at room temperature.

Table 1
Important bond lengths (Å) and bond angles (°) for **3** and **4** with estimated standard deviations

	3	**4**
Bond distances		
M–Cl(1)	2.425(3)	2.385(8)
M–Cl(2)	2.403(3)	2.382(8)
M–C(1)	2.416(8)	2.43(2)
M–C(2)	2.53(1)	2.50(3)
M–C(3)	2.54(1)	2.47(3)
M–C(4)	2.45(1)	2.45(3)
M–C(5)	2.421(1)	2.44(3)
M–C(7)	2.41(1)	2.38(3)
M–C(8)	2.526(9)	2.50(2)
M–C(13)	2.689(9)	2.69(3)
M–C(14)	2.673(9)	2.65(2)
M–C(19)	2.53(1)	2.45(3)
Zr–Cp [a]	2.16	2.152
Zr–Flu [a]	2.26	2.228
Bond angles		
Cp [a]–Zr–Flu [a]	118.56	119.8
Cl(1)–Zr–Cl(2)	99.1(1)	98.0(3)

[a] Cp = cyclopentadieny centroid; Flu = fluorenyl centroid.

pected range of angles observed for ansa-metallocene molecules with a single carbon as the bridging atom [1,3,4]. The small C(1)–C(6)–C(7) angle of 98.4° is probably due to the metallocenophane character. The fluorenyl ligand is η^5 bonded to the zirconium and the progressive increase in the Zr–C bond distances from the bridge head carbon C(7) (2.41(1) Å) to C(8) (2.526(9) Å), C(19) (2.53(1) Å), C(14) (2.673(9) Å) and C(13) (2.689(9) Å) should be attributed to the repulsive non-bonding interaction between the two chlorine atoms and the dorsal carbon and hydrogen atoms of the fluorenyl six-membered rings rather than to any haptacity change. The unusually large Zr–C bond distances for C(2) (2.53(1) Å) and C(3) (2.54(1) Å) indicate the stronger non-bonded interactions between the bulkier methyl substituents and the underlying chlorine atom. These apparently slight modifications in the interatomic parameters of **3** are significant for the stereoselectivity of the final catalyst (vide infra).

Table 2
Polymerization conditions and results [a] for **3** and **4**–methylaluminosane

Complex	Polymerization temperature (°C)	Melting point [b] (°C)	Molecular weight ($\times 10^3$)	*mmmm* (%)	*rrrr* (%)
3	40	135	54	16.9	23.2
3	60	126	42	15.1	22.5
4	60	123	227	24.2	19.3

[a] For more details about the polymerization conditions and explanations for the molecular weight, *mmmm* and *rrrr* see [1].

[b] Semi-amorphous opaque polymers with broad melting-point curves.

4. Polymerization behavior

Complexes **3** and **4** are active catalysts precursors for the homogeneous polymerization of α-olefins. When activated by methylaluminoxane (MAO) or other ionizing agents, they promote the polymerization of propylene to a semicrystalline polypropylene. Complex **3** shows higher polymerization activity, and **4** produces

