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Articles

Branching Formation in the Ethylene Polymerization with Meso Ansa Metallocene-Based Catalysts

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ABSTRACT: An investigation of the ethylene polymerization with meso ansa metallocenes of group 4 allows clarifying some aspects of the branching formation observed in the polyethylene produced with these catalysts. The meso structure of the zirconocene precursor is more effective in promoting the chain growing isomerization when indenyl ligands bear no substituents. But the same coordinating neighborhood when surrounding the Ti(IV) or Hf(IV) ion gives rise to complexes not effective in the ethyl-branched polyethylene synthesis. On the other hand, several activators in combination with *meso*-ethylenebis(1-indenyl)Zr$(CH_3)_2$ produce catalysts able to polymerize ethylene to ethyl-branched polyethylene. No difference has been detected in the amount of branches with respect to that observed with MAO-activated *meso*-ethylenebis(1-indenyl)$ZrCl_2$.

Introduction

The ability of the meso isomers of the ethylenebis(1-indenyl)zirconium dichloride and isopropylidenebis(1-indenyl)zirconium dichloride to promote the synthesis of branched polyethylene (LLDPE) in the ethylene polymerization has been recently disclosed.[1]

An isomerization mechanism involving β-hydrogen transfer from the growing chain to the incoming monomer followed by insertion of the unsaturated terminal into the formed ethyl−zirconium bond[1] could rationalize the significant formation of about 2 mol % ethyl branches, which are the only detected branching. Actually, the isomerization should take place when the growing chain is in the *inward* site, where, according to theoretical studies on similar systems,[2] the conformation suitable for the β-hydrogen transfer should be more populated (Scheme 1).

On the basis of this hypothesis, the branching mechanism should be more or less active depending on the constraints of the meso ligands environment.

Moreover, quaternary carbon centers can be generated when the *inward* site has more space at its disposal as is the case of *meso*-isopropylidenebis(1-indenyl)-zirconium dichloride.[1b] Such an unprecedented structural feature should be accounted by the reiteration of β-hydrogen transfer followed by insertion of the vinylidene terminal into the ethyl−zirconium bond. The complete picture of the ethylene polymerization with these systems includes a competition among three different pathways: skip to the *outward* site, insertion following the monomer coordination, and β-H transfer to the incoming monomer (Scheme 2).

It seems reasonable that even small differences in the features of the catalytic center could play a relevant role to direct this competition and so to determine the amount of branches. In the present paper we report the investigation of the behavior of some catalytic systems with respect to the branches formation in order to evaluate the effect of (a) the presence of substituents in the indenyl moieties of the zirconium complexes, (b) the coordinating strength of the counterion of the cationic catalytic center, and (c) the nature of the metal through the comparison among *meso*-ethylenebis(1-indenyl) complexes of group 4.

Results and Discussion

Influence of the Ligand Encumbrance on the Branches Formation. The zirconocene compounds reported in Figure 1 have structures resembling the previously described catalysts useful in the branched polyethylene synthesis.

They have been tested in the ethylene polymerization at different temperatures by using MAO as cocatalyst. In every case the products show a melting temperature around 135 °C (Table 1) and ^{13}C NMR spectra lacking evidence of branches, and so they can be safely considered HDPE's.

On the basis of the mechanism we proposed, the absence of branching could be related to the presence of methyl substituents or condensed aromatic rings on the indenyl ligands that, according to experimental[3] and theoretical[4] studies, seems to forbid β-H transfer to the coordinated monomer molecule. The results described herein and several other examples reported by Alt et al.[5] on the behavior of C_1 symmetric zirconocenes suggest that the mechanism of chain isomerization works in very few particular situations with the well-tailored coordination environment. Further examples of catalysts able to give ethyl-branched polyethylene have been recently reported by Wang and co-workers.[6] Also,

