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Journal of Molecular Catalysis A: Chemical 115 (1997) 129–154

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Geometric flexibility, ligand and transition metal electronic effects on stereoselective polymerization of propylene in homogeneous catalysis [1]

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Abstract

The stereotacticities of a series of polypropylene polymer chains produced with different categories of structurally characterized ansa-zirconocene and hafnocene procatalysts in homogeneous catalysis have been determined by statistical analyses of the methyl pentad signal intensity distributions of their ^{13}C NMR spectra. The polymers microstructural characteristics have been contrasted with the intramolecular parameters of the discrete metallocene molecules obtained from single crystal X-ray diffractions and different ^{1}H NMR measurements. For the first category, by contrasting the polymerization behavior of zirconocene–hafnocene pairs the origin of the stereospecificity differences have been discussed in terms of heavy atom electron configuration, lanthanoid shell contraction and relativistic effects operative on elements belonging to the sixth row of the periodic table. For the second category the observed changes in polymerization behavior for a pair of zirconocene based catalysts with ligand modification of irrelevant steric control have been correlated to the electron density redistribution on different aromatic carbons and the consequent change in flexibility of the catalyst framework, increase of the haptocity of M–C5 bonding and variation of the frontier orbital shape and diffusivity. For the third category, pairs of syndio- and isotactic specific ansa-zirconocene and hafnocenes have been selected in which the organic ligands are constructed with the same aromatic moieties joined with different bridges. The observed catalytic changes have been correlated to combined steric and electronic factors altering orbital energies and hybridizations. Finally, by introducing a fourth category, the Hf effect is demonstrated by comparing the catalytic olefin activities of two non-bridged hafnocene–zirconocene pairs.

Keywords: Propene; Electronic effects; Stereoselectivity

1. Introduction

Hitherto most articles treating the polymerization behavior of ansa-metallocene catalysts have investigated mainly the steric factors such as the size of the substituent of the ancillary ligand, the ionic radii of the transition metal (Ti, Zr, Hf) and the degree of the coverage of the active coordination positions by the substituents [1]. In this article we report, in a qualitative manner, the influence of electronic factors on stereospecific or non-stereospecific behavior of metallocene catalysis. By electronic factors we mean those which are related in one

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[1] A slightly modified version of this paper was first presented at the Int. Symp. on Catalyst Design for Tailor-made Polyolefins Kanazawa/Japan, March 10–12, 1994.

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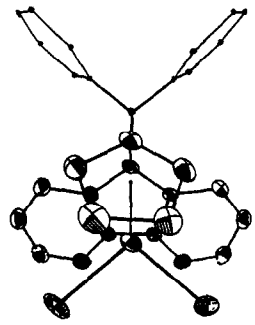
PII S1381-1169(96)00096-9



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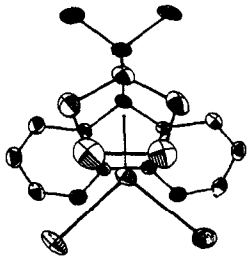

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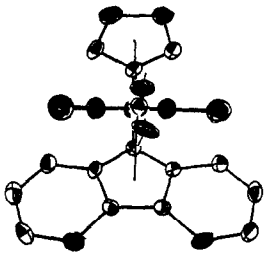

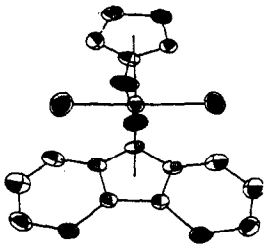

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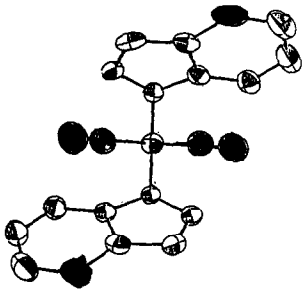

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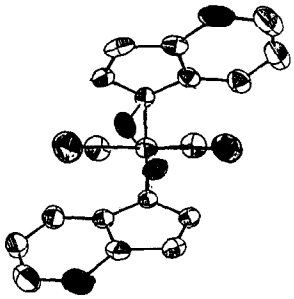

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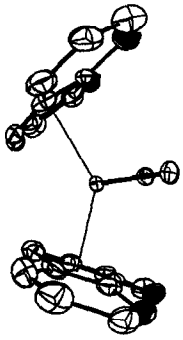

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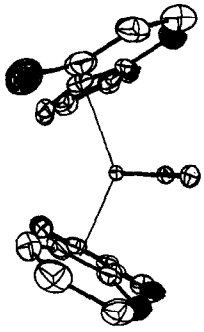

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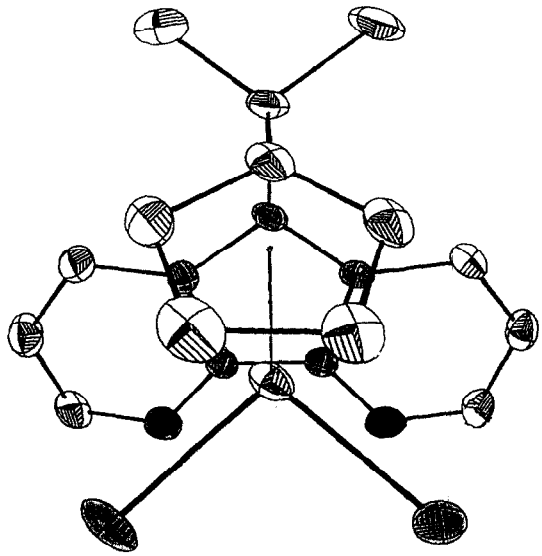
Scheme 1. Molecular structures of selected hafnocenes and zirconocenes.

way or another to the electron configuration of the central transition metal, its electrophilicity, the topology, energies and hybridizations of the frontier orbitals, and metal ion's capacity for oxidation state changes (redox behavior both in ground and transition state).

To that end, we have selected a series of metallocenes in which only one factor at a time (transition metal, substituent in the bridge, and the size of the bridge) has been modified and its influence on the polymerization behavior was investigated. While doing so we have been trying to remain as loyal as possible to our principal goal that mainly electronic factors should be affected by these changes even though ideally this condition is difficult to meet. We commence the discussion, for historical and chronological reasons but also on mechanistic grounds, with a general treatment of our syndiospecific complex pair isopropylidene(cyclopentadienylfluorenyl)MCl_2; M = Hf, Zr as the point of departure, and proceed with comparison of other structurally related catalyst pairs and extend the discussion to structurally different metallocene catalysts for generalization of the results. The metallocenes subject to these discussions are portrayed in Scheme 1.



$[(C_{13}H_8\text{-}\mu\text{-}CMe_2\text{-}C_5H_3Me)MCl_2]$

M = Hf (1), Zr (2)

Fig. 1.

2. Results and discussion

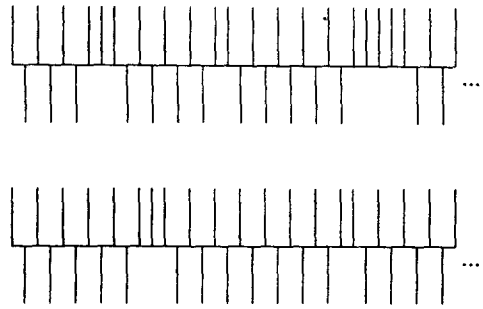
2.1. Isopropylidene(cyclopentadienylfluorenyl) MCl_2 (M = Hf(1), Zr(2)) (Hf vs Zr; lanthanoid contraction, relativistic effects)

The two title compounds whose molecular structures are displayed in Fig. 1 are the first examples of their kind prepared and investigated by us initially. They proved to be very active for polymerization of propylene to syndiotactic polypropylene after their activation with MAO or other appropriate ionizing agents. We have already reported on many occasions [2] their structural characteristics and catalytic properties from different perspectives. In this article we put the emphasis on the effect of electron configuration differences that stem from the position of the two central transition metals, Hf and Zr, in the periodic table and the correlation of these effects to the catalytic behavior as well as the macro- and microstructures of the resulting syndiotactic polymers.

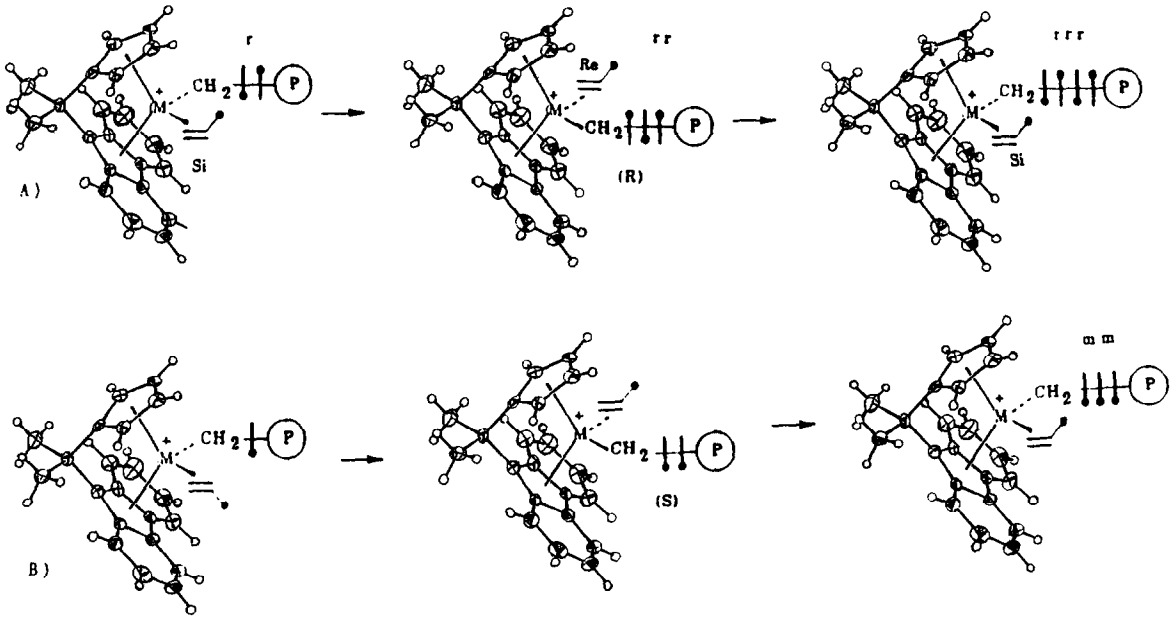
We have already shown [2] that the syndiospecificity of these catalysts emanates from the prochirality and the bilateral symmetry of the metallocene molecule (cf. Fig. 1) as well as the *S*,*R*-enantiomeric nature of the cationic active sites. The stereoregulation of the polymerization was shown to be governed by the geometry of the enantiomorphic sites and the continuous, insertion initiated, chain migration/site isomerization processes which result in alternating enchainment of monomers and formation of monomer sequences with inverted stereogenic centers (syndiotactic chain). The prochiral face selectivity has been shown to be dictated by the balanced and cooperative non-bonded interactions induced by the ancillary chelating ligand directing the conformation of the growing polymer chain and conducting

the coordination and insertion of the monomer with proper prochiral faces (Scheme 2) [3].

Table 1 compares selected bond distances and bond angles for **1** and **2**. Inspection of the data presented in this table reveals that the interatomic bond distances for **1** and **2** are very similar, but always (except for M–C5 distance) slightly shorter for the Hf–C bond. The ^{1}H NMR spectrum shown in Fig. 2 is representative for both complexes and confirms that the structural resemblance exhibited in solid state is also maintained in solution. In contrast to these structural similarities the polymerization results presented in Table 2(a,b) for **1** and **2** show major discrepancies with respect to the catalytic activities and polymer properties. The striking features in Table 2 are the high activity and stereospecificity of **2** (cf. Fig. 3) and the very high molecular weights of the polymers produced with **1**. Also noteworthy is the formation of short isotactic sequences in the backbone of the polymers produced at lower polymerization temperatures with **1** in addition to the ubiquitous enantiomorohic site stereochemical defects (meso triads) and the so-called single m defects (meso dyads) in the SPP polymers of **2**.