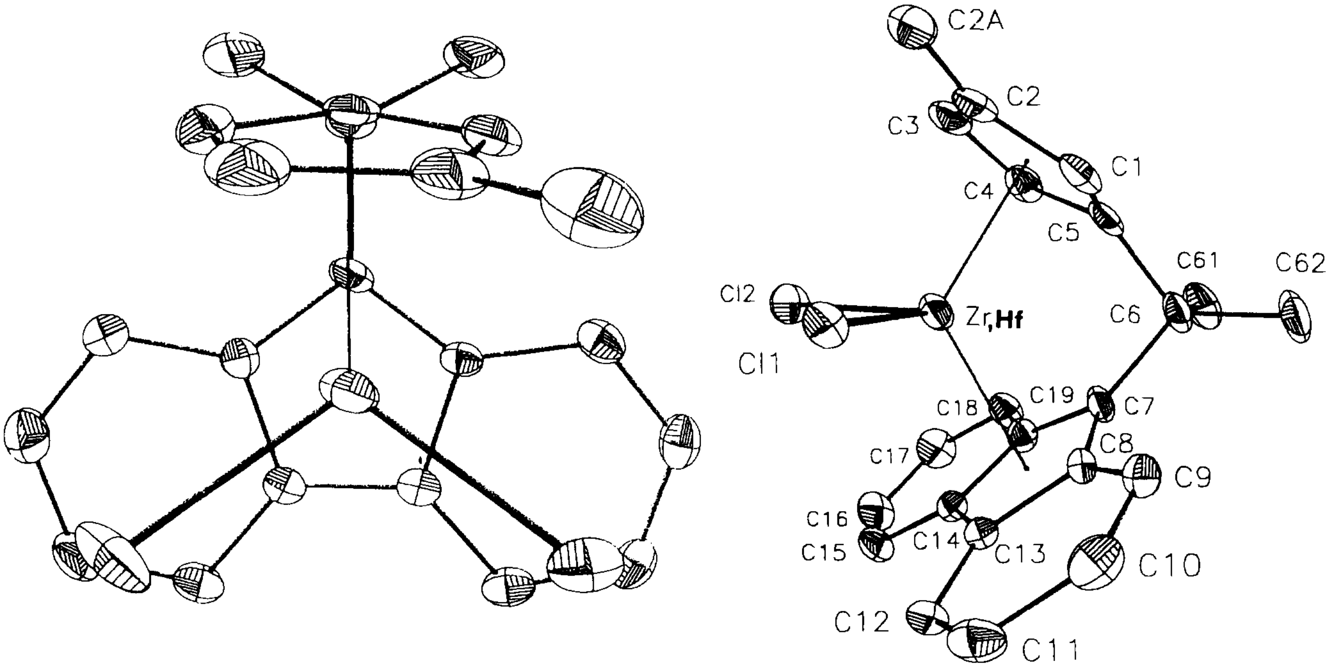
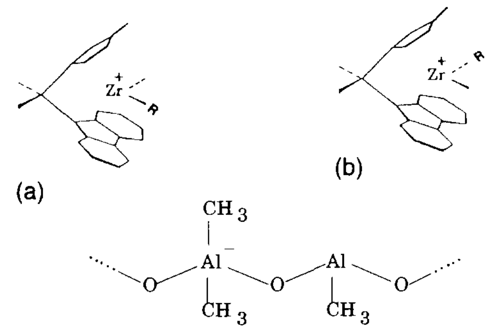


Fig. 2. Two perspective views of the molecular structures of **3** and **4** with atom numbering scheme.



Scheme 1. Hypothetical metalloceniumalkyl diasteroisomers with their methylaluminoxane counter-ion.

polymers with higher molecular weight (Table 2). The analysis of the ^{13}C NMR spectra of the polymers reveals that their chains are composed of alternating blocks of short sequences of isotactic (meso) and syndiotactic (racemic) diads.

5. Mechanistic aspects of the polymerization and the impact of the β substituent on the polymer chain stereoregularity

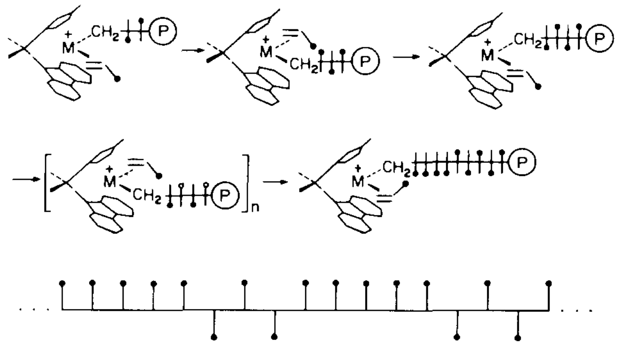
A comparison of the physical properties and stereoregularities of the polymers produced with **3** (and **4**) with the properties of the corresponding polymers reported for their unsubstituted metallocene counterparts [1] reveals that the catalytic performance of the latter has undergone substantial transformation upon introduction of the methyl group into one of the β positions of the cyclopentadienyl group. However surprising the effect of the β substituent may appear at first, by applying the general stereodifferentiation principles which are discussed below, the reasons for the modified catalytic behavior of **3** and **4** and the abrupt change in the nature of their polymers can be delineated satisfactorily.