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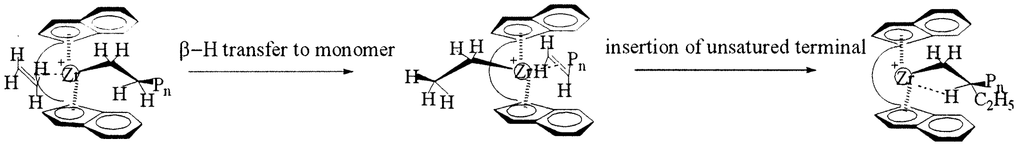
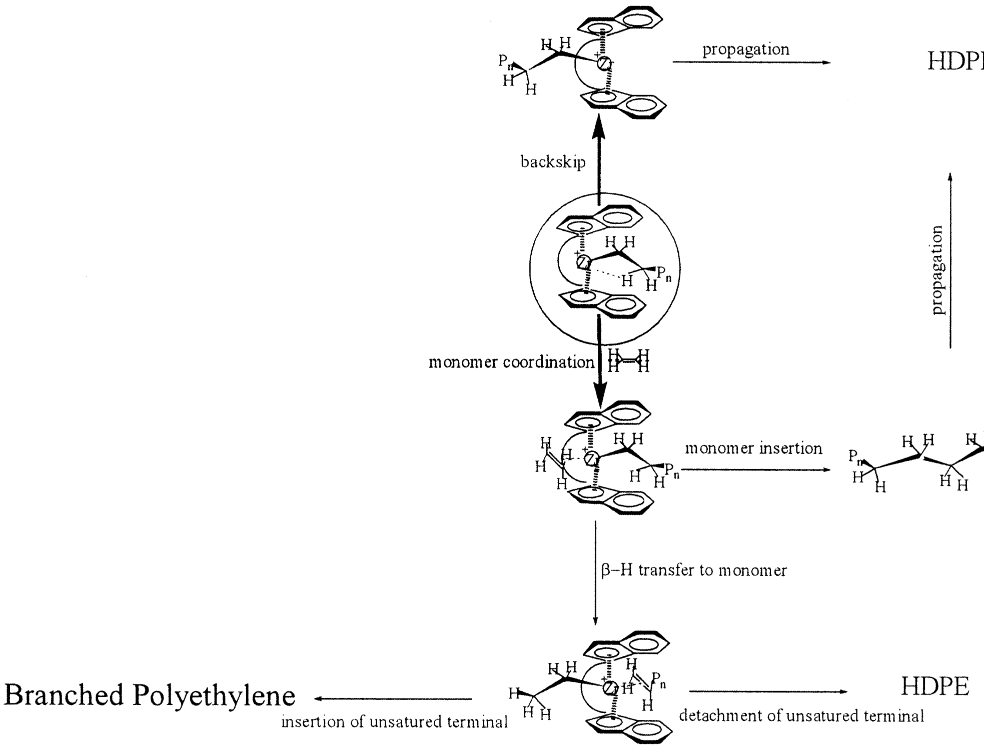
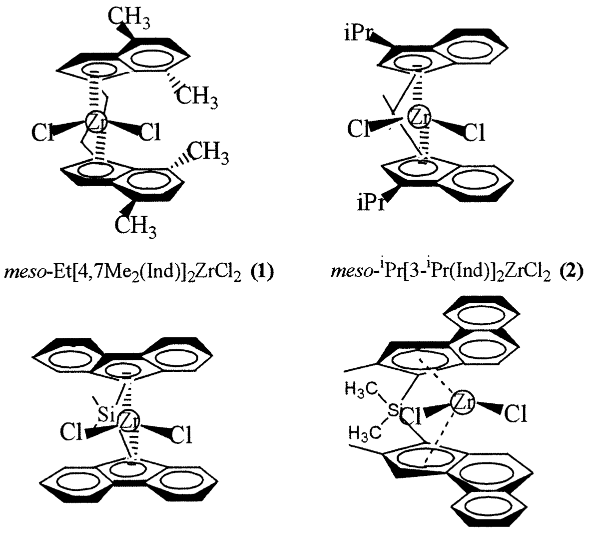
Scheme 1. Proposed Mechanism for the Formation of Ethyl Branches



Scheme 2. Competitive Pathways in the Ethylene Polymerization with *meso*-Zirconocene-Based Catalysts





meso-Et[4,7Me$_2$(Ind)]$_2$ZrCl$_2$ (**1**) *meso*-^{i}Pr[3-^{i}Pr(Ind)]$_2$ZrCl$_2$ (**2**)

Me$_2$Si(Flu)$_2$ZrCl$_2$ (**3**) *meso*-Me$_2$Si(2-Me-Benz[e]Ind)$_2$ZrCl$_2$ (**4**)

Figure 1. Substituted *meso*-zirconocenes used in ethylene polymerization.

in these cases the cyclopentadienyl and indenyl ligands bear no substituents. Such a circumstance seems mandatory for the occurrence of the chain growing isomerization.

Counterion Effect. It is well-known that the catalytic species of α-olefin polymerization derived from group 4 metallocene precursors is a 14-electron cation generated by mixing the metallocene dichloride with a large excess of methylalumoxane.

Table 1. Ethylene Polymerization Results as a Function of the Ligand Hindrance[a]

catalyst	run	*T* (°C)	T_m (°C)
1	1	20	133
2	2	20	133
3	3	20	133
4	4	20	135

[a] Using MAO as activator: Al/Zr = 1000, under 1 atm of ethylene, 25 mL of toluene.