The difference in catalytic activity, stereospecificity and molecular weights observed for two metallocene catalysts with exactly the same ligand framework and transition metals of the same family is rather surprising and is certainly related to thermodynamic and kinetic factors. Since the activity is directly proportional to the initiation and propagation rates, and the molecular weight is inversely related to the termination reactions rates, we have to examine possible



Scheme 2. (A) Enantiomorphic site stereochemical control mechanism, prochiral face selectivity and syndiotactic chain propagation.(B) Reverse prochiral face selectivity and formation of isotactic triad stereodefects.

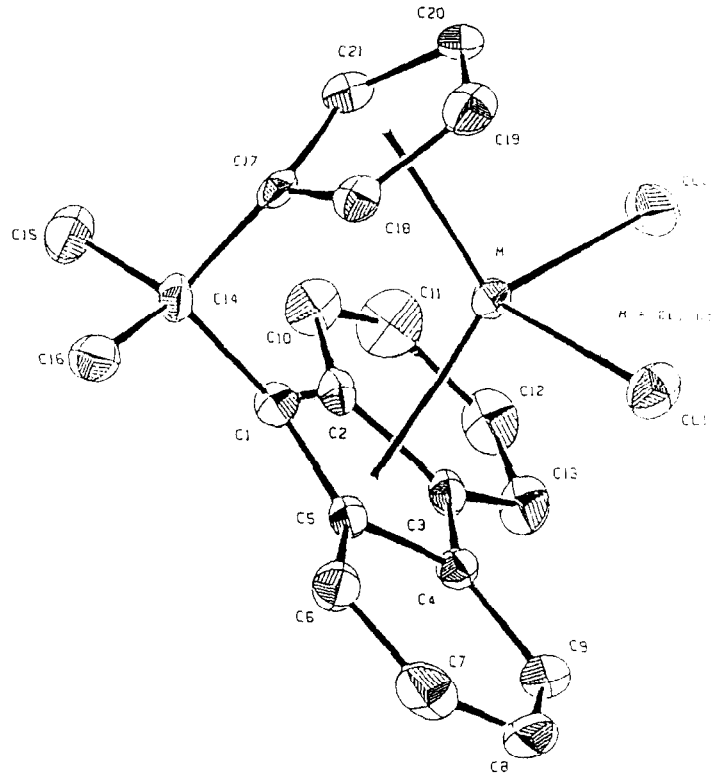
parameters which could act upon these reaction rates to elucidate the origin of these findings.

It is well known in organotransition metal chemistry that in the d-block transition metal series for each homologous triads, by descending from top to bottom, the M–C bonds become stronger (this phenomenon has its origin in lanthanoid contraction and relativistic effects and will be discussed in some length later). The weaker and more active Zr–C bond gives rise to a faster monomer insertion and more rapid chain propagation, but also to a higher termination rate. The net effect is that **1** produces longer chains at slower rates and **2** produces shorter chains at faster rates. Additionally **1** and **2**, due to different frontier orbitals spatial electron density distributions and ionization potentials, have different ability to undergo α(γ)- or β-agostic interactions in the transition and ground states. The active chain end α- and β-hydrides being differently oriented in space have different overlapping probabilities for the available frontier orbital and apparently their spatial orientation favors an α-agostic approach for Hf and a β-agostic interaction for Zr.

For the difference in stereospecificity a different type of argument is in order. As mentioned above the syndiotactic specificity of the catalysts formed with metallocenes **1** and **2** stems from the inherent symmetry and the unique steric arrangement of the ancillary chelating ligand, but also on the ability of the chain to migrate and the capacity of the sites to isomerize after each insertion. Whereas the static properties of the metallocene, bilateral symmetry and prochirality of the site are determinant

Table 1
Selected bond angles (degrees) and bond distances (Å) for **1** and **2**

	Hf	Zr
M–Cl	2.391(6)	2.422(3)
M–Cl	2.394(6)	2.425(2)
M–Cl	2.40(2)	2.401(8)
M–C2	2.49(2)	2.501(8)
M–C3	2.64(2)	2.655(7)
M–C4	2.64(2)	2.651(7)
M–C5	2.57(2)	2.528(8)
M–C17	2.46(2)	2.436(7)
M–C18	2.44(2)	2.444(8)
M–C19	2.50(2)	2.519(8)
M–C20	2.51(2)	2.528(8)
M–C21	2.41(2)	2.452(8)
Cl–M–Cl	97.5(2)	98.2(9)
Cp–M–Flu	119.4	118.6



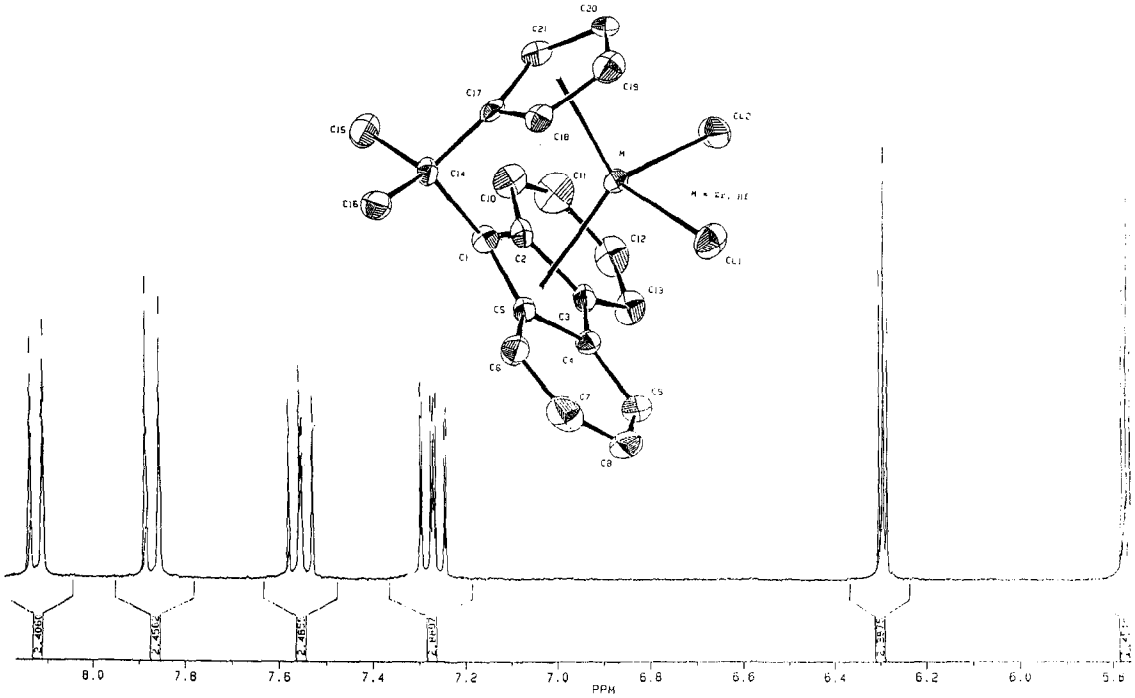


Fig. 2. ^{1}H-NMR spectrum of **1(2)** in CD_2Cl_2 (RT).

for the type of stereospecificity (syndiospecificity), the 'well' functioning of the dynamic properties of its activated form, site isomerization/chain migration processes, are responsible for the degree of the stereospecificity (syndiospecificity). The latter depends to a large extent on the polymerization conditions such as polarity of the diluent, the nature of the counter ion, the monomer concentration, and polymerization temperature as well as the effective nuclear charge, local Lewis acidity and steric environment of the sites.

A favorable contact ion-pairing equilibrium constant due to higher effective nuclear charge

Table 2
(a) Polymerization conditions [a] and results with **1** and **2**

	Pol. T (°C)	Act. (kg/g)	Mw ($\times 10^3$)	rrrr (%)
Zr	60	180	90	82
Zr	40	120	138	86
Hf	60	2.7	778	73
Hf	40	0.2	1322	64

(b) Variation of pentad stereosequece intensities distributions with polymerization temperature

	Pol. T (°C)	rrrr (%)	rrmr (%)	rmmr (%)	mmmm(%)
Zr	60	82	2.70	1.65	0.0
Zr	40	86	1.15	1.55	0.0
Hf	60	73	7.20	3.80	0.5
Hf	40	64	10.50	3.50	1.8

[a] 1 l liquid propylene; 5 ml MAO (11 wt% in toluene); 60 min.

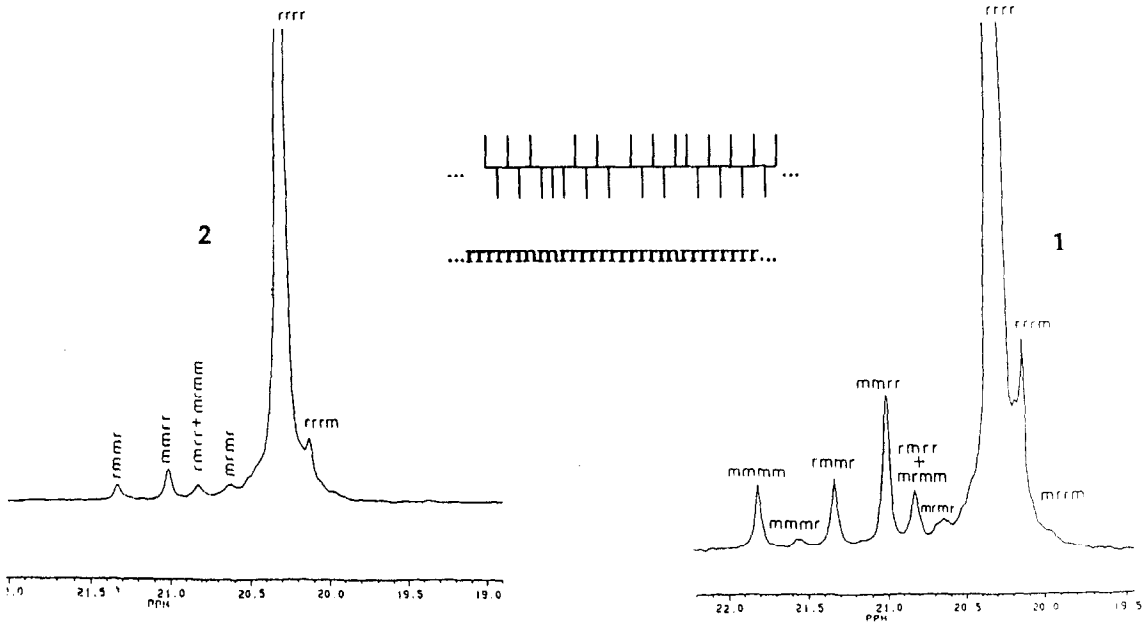
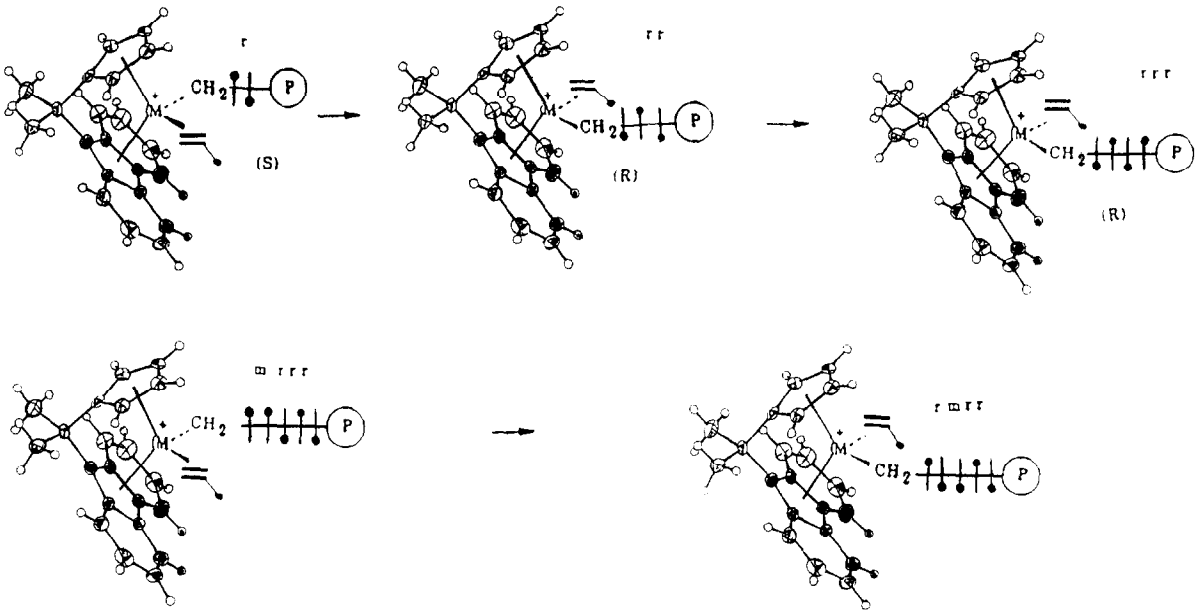