It is logical to assume that cationic species, similar to those reported for other metallocenes [5], are formed after the activation of **3** (or **4**) with MAO (Scheme 1). These cationic species are electronically and coordinatively very reactive and are believed to rearrange to a transitional metalacyclobutane complex, spontaneously after the coordination of an olefin. The reoccurrence of a certain spatial arrangement (stereoselectivity) of the substituents of the participating units in this hypothetical metallacyclobutane is assured via a selective non-bonding repulsion exerted by the distal and dorsal substituents of the aromatic ligand [6].

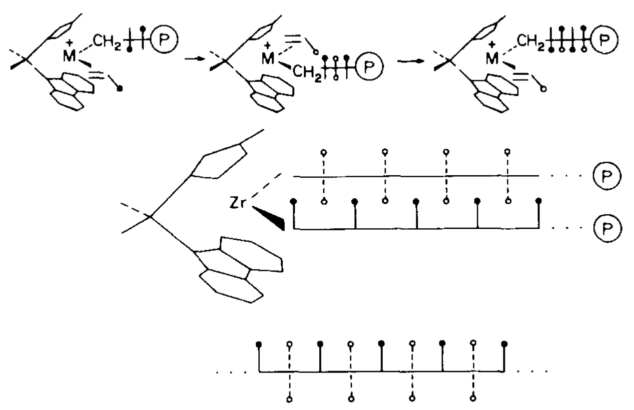
According to a mechanism similar to that proposed by Arlman and Cossee [7], catalytic sites of this nature should be capable of producing syndiotactic chains if after each and every monomer insertion, the alkyl chain and olefin complexation sites are systematically interchanged (chain migratory insertion). Conversely they should produce isotactic chains, whenever the exchange of the coordination sites is prevented and the chain growth occurs always at the same coordination position (chain stationary insertion). An intermediate situation arises if the site-switching mechanism and the chain migration are periodically blocked (e.g. by intermittent substitutional interactions). In this particular case the formation of polymer chains composed of sequences of alternating tacticity can be envisaged.

From the inspection of the position of the alkyl group in the two diastereoisomeres shown in Scheme 1 [8] it becomes obvious that the formation of the diastereoisomer **a**, for steric reasons, is energetically more favorable than that of the diastereoisomer **b** particularly if the R group is replaced by a bulky polymer chain. However, owing to the small size of the β-methyl substituent, the energy difference is probably not very large and could be surmounted if the non-bonded steric interactions between the growing chain (R!) and the substituent are alleviated either by slight rotation of the helical chain due to the newly inserted units or by a haptacity change of the C(5)–Zr bonding. These interactions, individually or concerted, permit the migration of the chain to the more crowded position by enlarging the non-bonding distances between the growing chain and the ligand's substituent. Since these interactions reappear periodically, a multiple of chain migratory insertions will be followed by few chain stationary insertion steps. Frequent repetition of this process can lead finally to the formation of a polypropylene chain composed of syndiotactic and isotactic blocks (Scheme 2).

An alternative microstructure (hemiisotactic [9]) and a different mechanism of formation have been proposed [10] for the polymers prepared with **3** (**4**). According to this mechanism the methyl substituent in the β position, which is suspended directly above one of the coordination positions, does not interfere with the migration of the chain but prevents it occasionally from adopting a preferred orientation in space (preferred conformation). The delicate steric and stereoregulating balance of non-



Scheme 2. The alternate chain migratory and chain stationary insertion and formation of syndiotactic–isotactic stereoblock polypropylene.