The same cationic species can be generated through reaction between the metallocene dimethyl complex and a strong Lewis acid.[7] Following the latter route, it is possible to have counterions with different coordinative abilities toward the positively charged metal center.[8]

Recent observations suggest that the polymerization behavior and the properties of the polymeric products are significantly influenced by the nature of the "cation–anion" interaction. A relevant example is the effect of ion pairing strength on the stereocontrol in propylene polymerization in the presence of the syndiospecific catalysts based on [i-Pr(Cp)(fluorenyl)]ZrCl$_2$/MAO. Fink et al. observed the stereospecifity of this catalyst system strongly decreases with increasing dielectric constant of the polymerization medium.[9] More polar solvents weaken the ion pair interaction, and consequently the frequency of the growing chain skip to the unoccupied site increases. The effect of such a skip is the catalytic site isomerization and the stereoerror in the incoming monomer insertion. More recently, Marks and coworkers analyzed the behavior of the same cationic syndiospecific metal center when different anions work

Table 2. Ethylene Polymerization Results as a Function of Anion Structure[a]

run	catalyst[b]	cocatalyst	counteranion	T_{mp} (°C)	% branches[e]
5	*meso*-EBIZrCl$_2$	MAO[b]	MAOCl$^-$	121	1.1
6	*meso*-EBIZrCl$_2$	MMAO[c]	MMAOCl$^-$	123	1.1
7	*meso*-EBIZrMe$_2$	B(C$_6$F$_5$)$_3$[d]	MeB(C$_6$F$_5$)$_3{}^-$	123	1.2
8	*meso*-EBIZrMe$_2$	[Ph$_3$C][B(C$_6$F$_5$)$_4$][d]	B(C$_6$F$_5$)$_4{}^-$	121	1.4
9	*meso*-EBIZrMe$_2$	[Ph$_3$C][B(C$_6$F$_4$Si^{i}Pr$_3$)$_4$][d]	B(C$_6$F$_4$Si^{i}Pr$_3$)$_4{}^-$	121	1.4

[a] Under 1 atm of ethylene, T = 50 °C. [b] EBI = ethylenbis(1-indenyl). [c] Al/Zr = 1000, 25 mL of toluene. [d] 10 mL of toluene, 40 μmol of Al(i-Bu)$_3$. [e] Calculated according to ref 1a.

Table 3. Ethylene Polymerization Results with *meso*-EBIZrCl$_2$ + Indicated Cocatalysts as a Function of Different Solvents[a]

run	cocatalyst	counteranion	solvent	T (°C)	T_{mp} (°C)	% branches
10	MAO[b]	MAOCl$^-$	toluene	25	122	1.3
11	MAO[b]	MAOCl$^-$	CH$_2$Cl$_2$	25	124	1.5
12	MMAO[c]	MMAOCl$^-$	toluene	50	123	1.1
13	MMAO[c]	MMAOCl$^-$	heptane	50	123	1.1

[a] Under 1 atm of ethylene, Al/Zr = 1000, 25 mL of solvent.

as counterions.[10] The authors observed a wide range of stereoregularity for the different catalytic systems. In agreement with the findings of Fink, they argued that the more tightly bound anion should depress epimerization rates (chain skip) whereas in the presence of a loose ionic pair a considerable amount of stereoerrors occurs.

In light of the mechanism suggested for ethyl branches formation with *meso*-zirconocene-based catalysts, the coordination power of the counterion could play a role in driving the polymer growth toward the linear chain or the branched one. This should happen by influencing the back skip rate of the growing chain from the *inward* to the *outward* site. Aimed at obtaining experimental evidence about a possible relationship between the ionic pair strength and the branches formation, we have tested different activators in association with the *meso*-ethylenebis(1-indenyl)zirconium dimethyl or with the respective dichloride also changing the polarity of the solvent. The results are summarized in Tables 2 and 3.

On the basis of ^{13}C NMR data and calorimetric evidence, one can argue that the polyethylenes produced with the different catalysts are substantially similar, and in particular they contain similar amounts of branches. From a mechanistic point of view, these findings seem to indicate that with the examined catalysts the back skip rate of the growing chain is considerably lower than the propagation rate.[11]

NMR Experiments. The solution structure of *meso*-ethylenebis(1-indenyl)zirconium dimethyl has been determined by ^{1}H NMR. The ambient temperature spectrum in benzene-d_6 (Figure 2a) shows two remarkable quite distinct singlets for the diastereotopic methyl groups. The signal upfield (δ = −2.18 ppm) has been assigned to the methyl in the *inward* site and the other one (δ = 0.14 ppm) to that in the *outward* site.

Such an assignment arises from the comparison with the ^{1}H NMR chemical shift of some dimethylzirconocene compounds (Table 4). The shift to higher field of the methyl groups may be related to enhanced shielding owing to the magnetic field resulting from the aromatic ring current effect of the two π-indenyl ligands. Such an effect is particularly strong in the case of the methyl in the *inward* site of the meso complex.