Fig. 3. The methyl region of ^{13}C-NMR spectra of the SPP produced with **1** and **2**.

and an increased steric encumbrance resulting from smaller size of the Hf cation are detrimental to the chain migratory insertion and favors intermittently double and/or multiple insertion at the same enantiomeric site (chain stationary insertion). This situation leads to the formation of the so-called single m defects in **2** and/or short isotactic sequences in **1** particularly at

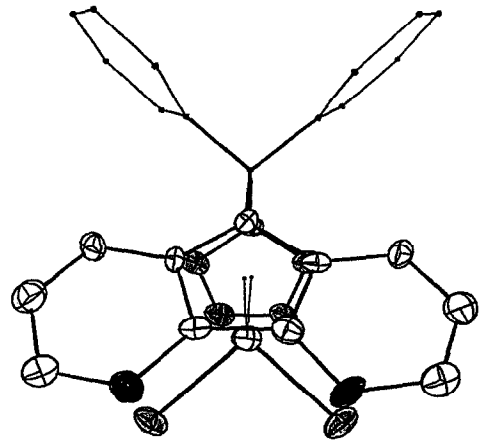


Scheme 3. Chain migratory insertion/site siomerization with occasional chain stationary insertion and formation of isotactic dyads.

lower polymerization temperatures (Scheme 3). At higher polymerization temperatures, however, the ion pairing of Hf^+ with MAO^- is less favored, the steric barrier for migration can be surmounted, the formation of isotactic sequences is strongly suppressed, and the polymers have higher stereoregularity (cf. Table 2b).

2.2. *Diphenylmethylidene(cyclopentadienylfluorenyl)MCl_2 (Hf(3), Zr(4)) (phenyl vs methyl; haptotropy and electronic rigidity)*

The molecular structures and the aromatic region of the ^1H NMR spectra of 3 and 4 are displayed in Figs. 4 and 5. Despite the substitution of the two methyl groups in the parent complexes with two phenyl substituents the basic structural characteristics, prochirality and bilateral symmetry, prerequisites for the syndiospecificity, have been maintained. Consequently, after activation, **3** and **4** promote the polymerization of propylene to syndiotactic polypropylene efficiently (Fig. 6) according to the same mechanism operative for **1** and **2**. The polymerization conditions, results and polymer analyses given in Table 3(a,b) indicate, however, that the syndiotactic polymers produced with **3** and **4** differ in some respects from the corresponding polymers of **1** and **2**. The new polymers expose substantially higher molecular weights and slightly higher stereoregularities. Here again, the polymers made with hafnium based catalyst **3** have much higher molecular weights.



[(C13H8-μ-CPh2-C5H4)MCl2]

M = Hf (3), Zr(4)

Fig. 4.

The differences in the macro- and microstructural characteristics of the polymers produced with **2** and **4** are obviously originating from the particular structural modifications that have been performed on the ligand framework of the individual metallocene procatalysts. The impact of the phenyl and methyl substituents in the bridge

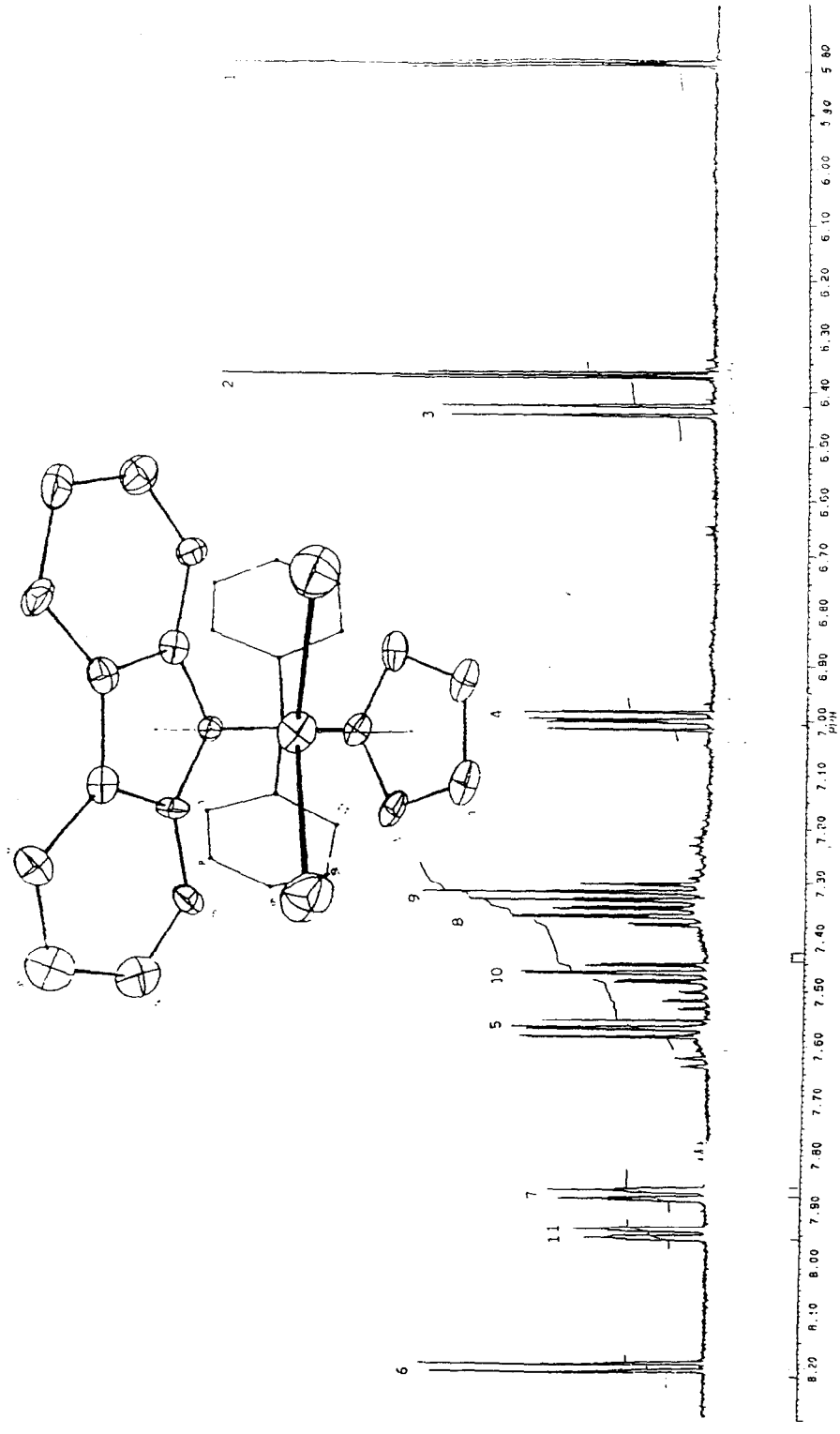
Table 3
(a) Polymerization conditions [a] and results for **3** and **4**

	Temp. (°C)	Act. (g/g)	Mw ($\times 10^3$)	Mp (°C)	rrrr (%)
Zr	20	11 800	1243	145.60	91.04
Zr	40	26 700	785	144.45	89.74
Zr	60	138 000	478	133.40	86.78
Hf	40	17 500	2863	103.81	76.60
Hf	60	27 500	1950	102.17	74.03

(b) Variation of methyl pentad stereosequence intensity distributions with polymerization temperature

	Pol. *T* (°C)	rrrr (%)	rmrr (%)	rmmr (%)	mmmm(%)
Zr	20	91.04	1.07	0.92	0.00
Zr	40	89.74	1.21	2.08	0.00
Zr	60	86.78	1.95	2.40	0.11
Hf	40	76.60	2.71	4.55	0.58
Hf	60	74.03	1.37	3.46	0.86

[a] 1 l liquid propylene; 10 ml MAO (11) wt% in Toluene); 60 min.



^{1}H-NMR Spectrum of 3 (4) in CD_2Cl_2 (RT)

Fig. 5. ^{1}H NMR spectrum of **3**(**4**) in CD_2Cl_2 (RT).