Scheme 3. Stereoselective and non-stereoselective diastereoisomeric coordination sites and formation of hemi-isotactic polypropylene.

bonded interactions that exists for both coordination positions in the parent unsubstituted catalysts [1] act in **3** (**4**) upon one of the coordination sites only. While preserving its stereoselectivity, this site continues to coordinate and insert preferentially propylene molecules with only one type of prochiral face (*si* or *re*). After this stereoselective insertion and as a consequence thereof the alkyl chain moves to its new positions. In this position, however, the chain interacts, in a non-bonded manner, with the methyl substituent and adopts an accidental orientation in space. In the backbone of such a hemi-isotactic polypropylene chain every other tertiary carbon has the same chirality, whereas the tertiary carbon atoms as their closest neighbors are of random configurations (Scheme 3).

The ^{13}C NMR of the polymer formed according to Scheme 3 with the proposed hemiisotactic microstructure is not distinguishable from the ^{13}C NMR (Fig. 3) of the syndiotactic–isotactic block polymer discussed above and the interpretation of the results obtained from statistical analysis based on the methyl pentad intensity distributions predict the same outcome in both cases. Consequently both mechanisms could be regarded as valid, although some of the physical properties of the polymers and results obtained from similar catalytic systems tend more toward the periodic site-switching mechanism and syndiotactic–isotactic block polymer notion.

6. Experimental details

All operations were performed routinely under an inert gas by the glove-box or Schlenk technique. Pentane and methylene chloride were dried over calcium hydride. Toluene and (THF) were dried over sodium–benzophenone. All solvents were freshly prepared before use. $HfCl_4$ and $ZrCl_4$ were obtained from Comprehensive Research Chemical Corporation, PO Box 4591, Anaheim, CA, USA. The NMR spectra were recorded on a Bruker 300 MHz instrument.