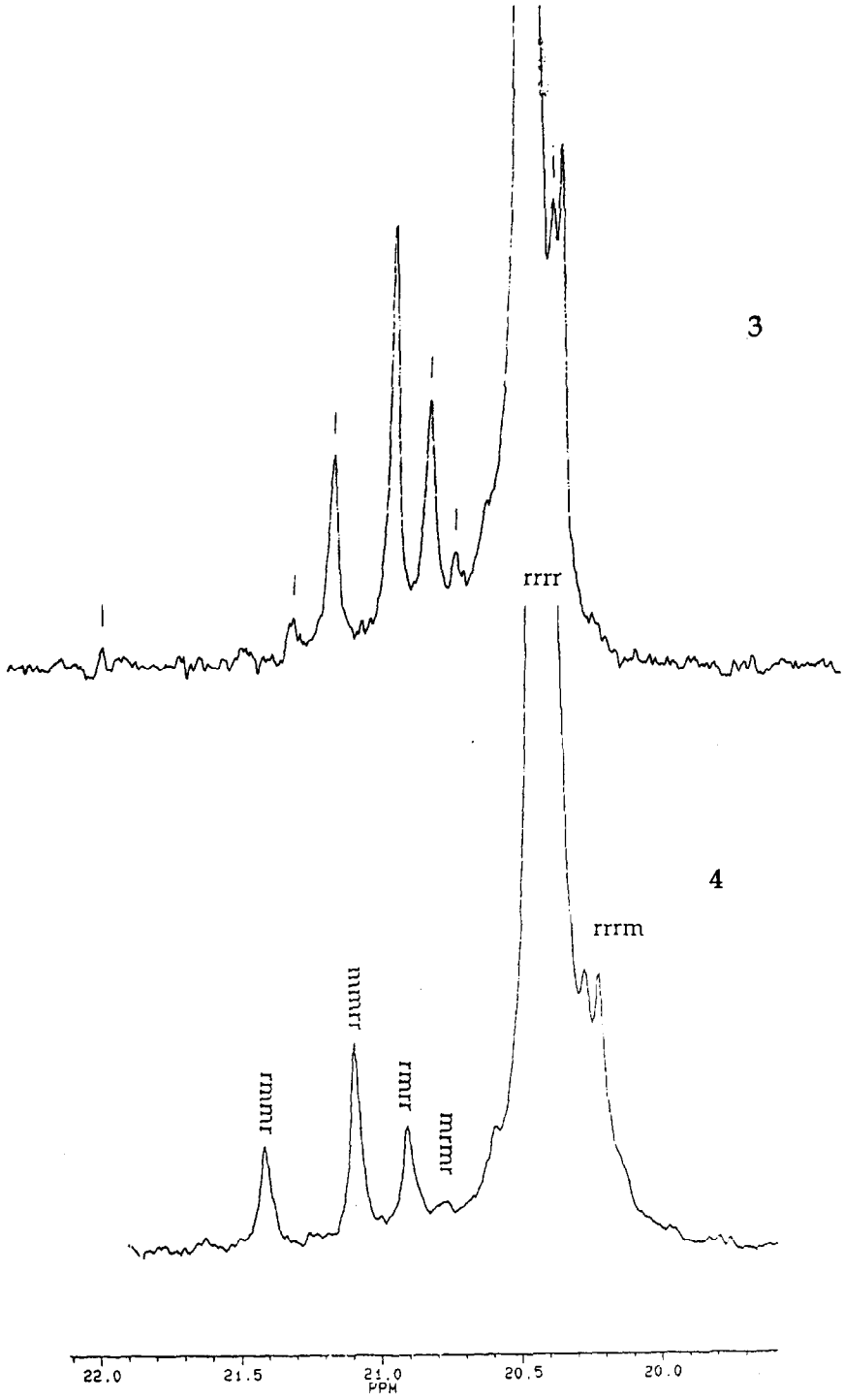
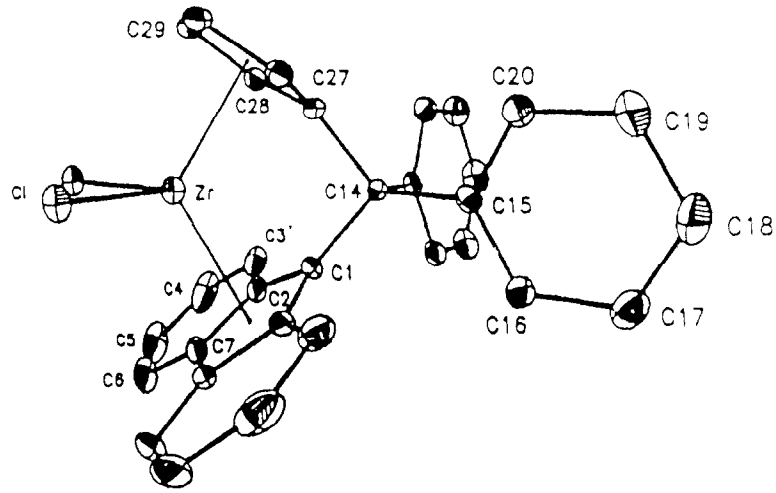


Figure 6. The Methyl Region of the ^{13}C-NMR Spectra of the Polymers Produced with 3 and 4

Table 4
Selected bond angles (degrees) and bond distances (Å) for **3** and **4**

	Hf = 3	Zr = 4
3M–C1	2.403(2)	2.424(2)
M–C1	2.410(1)	2.417(8)
M–C2	2.511(9)	2.513(6)
M–C7	2.670(1)	2.680(6)
M–C27	2.440(1)	2.452(8)
M–C28	2.439(9)	2.450(6)
M–C29	2.505(9)	2.523(6)
Cp–M–Flu	118.2	117.6
Cl–M–Cl	95.6	96.6



on the polymerization characteristics of the final catalysts influence the catalyst structure–polymer property interrelation. This can be rationalized by the interpretation of the intramolecular data of **2** and **4** (both in static and dynamic states) in conjunction with the processing of the analytical data of their polymers.

A cursory inspection of the interatomic parameters of **4**(**3**) given in Table 4 and their comparison with those of **2**(**1**) shown in Table 1 reveals that upon introduction of the phenyl groups in the bridge the important M–C bond distances do not undergo palpable changes and the observed variations are well within the expected experimental uncertainties. However, the cent-Zr-cent and Cl-Zr-Cl angles have been decreased from values of 118.60° and 98.20° for **2** to values of 117.60° and 96.60° for **4** by 1.00° and 1.60°. These angular changes imply that in **4** the Zr atom has moved slightly out of the mouth of the ligand and is less electrophilic [4]. Thus in solid state, under compacting crystal effect, the two metallocene molecules do not much differ structurally from each other (cf. Fig. 7). Surprisingly this is not the case any more once they are dissolved in an organic solvent.

A comparison of the ^{1}H NMR spectrum of **3**(**4**) with the ^{1}H NMR spectrum of **2**(**1**) is given in Fig. 8. For both molecules the protons related to the C_5H_4 groups show the same coupling pattern (two virtual triplets) and very similar chemical shift values. Nevertheless, the examination of the remaining section of the spectra reveals major alteration for the chemical shifts of the proton signals belonging to the $C_{13}H_8$ moiety of **4**. These protons have been subjected to different shielding and deshielding forces under the influence of the magnetic field anisotropy that has been caused by the ring currents of the two phenyl substituents in the bridge. Proton 3, closest to the phenyl groups, has experienced the most dramatic upfield shift. Its signal appears at 6.43 ppm and is more than 1.5 ppm shifted to the higher field. The signal related to the nearby proton 4 is too shifted to

Fig. 6. The methyl region of ^{13}C-NMR spectra of the SPP produced with **3** and **4**.

higher field but only by about 0.5 ppm. The chemical shift variations for protons 5 and 6 are less pronounced. Another interesting feature of these ^{1}H NMR spectra concerns the fluorenyl proton signal patterns of **4** and **2**. Whereas a doublet triplet–triplet doublet pattern extending from 6.43 ppm to 8.19 ppm is observed for the former the latter show a doublet–doublet triplet–triplet pattern within the 5.7 to 8.2 ppm range.

Apparently the electromagnetic fields induced by the ring current of the phenyl groups in the C1 bridge have not only caused the deformation of the aromatic π system of the fluorenyl six membered rings but also have provoked a redistribution (a more homogeneous partition) of the electron densities concentrated on the carbon atoms of the fluorenyl group. The bonding between the individual five carbon atoms of the fluorenyl five membered ring to the Zr ion in **4** is more balanced and should have similar length and strength in solution. In other words the cyclopentadienyl ring of the fluorenyl has become 'fully' aromatic and its six membered rings have adopted a more butadiene like character (cf. signal pattern). This means that in **4(3)** the fluorenyl five membered ring is pentahapto bonded to Zr. The easy hydrogenation of **4** and its transformation to the corresponding diphenylidene(cyclopentadienyl-octahydrofluorenyl)$ZrCl_2$ and the formation of very stable cations with Turner's reagents corroborate this conclusion.

The change from trihapto bonding in **2(1)** to pentahapto bonding in **4(3)** is probably the main source of the modified catalytic performance. As a consequence of penthapto bonding the active sites formed with metallocene **4(3)** are less Lewis acidic, coordinatively more saturated, electronically less flexible and thermodynamically and kinetically more stable than those of the corresponding sites formed by **2(1)**. All these characteristics of course favor the formation of shorter and less stereoregular chains with **1** and **2** and production of longer, more stereoregular chains for **3** and **4**.

The electromagnetic field perturbations caused by the phenyl substituents can furthermore alter the shape, spatial extension and diffusivity of the more exposed frontier orbitals of the Zr cation [5] in **4** and change the course of the polymerization reactions. It has been widely accepted that the electronically and coordinatively unsaturated, highly reactive cationic cen-

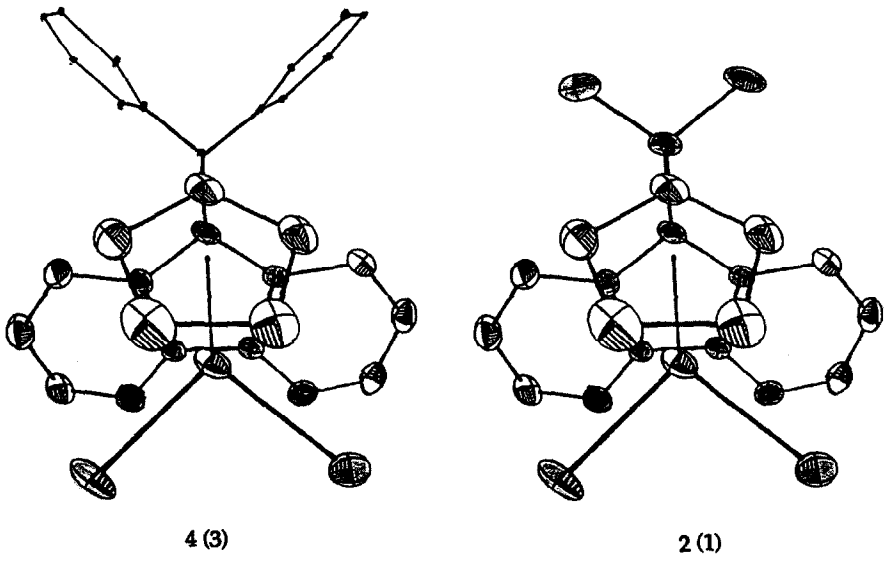


Fig. 7. Structural comparison between **2(1)** and **4(3)**.

ters are stabilized by agostic interactions with the hydrides at α(γ) or β position on the reactive end of the polymer chain [6]. These C–H bonds act as ligands with a 'pair' of electrons. The occurrence and the frequency for each of these interactions depend on the shape and the extension of the available frontier orbitals, can change the mechanism of propagation and termination reactions and affect the molecular weight and stereoregularity of the polymer chain dramatically. An α(γ)-agostic interaction that would maintain the active center intact during the time lapse between two coordinations and yet would give way to the incoming monomer for successive insertion, is crucial for the formation of the polymers with high molecular weights. Conversely, β-hydride agostic interactions could lead to β-hydride eliminations and the formation of chains with lower molecular weights.

The same line of reasoning can be employed when comparing the catalytic properties of the

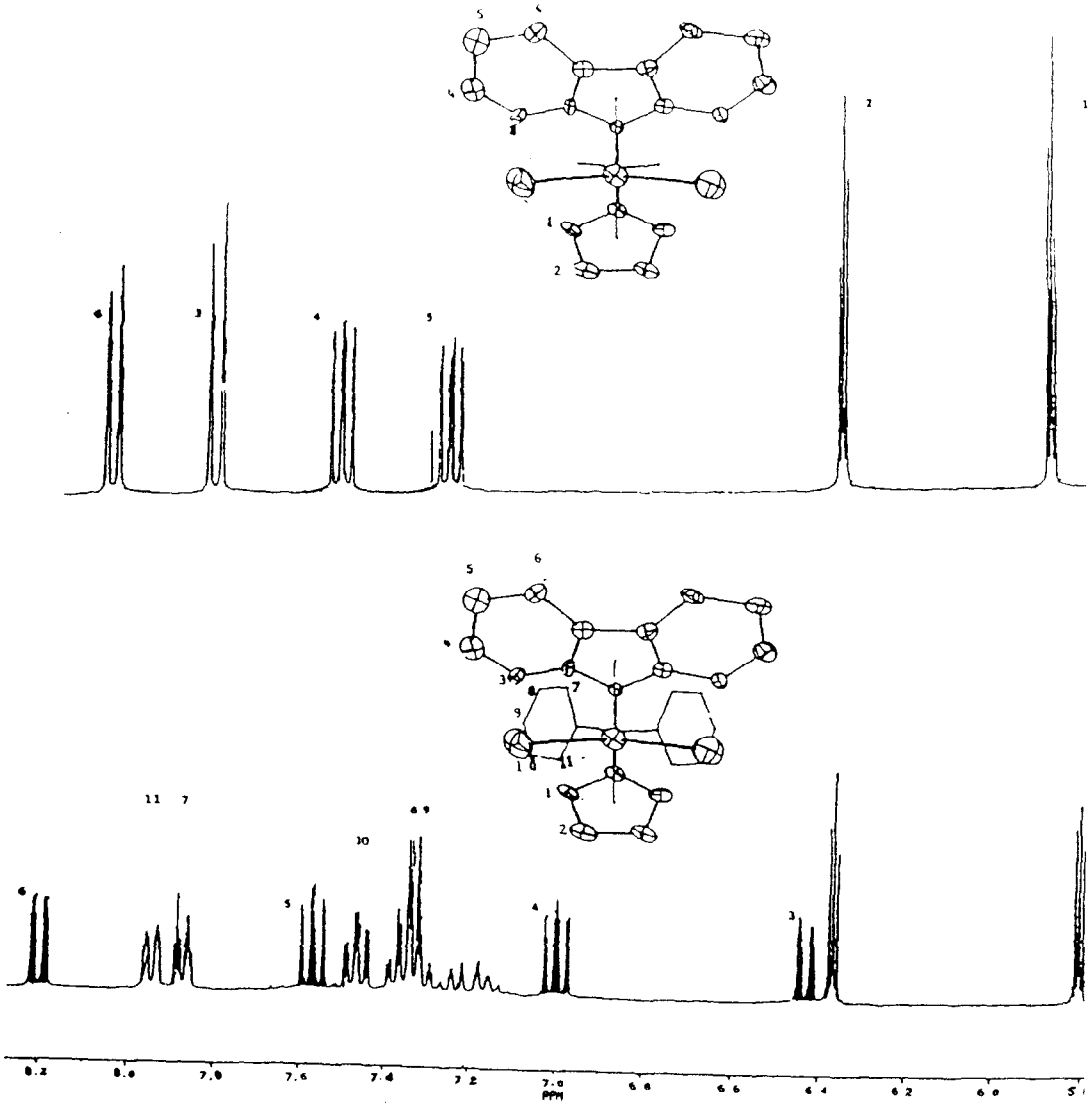
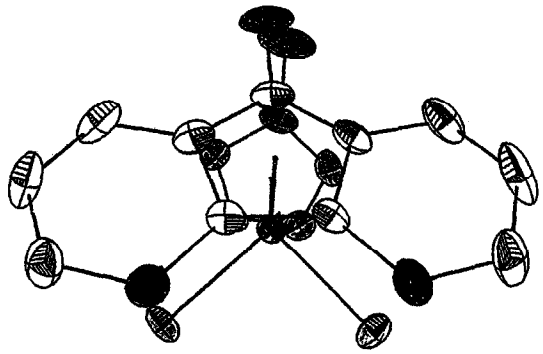


Fig. 8. Comparison between ^{1}H NMR of **1**(**2**) and **3**(**4**).

hafnocenes **1** and **3** with an additional remark regarding the tacticity data presented in Table 4b. The tacticity values indicate that the syndiotactic polymers produced at 40°C with **3** contain fewer isotactic sequences than the polymers of **1**. The most likely explanation could be that the pentahapto bonded, coordinatively and electronically more satisfied Hf cation in **3** is less prone to contact ion pairing. In this case the chain migrations proceed with less restriction. At 60°C the steric factors become predominant and the percentage of mmmm pentads is slightly higher for the polymer produced with **3**.



[(C13H8-μ-CH2CH2-C5H4)ZrCl2]

Fig. 9.

2.3. *[1,2-(cyclopentadienylfluorenyl)ethane] $ZrCl_2$ (5) (ethano bridge vs isopropylidene bridge; structural flexibility)*

The molecular structure and ^{1}H NMR spectrum of **5** is displayed in Figs. 9 and 10. The molecule is prochiral and can be cut in two almost equivalent halves by a mirror plane bisecting the Cl–Zr–Cl angle (only the two carbon atoms in the bridge lie on a skew line with respect to the mirror plane and are not symmetry related). In this respect **5** bears close resemblance to **2** (and **4**) and behaves accordingly by polymerizing propylene to syndiotactic polypropylene after activation (cf. Figs. 11 and 12). The polymers it produces have higher molecular weights and broader polydispersities

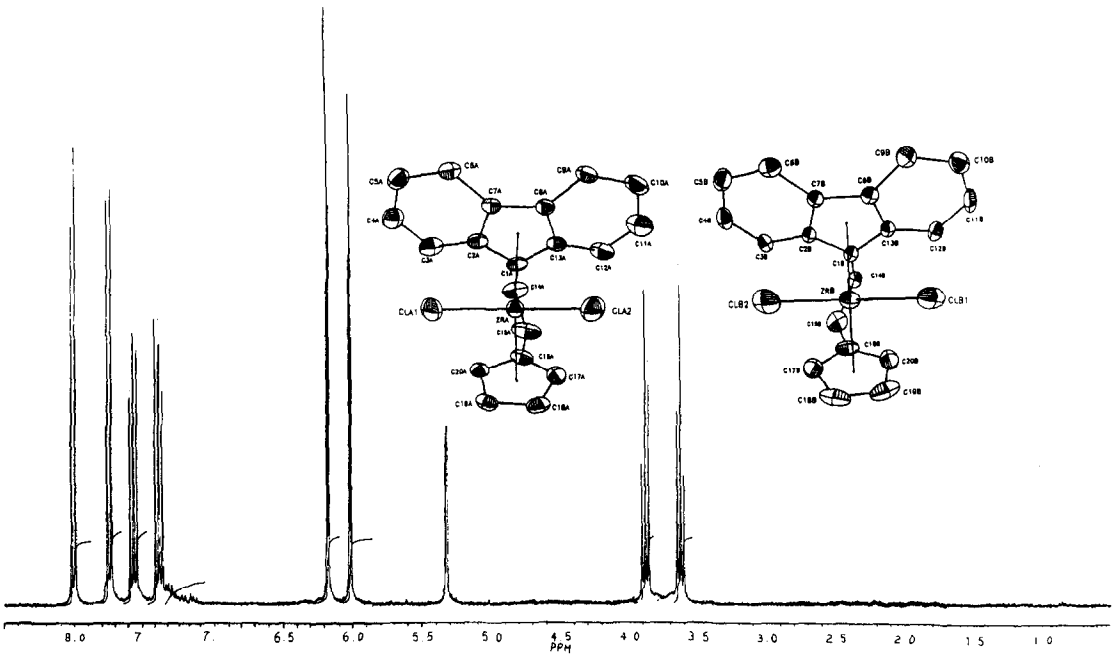


Fig. 10. ^{1}H NMR spectrum of **8** in CD_2Cl_2 (RT).

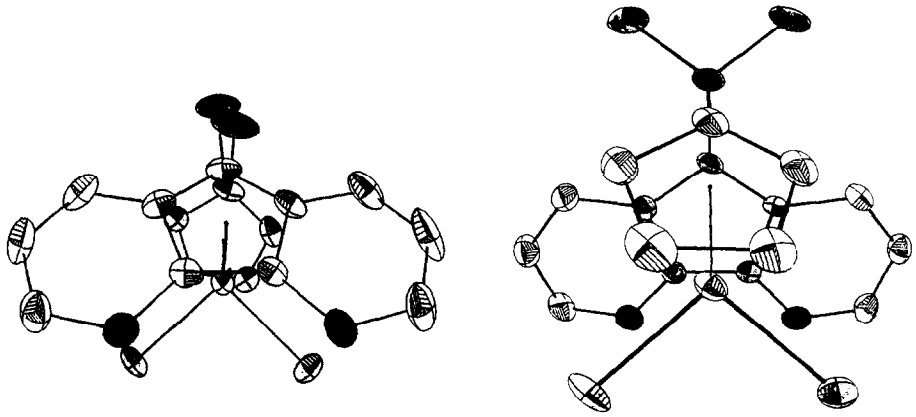
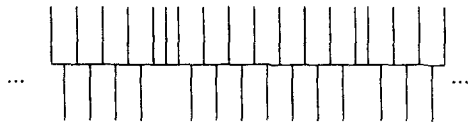


Fig. 11. Top view structural comparison of **9** and **2** exposing their bilateral symmetry and chirality.

though with somewhat lower stereoregularities (cf. Table 5a,b).



The general polymerization properties of **5** have been discussed already [7]. They will be highlighted here briefly to point out the geometric variations that are expected when the size (and flexibility) of the interannular bridge is adjusted, and to serve as a comparative example for the later introduced isospecific catalysts that have undergone identical ligand modification.

We begin the discussion of **5** with the explanation of the relatively large polydispersities (up to 4.7) observed for its polymers. It follows from the Shultz–Flory equation that for a single

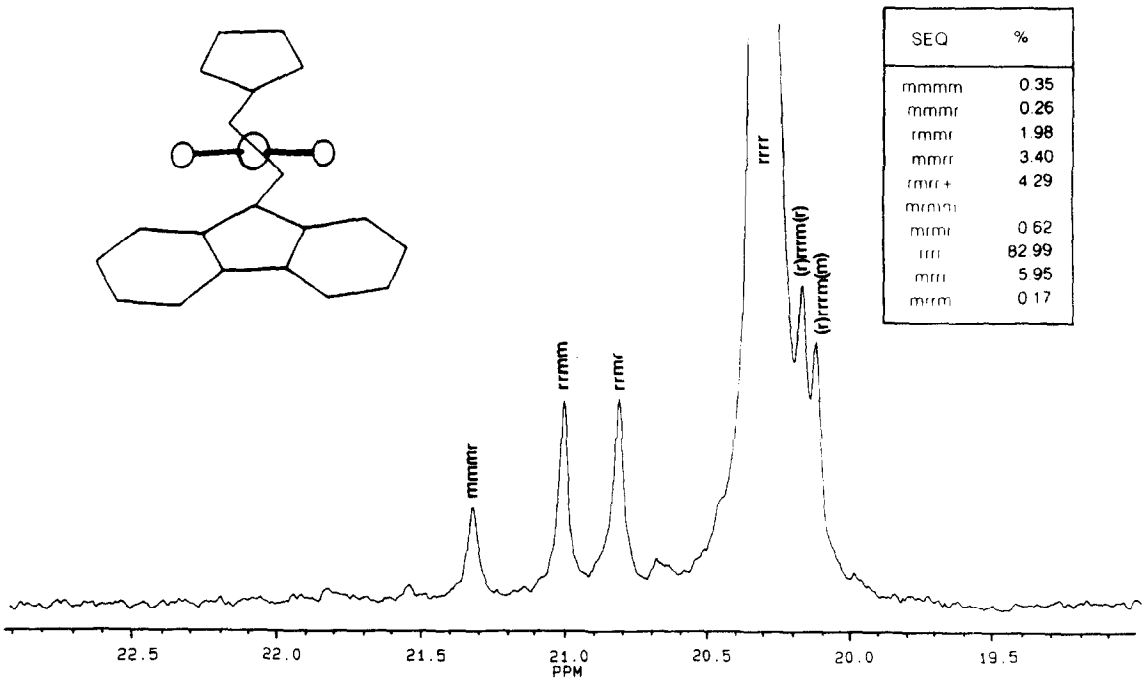


Fig. 12. ^{13}C NMR spectrum of the methyl region of sPP polymer produced with **5** at 40°C.