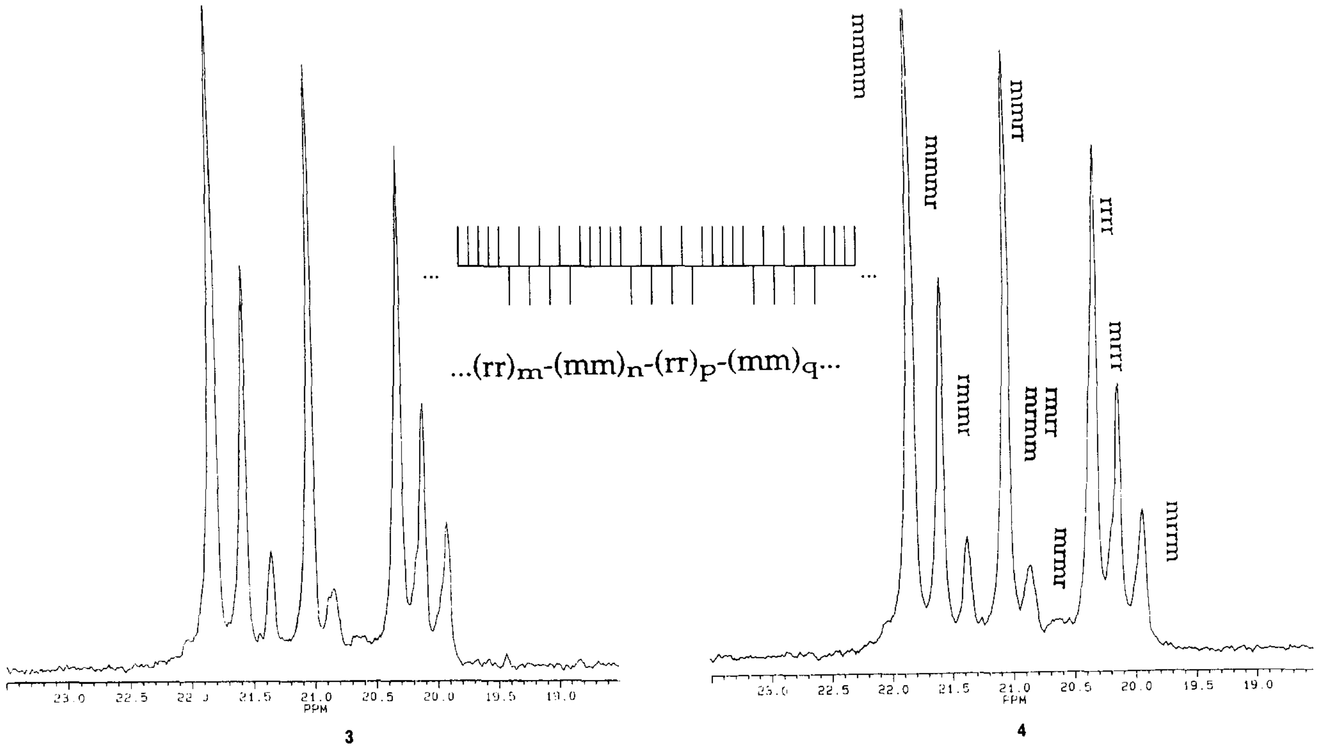


Fig. 3. ^{13}C NMR spectrum of the polymer produced with **3** and **4** at 60°C.

Table 3
Crystal data for [($C_{13}H_8$-μ-CMe_2-C_5H_3Me)$ZrCl_2$]

Space group	$P2_1/c$
Cell constants	
a (Å)	9.024(5)
b (Å)	11.392(6)
c (Å)	18.369(6)
β (°)	100.29(1)
V (Å^3)	1858
Number of molecules per unit cell	4
D_c (g cm^{-3})	1.60
μ_c (cm^{-1})	3.1
Radiation	Mo Kα
Maximum crystal dimensions (mm)	0.15 × 0.25 × 0.30
Scan width (°)	0.80 + 0.20 tan θ
Standard reflections	200, 060, 004
Decay of standards	< 2%
2θ range (°)	2–50
Number of reflections collected	3682
Number of observed reflections	1903
Number of parameters varied	235
R	0.049
R_w	0.062

Table 5
Crystal data and summary of data collection for [($C_{13}H_8$–μ-CMe_2–C_5H_3Me)$HfCl_2$]

Molecular weight	533.8
Space group	$P2_1/c$
Cell constants	
a (Å)	9.034(2)
b (Å)	11.351(4)
c (Å)	18.433(8)
β (°)	100.57(3)
V (Å^3)	1858
Number of molecules per unit cell	4
D_c (g cm^{-3})	1.92
Radiation	Mo Kα
Maximum crystal dimensions (mm)	0.10 × 0.20 × 0.30
Scan width (°)	0.80 + 0.20 tan θ
Decay of standards	< 2%
2θ range (°)	2–46
Number of reflections collected	3282
Number of observed reflections	1640
Number of parameters varied	235
R	0.071
R_w	0.081

6.1. Preparation of 2-(methyl-3-cyclopentadienyl)-2-(fluorenyl)propane (1)

A 1 l round-bottom flask equipped with a side arm, addition funnel and magnetic stirring bar was charged with 50 g (0.3 mol) of fluorene dissolved in 200 ml of THF, under nitrogen. 180 ml of a 1.6 molar solution of methyllithium in ether was added dropwise at room temperature. The resulting red solution was stirred for 6 h until gas evolution had completely ceased. Subsequently a solution of 36 g (0.3 mol) 3,6,6-trimethylfulvene in 100 ml of THF was added dropwise. The reaction mixture was stirred for a further 6 h. It was then treated with a saturated solution of ammonium

Table 4
Final fractional coordinates

Atom	x	y	z	U_{eq}
Zr	0.2567(1)	0.16399(8)	0.13218(6)	0.048(8)
Cl(1)	0.0493(3)	0.2280(3)	0.0378(2)	0.054(10)
Cl(2)	0.1206(4)	0.0378(3)	0.2018(2)	0.074(13)
C(1)	0.418(1)	0.1377(9)	0.0415(6)	0.051(1)
C(2)	0.318(1)	0.039(1)	0.0271(6)	0.051(1)
C(2)A	0.219(3)	0.012(2)	−0.036(1)	0.062(5)
C(3)	0.349(1)	−0.031(1)	0.0899(7)	0.062(17)
C(3)A	0.273(3)	−0.147(2)	0.092(1)	0.057(20)
C(4)	0.464(1)	0.022(1)	0.1433(7)	0.054(13)
C(5)	0.511(1)	0.1285(9)	0.1120(6)	0.049(10)
C(6)	0.598(1)	0.227(1)	0.1567(6)	0.048(15)
C(61)	0.721(1)	0.183(1)	0.2174(7)	0.071(27)
C(62)	0.673(1)	0.308(1)	0.1070(7)	0.068(21)
C(7)	0.466(1)	0.2870(9)	0.1846(5)	0.041(7)
C(8)	0.362(1)	0.3698(8)	0.1456(5)	0.034(6)
C(9)	0.353(1)	0.4348(9)	0.0775(6)	0.045(3)
C(10)	0.236(1)	0.5064(9)	0.0535(6)	0.050(9)
C(11)	0.116(1)	0.5205(9)	0.0921(6)	0.049(8)
C(12)	0.116(1)	0.4611(9)	0.1547(6)	0.046(12)
C(13)	0.238(1)	0.3837(8)	0.1832(5)	0.035(3)
C(14)	0.264(1)	0.3112(8)	0.2461(5)	0.035( )
C(15)	0.179(1)	0.294(1)	0.3027(6)	0.050(5)
C(16)	0.231(1)	0.222(1)	0.3577(6)	0.061(12)
C(17)	0.365(1)	0.162(1)	0.3610(6)	0.063(9)
C(18)	0.453(1)	0.176(1)	0.3079(6)	0.052(4)
C(19)	0.405(1)	0.2525(8)	0.2491(5)	0.040(5)

Table 6
Final fractional coordinates

Atom	x	y	z
Hf	0.2578(1)	0.16231(9)	0.13196(6)
Cl(1)	0.0519(8)	0.2257(7)	0.0402(4)
Cl(2)	0.120(1)	0.0394(7)	0.2007(5)
C(1)	0.418(3)	0.139(3)	0.040(1)
C(2)	0.312(3)	0.036(3)	0.029(2)
C(2)A	0.201(7)	0.028(7)	−0.030(4)
C(3)	0.341(4)	−0.029(3)	0.089(2)
C(3)A	0.258(7)	−0.159(5)	0.092(3)
C(4)	0.460(4)	0.016(3)	0.139(2)
C(5)	0.512(4)	0.118(3)	0.112(2)
C(6)	0.596(3)	0.220(3)	0.153(2)
C(61)	0.725(3)	0.177(3)	0.211(2)
C(62)	0.668(4)	0.305(3)	0.104(2)
C(7)	0.466(3)	0.286(2)	0.180(1)
C(8)	0.363(3)	0.367(2)	0.144(2)
C(9)	0.353(3)	0.432(3)	0.077(1)
C(10)	0.245(4)	0.505(3)	0.052(2)
C(11)	0.117(3)	0.522(3)	0.094(2)
C(12)	0.114(3)	0.460(2)	0.157(2)
C(13)	0.236(3)	0.384(2)	0.181(1)
C(14)	0.266(3)	0.309(2)	0.245(1)
C(15)	0.173(3)	0.295(3)	0.301(2)
C(16)	0.227(4)	0.222(3)	0.359(2)
C(17)	0.361(4)	0.158(3)	0.357(2)
C(18)	0.447(3)	0.173(3)	0.306(1)
C(19)	0.397(3)	0.249(2)	0.246(2)

chloride in 200 ml of water. The organic phase was extracted with ether and dried over $MgSO_4$. After evaporation of the solvents an off-white solid was obtained. Recrystallization from a chloroform–methanol solvent mixture yielded 9.17 g (20%) of spectroscopically pure white needles.

6.2. *Preparation of the dianion* **2**

A 500 ml round-bottom flask equipped with a side arm, addition funnel and magnetic stirring bar was charged with 5 g (0.0175 mol) of 1 in 200 ml of THF. To this solution, 21.9 ml (0.035 mol) of a 1.6 M solution of methyllithium in ether was added dropwise. The resulting red solution was stirred overnight. The evaporation of the solvents yielded the dianion quantitatively as an orange solid.