Table 5
(a) Polymerization conditions [a] and results with **5** compared with **2**

Cat	Pol. T (°C)	Act. (kg/g)	Mw ($\times 10^3$)	MWD	mp (°C)	rrrr (%)
5	40	35	248	3.4	125	82.99
5	60	50	171	3.6	111	74.31
2	40	120	138	1.8	140	85.99
2	60	180	90	2.1	137	81.16

(b) Variation of methyl pentad stereosequence intensity distributions with polymerization temperature for **5** and **2**

	Pol. T (°C)	rrrr(%)	rrmr(%)	rmmr(%)	mmmm(%)
5	40	82.99	4.29	1.98	0.35
5	60	74.31	6.91	2.48	0.40
2	40	85.99	2.93	1.55	0.00
2	60	81.16	2.70	1.65	0.00

site type catalyst the expected molecular weight distribution should have values around **2**. This has been observed generally for polymers produced in homogeneous catalysts with metallocenes. Large deviations from this value are indicative for the existence of more than one active species in the polymerization medium.

The inspection of the crystal structure of **5** has revealed that the unit cell of the crystal lattice accommodates two types of molecules, two conformers. The determined interatomic bond angles and distances of these conformers are different enough to be considered as two structurally different molecules. These conformers, as neutral molecules, interconvert very quickly in solution at room temperature (cf. Fig. 10) and are indistinguishable (from −80 to 90°C) in the NMR time scale. However, after the activation with MAO, the mobility of their cationic species will be severely restricted due to contact ion pairing between the zirconium alkyl cation and the MAO anion (Fig. 13) [8].

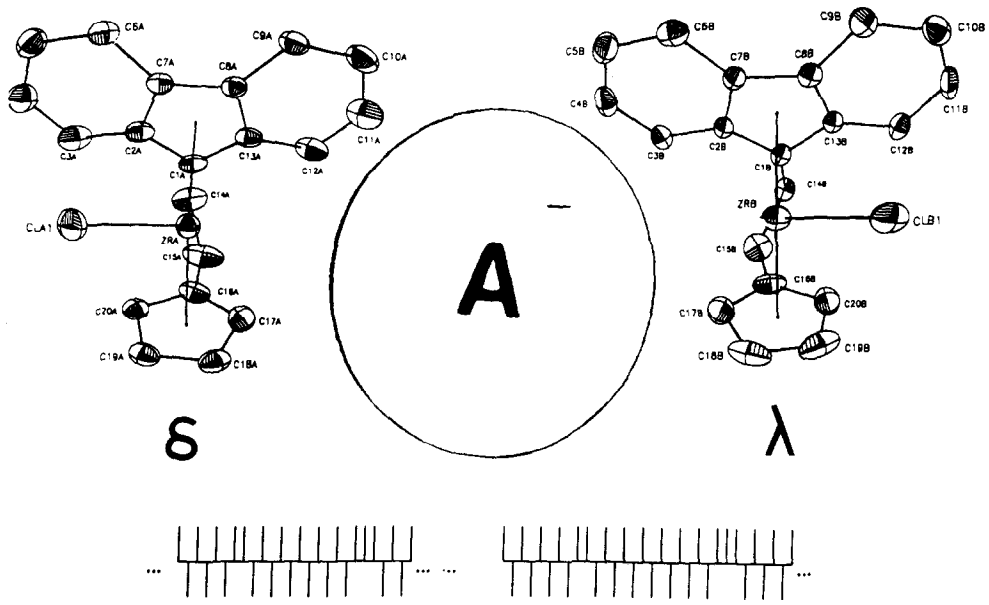
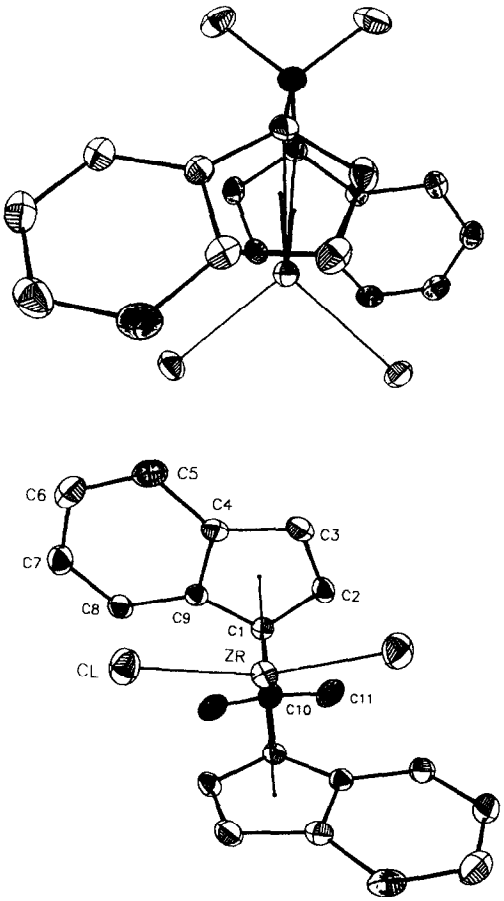


Fig. 13. Ion-paired cationic conformer produced with **9** and MAO.

These cationic conformational isomeric species have different receptibility towards agostic interactions and produce chains of different lengths. In this respect the catalytic system generated with **9** and MAO resembles very much a multi-site system. At temperatures above 40°C, however, the energy for overcoming the interconversion barrier is provided and the polydispersity begins to decrease as the number of active species decreases with the gradually increasing polymerization temperature. At 90°C the catalyst produces an amorphous polymer which contains large portion of atactic pentads.

For the formation of the longer polymer chains with lower stereoregularities with **5** the increase of cent–Zr–cent angle by several degrees is accountable. With two carbon atoms in the bridge the cyclopentadienyl and fluorenyl moieties are pushed further away, and adopt a more parallel position. Under these conditions more ligand coverage is provided for the coordination sites (Fig. 11). The increase of the cent–Zr–cent angle at the same time is accompanied by a change of the frontier orbital energies and hybridizations [9] (vide infra). Thus both from a steric and a valence orbital energetic point of view the approach and subsequent orbital overlap between chain end hydrides σ orbitals and transition metal orbitals for a proper agostic interaction (of any kind) will be less favored for the new catalyst. The lower probability of α-agostic interaction combined with increased structural flexibility of the catalyst framework explains the lower stereospecificity. The lower probability of β-agostic interaction (β-hydide elimination) results on the other hand in the formation of longer chains.



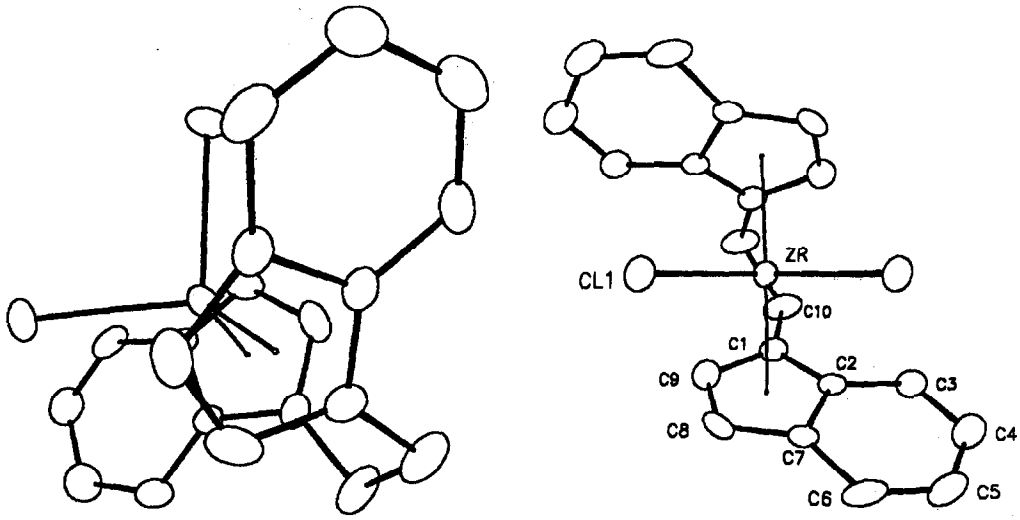
[(C9H6-μ-CMe2-C9H6)ZrCl2]

Fig. 14.

The increased steric crowding of the coordination positions with the ethano-bridged ligand is probably responsible for the difficulties encountered during the synthesis of the Hf analogue of **5**. Here again the smaller size and modified fragment orbital configuration of the Hf cation play a decisive role for the instability of the putative Hf complex.

2.4. *[Isopropylidene(bisindenyl)]MCl_2; M = Hf(6), Zr(7) (isopropylidene vs ethano bridge; aperture angle and activity)*

The replacement of the isopropylidene interannular bridge with an ethano bridge in syndiospecific catalysts **2**, as we saw, is accompanied with a decrease of stereospecificity of the catalyst as well as an increase of the molecular weight and molecular weight distribution of the syndiotactic polypropylene. It appeared intriguing to see how such a ligand modification (change from ethano-to isopropylidene bridge) would affect the stereospecificity of an isotactic



[(C9H6-μ-CH2CH2-C9H6)ZrCl2]

Fig. 15.

specific catalyst and its polymerization behavior. For this purpose the title complexes **6** and **7** have been prepared and their structures and polymerization behaviors have been compared with the corresponding data for Brintzinger type ethano bridge metallocenes [1,2-

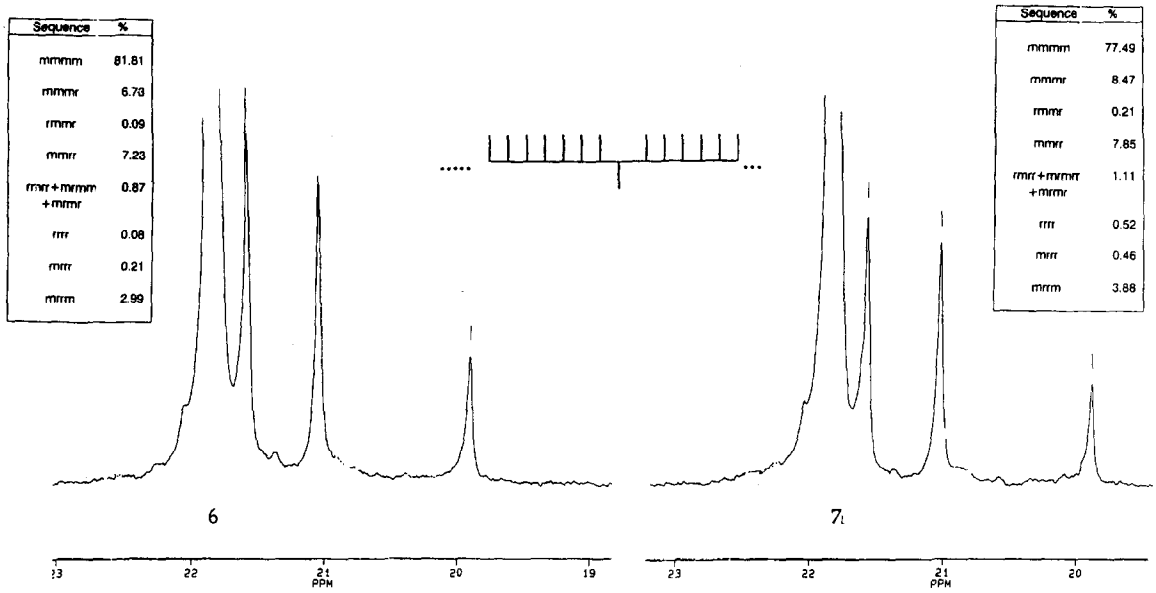


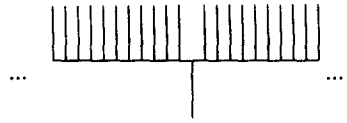
Fig. 16. Methyl region of the ^{13}C NMR spectra of IPP formed with **6** and **7** at 60°C.

Table 6
Polymerization conditions and results for **6** and **7** (top) compared with **6′** and **7′** (bottom)

Cat.	Poly. T (°C)	Act. (kg/g)	Mw ($\times 10^3$)	Mp (°C)	mmmm (%)
Zr	40	6	15	130	84.04
Zr	60	35	9	124	77.49
Hf	40	2	138	127	79.88
Hf	60	3	114	126	81.81
Zr	60	150	32	128	80.80
Hf	60	29	450	133	83.16

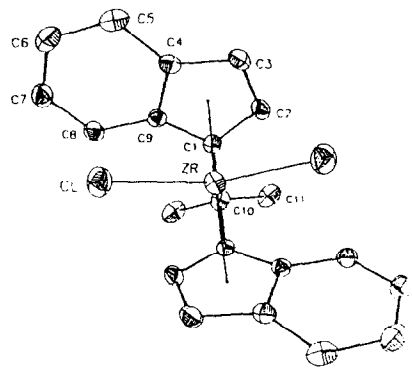
(bisindenyl)ethane]MCl_2, M = Hf(**6′**), Zr(**7′**) [10].

Compounds **6** and **7** exist both in racemic and meso form of which only the racemic isomers will be discussed here. They have been identified by their ^{1}H NMR spectra and the molecular structure of **7** determined by single crystal X-ray diffraction method (Fig. 14). The general symmetry of the metallocene **7** is similar to that of the corresponding ethano bridged complex **7′** whose molecular structure is portrayed in Fig. 15; hence it too produces isotactic polypropylene after its activation with MAO. Fig. 16 represents the ^{13}C NMR of the polymers produced with **6** and **7**.

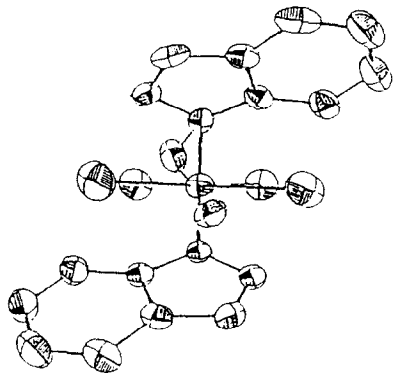


The microstructure of the polymer chain indicate that both polymers have been produced according to the enantiomorphic site stereochemical control mechanism. Table 6 shows the polymerization conditions and some polymer analyses for the two compounds. At the bottom of the table the corresponding data for the known ethano bridge complexes **6′** and **7′** are given. These data indicate that, as usual, for both systems the Hf sites produce higher molecular

Table 7
\Comparison of selected bond angles (degrees) and bond distances (Å) for **7** and **7′**



7



7′

M–Cl	2.428(1)	2.417(1)
M–C1	2.439(4)	2.498(6)
M–C2	2.453(4)	2.459(6)
M–C3	2.546(5)	2.530(5)
M–C4	2.614(4)	2.627(5)
M–C9	2.528(4)	2.569(5)
Ct–M–Ct	117.943	125.39
Cl–M–Cl	97.30(2)	98.58(2)

weight polymers and are slightly more stereospecific than the corresponding Zr sites. More interesting is, however, the comparison of the activities of the two catalysts systems, **6, 7** with **6′**, **7′** and the molecular weights of their polymers. As a general trend the activities and molecular weights of the polymers are much lower in the case of isopropylidene bridged **6** and **7** which contain like their ethylene bridged counter parts appreciable amount of 2-1 and 1-3 regioirregular placement in their backbone.

Table 7 compares the important bond angles and bond distances for **7** and corresponding ethano bridged **7′**. There is nothing unusual about the structures of the two molecules. Both molecules reside on the crystallographic two fold axis and have only one independent set of bond distances. The only important feature is the relatively large difference between their centroid–Zr–centroid angles with values of 117.94° for **7** about 7° smaller than the value of 125.39° found for **7′**. We believe it is this parameter which should be held responsible for the observed changes in the catalytic performance. The interannular bridge not only decreases the mobility of the aromatic rings (gliding across the fragment orbital surface) but can also, depending on its size, significantly influence the degree of the ring canting as well as orbital energies and hybridizations. The closing of the cent–Zr–cent angle in the dorsal part of the molecule necessitates an opening of the frontal aperture angle and constitutes a larger bite for the corresponding final catalyst.

With this ligand modification the active coordination sites are relieved partly from the steric encumbrance exerted by the distal substituents, and can undergo more easily both α- and β-agostic interactions due to favorable steric but also orbital energetic reasons. The decrease of the cent–Zr–cent angle reduces the energies of the fragment orbitals substantially [7,9], and the lower steric congestion around the propagating site allows a closer approach of the growing chain substituents. Thus the chances for an adequate overlap between the corresponding metal frontier orbitals and hydride σ-orbitals for both α and β-agostic exchange increases. The higher probability of β-agostic interaction is detrimental to formation of longer chains. On the other hand the effect of increased probability of α-agostic approach, which should theoretically increase the stereospecificity of the catalyst [11], has been apparently cancelled out by the decreased steric influence of the ligand and its lower directing influence on the conformation of the growing chain and monomer prochiral face selectivity.

Another surprising effect of this ligand modification is the unexpectedly lower activities of the isopropylidene catalyst both for propylene and ethylene polymerizations. It is not very clear why a simple alteration of the bridge, replacement of the ethano group by an isopropylidene group, one of the most active catalysts for ethylene and propylene polymerization, **7′**, is turned to a catalyst of poor activity. The identical alteration for syndiospecific catalysts had a much less dramatic effect in this respect (vide supra) [7]. Apparently this is another distinct particularity of the two systems indicating that probably something fundamentally different exists between mechanisms of syndiospecific and isospecific polymerization (we have already pointed out the difference between the regiospecificity of the two metallocene catalyst systems [7]). It is possible that beside stereoelectronic factors, different contact ion-pairing between metallocenium cations with MAO anion bare the responsibility for this behavior but the subject deserves a more in-depth investigation before any assertive statement can be made.

The phenomenon of formation of two conformers in solid state for the syndiospecific procatalyst, [1,2-(cyclopentadienylfluorenyl) ethane]$ZrCl_2$, **5** has not been detected for the isospecific counter part, [1,2-bis(indenyl)ethane]$ZrCl_2$, **7′**. The polymers' polydispersities indicate that even the formation of cationic contact ion pair after its activation has not been favoring the formation of two distinct conformational species. The interconversion energy bar-

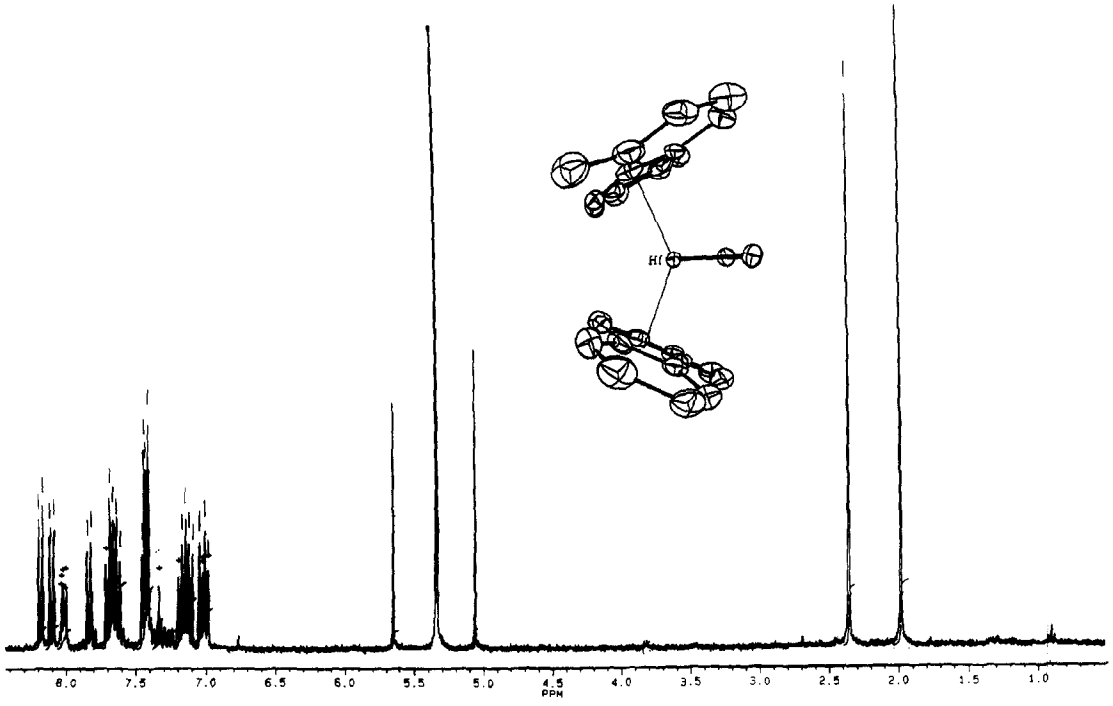


Fig. 17. ^{1}H NMR spectrum of 14(CD_2Cl_2 RT) showing the presence of two torsional isomers.

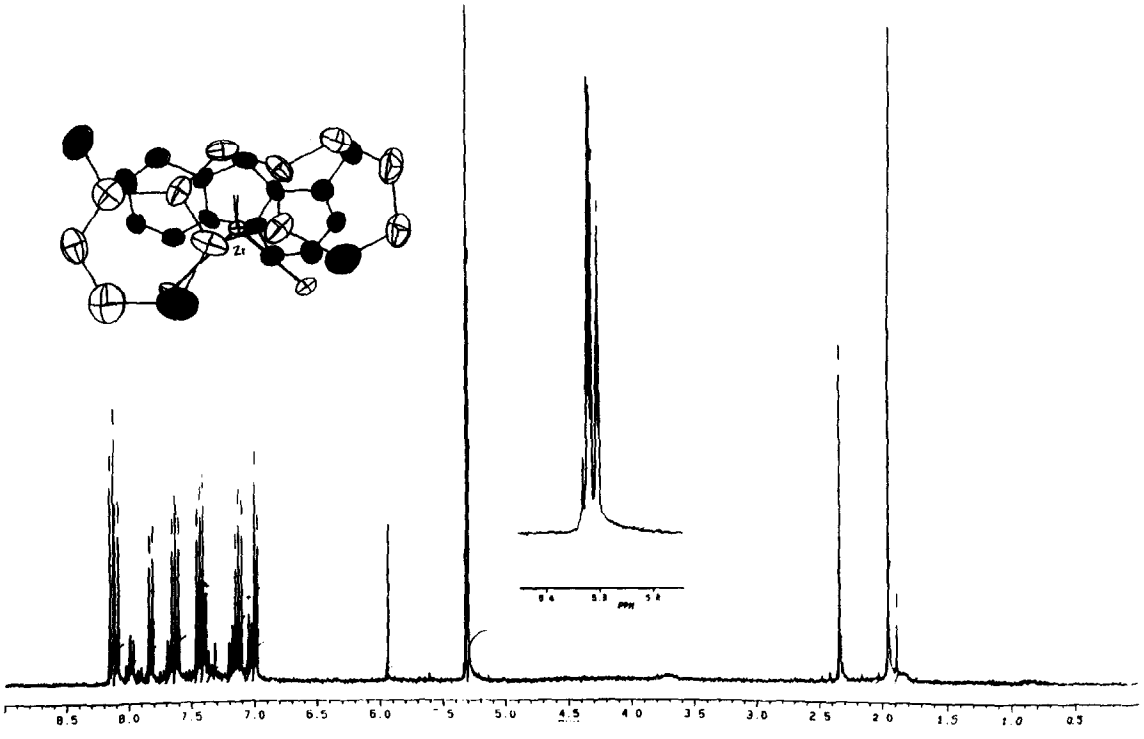


Fig. 18. ^{1}H NMR spectrum of 15(CD_2Cl_2 RT) showing the presence of two torsional isomers.

rier for the conformers of **7′** must therefore be very low. This difference between **5** and **7′** is most likely related to the balanced structure (two indenyls) and unbalanced structure (one cyclopentadienyl and one fluorenyl) of the aromatic moieties in their ligands.