6.3. *Preparation of* **3**

To a suspension of 0.0175 mol of 2 in 200 ml of dry pentane in a 1 l round-bottom flask equipped with a magnetic stirring bar was added a suspension of 4.9 g (0.0175 mol) of $ZrCl_4$ in 200 ml of pentane. The mixture was stirred for 6 h. The pentane was decanted, and the remaining red solid was extracted with methylene chloride. Cooling of the extract to −20 °C gave analytically pure red crystals with a quantitative yield.

6.4. *Preparation of* **4**

A similar procedure to that used for the preparation of **3** was used but with $HfCl_4$. A yellow analytically pure product was yielded after recrystallization from methylene chloride.

6.5. *X-ray data collection, structure solution and refinement of* **3**

Single crystals of **3** were sealed under N_2 in thin-walled glass capillaries as a precaution, although the crystals appear rather stable in air. Data were collected on an Enraf–Nonius CAD4 diffractometer by the Θ–2Θ scan technique as previously described [11]. The structure was solved by the application of the standard Patterson methods. The crystals diffracted well. All non-hydrogen atoms were treated with anisotropic thermal parameters. Hydrogen atoms (except for those of the disordered methyl groups) were located on a difference Fourier map, but their parameters were not refined. The methyl group on the cyclopentadienyl group was disordered (50:50) over two sites. A final difference Fourier map showed no unaccounted electron density. A summary of data collection parameters and positional parameters are given in Tables 3 and 4. Calculations were carried out with the SHELX system of computer programs [12].

6.6. *X-ray data collection, structure solution and refinement for* **4**

Data collection and structure solution and refinement were accomplished as for the zirconium analogue, with which this compound is isostructural. A summary of data collection parameters and positional parameters are given in Tables 5 and 6.

References

[1] A. Razavi and J. Ferrara, *J. Organomet. Chem., 435* (1992) 292.

[2] J.A. Ewen, L.R. Jones and A. Razavi, *J. Am. Chem. Soc., 110* (1988) 6255.

[3] A. Razavi and J.L. Atwood, *J. Organomet. Chem., 459* (1993) 117.

[4] A. Razavi and U. Thewalt, *J. Organomet. Chem., 445* (1993) 111.

[5] R.F. Jordan, C.S. Bajgur, R. Willet and B. Scott, *J. Am. Chem. Soc., 108* (1986) 7410; G.G. Hlatky, H.W. Turner and R.R. Eckman, *J. Am. Chem. Soc., 111* (1989) 2728; M. Bochman, *Nachr. Chem. Tech. Lab., 38* (1990) 1238; X. Yang, C.L. Stern and T.J. Marks, *Organometallics, 10* (1991) 840; P.G. Gassman and M.R. Callstrom, *J. Am. Chem. Soc., 109* (1987) 7875; R. Taube and L. Krukowka, *J. Organomet. Chem., 347* (1988) C9.

[6] L. Cavallo, C. Guerra, M. Vacatello and P. Corradini, *Macromolecules, 24* (1991) 1784.

[7] E.J. Arlman and P. Cossee, *J. Catal., 3* (1964) 99.

[8] Theoretically four diastereoisomeric minimum-energy conformations are possible (cf. [6]).

[9] M. Farina, G. Silvestro and P. Sozzani, *Macromolecules, 15* (1982) 1452; M. Farina, G. Silvestro and P. Sozzani, *Macromolecules, 18* (1985) 923.

[10] J.A. Ewen, M. Elder, R.L. Jones, L. Haspeslagh, J.L. Atwood, S.G. Bott and K. Robinson, *Makromol. Chem., Makromol. Symp., 48–49* (1991) 253.

[11] J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Dalton Trans.,* (1979) 46.

[12] G.M. Sheldride, *SHELX, a System of Computer Programs for X-ray Structure Determination*, 1976.