2.5. Bis(1-Rfluorenyl)MCl_2; R = H, M = Hf(8), Zr(9) R = Me, M = Hf(10), Zr(11)

The synthesis and molecular structure of (fluorenyl)$_2$$ZrCl_2$, **9** had been reported in 1974 [12]. The application of a new synthetic procedure has enabled us to synthesize it and its hafnium analogue, **8** including their methyl substituted counterparts **10** and **11** in higher yields and purities. Under our polymerization conditions **8** and **9** did not show any activity for propylene polymerization. Towards ethylene polymerization the Zr complex is inactive yet the corresponding Hf analogue show tangible activity.

Metallocenes **10** and **11** whose identities were confirmed by single crystal X-ray diffraction methods and ^{1}H NMR spectroscopy (Figs. 17 and 18) exhibit similar behavior with respect to ethylene polymerizations, only Hf procatalyst **10** is active. Nevertheless, they show different behavior with respect to propylene polymerization. Both **10** and **11** (which exist as two torsional isomers cf. ^{1}H NMR!) produce ipp after activation with MAO however, the isotactic polypropylene produced with **10** has higher molecular weight and stereoregularity. The polymerization proceeds in both cases according to enantiomorphic site stereochemical control mechanism, and the stereochemistry of insertion is dictated by the chirality of the organometallic part of the catalyst imposed by the unique steric arrangement of the fluorenyl ligands framing the central transition metals [13].

The question of why the methyl substituted complexes **10** and **11** are active and isotactic specific for propylene polymerization has been answered satisfactorily [13] by employing torsional angle and steric arguments. It remains to discuss the activity of the hafnocenes **8** and **10** and the inactivity of the zirconocenes **9** and **11** toward ethylene polymerization. We have been reiterating all along the smaller size of Hf in hafnocene cations and its different electronic characteristics as being the source of its different catalytic behavior; we shall continue with this approach while admitting that the conclusion is more or less an empirical one.

By reviewing our own results and the literature data [14], it seems that the tighter the coordination space around the transition metal in metallocene based catalysts the more active they are for polymerization of ethylene rather than propylene. All open structure isopropylidene bridged metallocenes, including those reported in this manuscript, have much lower activities towards ethylene polymerization than those prepared with an ethano-bridged ligand with smaller aperture angles. It seems that for some orbital energetic reasons the narrower the labyrinth through which the monomer passes to reach the active site, the more active it becomes for polymerization of ethylene. A proper monomer coordination approaching angle and a more effective overlapping of the orbitals which is probably reached in such a case could be crucial, however, none can be unequivocally ascertained. Based on these empirical observations we can say that the smaller coordination sphere of the bisfluorenyl hafnium dichlorides (both substituted and unsubstituted) satisfy in this respect the conditions for ethylene activation.

2.6. The origin of the catalytic differences between Hf and Zr (lanthanoid contraction, relativistic effects, redox nobility, triplet instability)

The anomalous differences that have been noted for the catalytic behavior of Hf and Zr can be traced back to two basic phenomena operative on all heavy transition metal atoms starting from the post lanthanides in the sixth row of periodic table.

1. The introduction of 4f orbitals in the sixth

row and their gradual filling with fourteen electrons provides the third d-block transition elements with a 'transparent' ($4f^{14}$) subshell. As a result of the incomplete shielding of the nucleus by the electrons in 4f orbitals, the valence orbitals of these elements 'feel' a larger effective core charge and contract accordingly.

2. The very high positive charge accumulated on the nucleus of the heavy atoms substantially contracts the inner s orbitals. This forces the electrons to move at speeds comparable to the speed of light, creating relativistic effects which contract the remaining s (and to a lesser extent p) orbitals both inside and outside the d (and f) shells. Consequently, in these elements a more effective shielding of the nuclear charge from reaching the d electrons is attained. The d orbitals expand radially due to the weaker attraction forces and become energetically destabilized (increased radii and lower ionization potentials). The two phenomena, lanthanoid contraction and relativistic effects, act in a complementary way for the s (and p orbitals) and in a contradictory manner for the d (5d) orbitals (lanthanoid contraction, relativistic expansion!), though with different weights. The relativistic effects modify also the shape and spatial extensions of the orbitals. Thus, the hybridized orbitals (fragment orbitals!) formed from 6s and 5d have different energies and directionalities depending on the extent of their s and d character.

As a consequence, some minor differences between Hf, a transition element of the sixth row compared to Zr, an element above it, from the fifth period can be distinguished: Hf has slightly smaller atomic and ionic radii, forms stronger σ-bonds, and is more resistant to reduction. These differences do not manifest themselves in the general chemistry of the two elements and in most chemistry text books [15], only the cancelling out of 6th period's shell expansion by the lanthanoid contraction and the similar size and chemistry of Hf and Zr is mentioned. Few articles consider the relativistic effects when comparing these two elements. They too emphasize the opposing nature of the relativistic effects to lanthanoid contraction forces for the d orbitals and come more or less to the same conclusion [16].

We believe, however, that precisely these 'minor' differences are at the origin of the major differences that we have been observing for the catalytic properties of these two elements. Thus the exploitation of the distinct electronic characteristics underlying these effects can be very helpful for the rationalization of the differences in the catalytic behavior of their metallocene catalysts. The smaller size of the hafnium cation, confirmed by all X-ray diffraction data reported in this paper, combined with a more effective nuclear charge favors the formation of contact ion pairing. Furthermore the active coordination positions of the smaller Hf cation receive a more efficient ligand coverage and are sterically more crowded. Thus for both electrostatic and steric reasons effective on Hf, the lateral displacements of the chain is more hindered than in the case of Zr. For the syndiotactic specific catalysts that would mean of course a decrease in stereoregularity (formation of larger number of meso dyad stereodefects and isotactic sequences) as seen for syndiotactic polymers prepared with 1. For isospecific catalysts, however, the occasional restriction of the chain migration either has no bearing on the stereoregularity of the polymer or will improve it (cf. isotactic polymers formed with hafnium compounds **6** and **6′** with **7** and **7′**). Our assumption is that an 'unnecessary' chain migration can only be detrimental to isospecificity.

The much lower activities and higher molecular weights of the polymers prepared with hafnocenes **1**, **3**, **6** and **6′** compared to their zirconium counterparts **2**, **4**, **7** and **7′** have, as stated above, their origin in stronger Hf–C σ-bond involving fragment orbitals with larger participation of energetically stabilized 6s orbital. The stronger Hf–C bond slows down both bond making and bond breaking processes and results in lower activity and higher molecular weight. Additionally the spatially more ex-

panded and more diffuse frontier orbitals (basically formed from 5d atomic orbitals) provide a better overlapping probability for chain end hydrides with α-agostic tendencies favoring again the formation of longer chains with more electrophilic Hf centers. The assumption that different frontier orbital geometry and 'diffusivity' of Hf could have been partly the cause of the increase in molecular weight is best corroborated when the catalytic behaviors of the zirconocenes, **1** and **3**, are compared. The fact that the substitution of an isopropylidene with a diphenylmethylidene group in the bridge has provoked a four fold increase of the molecular weight strongly suggests that the perturbations of the frontier orbitals of the Zr cation in **3** (vide supra) have affected their geometry in such a way that has rendered these orbitals more accessible to an α- rather than a β-agostic exchange.

This interesting finding indicates that via proper modifications performed upon the ancillary aromatic ligand we may be able to manipulate the electron density and the valence orbital characteristics of the transition metal in such a way that its bonding relation to the remaining ligands (monomer and growing chain) becomes very similar to that of its heavier homologue, Hf. In this particular case, the frontier orbital energies, shapes and spatial extensions of Zr in zirconocene **3** apparently bear more resemblance to the corresponding frontier orbitals characteristic of Hf in hafnocene **1** than to those of Zr in zirconocene **2**. Thus it is not surprising when **1** and **3** produce syndiotactic polypropylene polymers with molecular weights of the same order of magnitude.

At the end of this chapter it is important that a brief discussion about the stability of different oxidation states for zirconocene and hafnocene is included. Under ordinary reducing condition, contrary to zirconocene and titanocene, it is not possible to reduce Hf(IV) in hafnocene dichloride to Hf(III) species. Attempts for producing it under similar reaction conditions e.g. with Mg/THF, or electrochemical methods have failed so far. At the origin of this 'redox nobility' is probably the lower kinetic stability of Hf(III), its smaller size, and its poorer ability to stabilize itself by undergoing coordinative solvatation. These properties on the other hand are related to lanthanoid contraction and relativistic effects which have a double contraction influence on 6s electrons (non-relativistic radius 2.153 Å, relativistic radius 1.955 Å [16]) leading to smaller radius and larger ionization potentials for $6s^2$ orbital ('inert pair'). Since oxidation state changes are important during catalytic processes in the transition states the catalytic particularities of hafnocenes are to a certain extent related to this redox nobility. As a matter of fact D'yachkovskii et al. [17] propose that the elongation of the Ti–C bond in the activated Ziegler–Natta catalysts during the metalcyclobutane formation leads to a charge separation and an effective reduction of the transition metal to oxidation state III. With this phenomenon which they call triplet instability an elegant explanation for the existing dilemma for explaining the contradiction between the high thermodynamic stability of the transition metal carbon bond and their high kinetic lability in olefin polymerization reactions is provided. According to their calculations of bond dissociation energy of the Ti–C bond in $TiCl_3CH_3$ by unlimited Hartree–Fock method the elongation of the M–C bond in the transition state during the bond dissociation/olefin insertion process results in rapid rearrangement of the transition metal electron structure. Electrons of the singlet couple of the M–C bond start to separate in space. One of the electrons is more localized on the carbon hybrid orbital and the other on the Ti d-orbital. This means, that the M–C bond, while remaining in the ground state, acquires triplet characteristics, and the M atom become effectively reduced. These results which have been confirmed recently by other research groups [18,19] can be with some modification extended to Zr and Hf carbon bond [20]. In the light of the triplet instability logic it appears obvious that due to the 'nonreducibility' of Hf(IV) to Hf(III) its catalytic activity should be much

lower because of significantly lower gain in bond activation.

3. Conclusion

A qualitative account has been given for the activities, stereospecifities and molecular weights which have been observed for hafnocenes and zirconocenes based catalysts and their corresponding polymers. These properties have been contrasted with the electronic characteristics of the metallocenes in static and dynamic states and the influence of the inherent electron configurational differences of Hf and Zr which stem from their position in the periodic table. The complementary and contradictory effects of the lanthanoid contraction and relativistic effects (contraction of s and expansion of d orbitals) and their influence on the ionization potentials and frontier orbital geometry and diffusivity, have been suggested as being the determining factors for the bond making and bond breaking processes. The ligands electronic effects and their mode of action in changing the electronic characteristics of the central transition metal and creation of Hf-like Zr sites by the example of the introduction of aromatic groups in the bridge have been discussed. The resulting change in the haptocity of the M–C5 fluorenyl bonding and orbital geometry and spatial directionality and their influence on the catalytic performance is delineated. The influence of the size of the interannular bridge on the alteration of the orbital energies and hybridization and their distinct influence on syndiospcific and isospecific system with respect to the catalytic activity toward ethylene and propylene, stereocecificity, molecular weight, molecular weight distribution, is elaborated. The influence of electron density surface topology and frontier orbital geometry difference as well as local Lewis acidity on the polymerization behavior of the new bisfluorenyl system is briefly indicated.

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