The cationic C_1 species *meso*-ethylenebis(1-indenyl)-zirconium methyl has been generated by reaction of the dimethyl complex with B(C$_6$F$_5$)$_3$ and has been analyzed by ^{1}H NMR. The spectrum in benzene-d_6 is reported in Figure 2b. For characterization purposes the relevant resonances are the signals assigned to the methyl groups. They are the sharp peak at high field (−1.81 ppm) and the broad peak at δ = 0.41 ppm. The shape of this latter clearly denotes a quadrupolar coupling with the boron atom and can be safely assigned to the methyl group abstracted by the Lewis acid. Besides, the chemical shift value can be regarded as a measure of the anion−cation interaction strength. In fact, according to Brintzinger and co-workers[12] in contact ion pairs with a strong μ-Me coordination, the resonance of CH$_3$B-(C$_6$F$_5$)$_3{}^-$ appears at ca. δ = 0.1 ppm (as in Cp$_2$ZrCH$_3{}^+$B-(C$_6$F$_5$)$_3$CH$_3{}^-$) while signals at δ = 1.3−1.4 ppm are found when there is a loose ion pair.

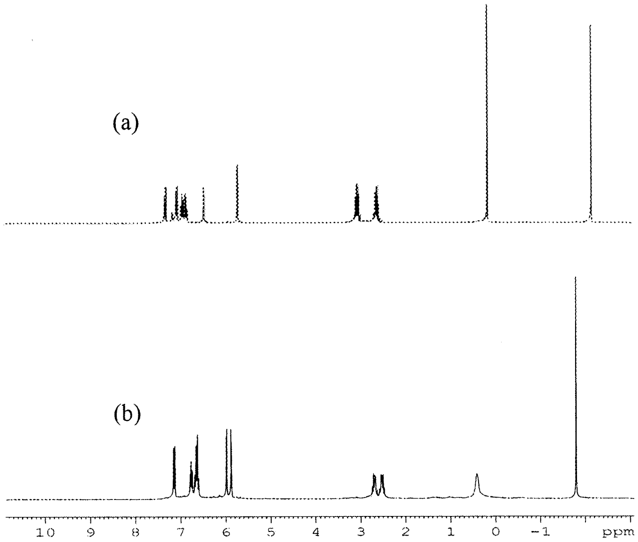


Figure 2. ^{1}H NMR spectra of (a) *meso*-EBIZr(CH$_3$)$_2$ and (b) *meso*-EBIZrCH$_3{}^+$B(C$_6$F$_5$)$_3$CH$_3{}^-$.

Table 4. ^{1}H NMR Data for L$_2$Zr(CH$_3$)$_2$ in C$_6$D$_6$ at 25 °C

complex	$\delta_{\mathrm{Zr-CH_3}}$ (ppm)	ref
Cp$_2$Zr Me$_2$	−0.12	13
rac-EBIZrMe$_2$	−0.96	14
meso- EBIZrMe$_2$	−2.18	this work

The chemical shift of the sharp signal at δ = −1.81 ppm seems to indicate the *inward* placement of this methyl group, and consequently the abstraction by B(C$_6$F$_5$)$_3$ is made on the *outward* methyl group. It seems reasonable that the polymerization occurs through the olefin separated ion pair.

The Nature of the Catalytic Metal. Ansa-metallocene derivatives of all the metals of group 4 are able to polymerize ethylene and α-olefin. We have synthesized and tested in polymerization the *meso*-ethylenebis-(1-indenyl) dichloride complexes of titanium and hafnium in order to compare their ability to give branched polyethylene when activated by methylalumoxane. The synthesis of the *meso*-hafnium complex has been carried

Table 5. Ethylene Polymerization Results as a Function of the Group 4 Metals[a]

run	catalyst	P_{ethylene}[b] (atm)	C_{ethylene} (mol/L)	T_{mp} (°C)	$M_v \times 10^{-3}$
14	*meso*-EBIZrCl$_2$	1	0.14	121	22
15	*meso*-EBIHfCl$_2$	1	0.14	132	186
16	*meso*-EBITiCl$_2$	1	0.14	131	87
17	*meso*-EBITiCl$_2$	3.8	0.61	133	270
18	*meso*-EBITiCl$_2$	6	1.03	136	610
19	*meso*-EBIHfCl$_2$	2.2	0.34	133	212
20	*meso*-EBIHfCl$_2$	3.8	0.61	132	224
21	*meso*-EBIHfCl$_2$	4.9	0.82	130	175
22	*meso*-EBIHfCl$_2$	6	1.03	134	270

[a] Using MAO as activator: Al/Zr = 1000, toluene = 30 mL for the runs under 1 atm of monomer and 80 mL for the other runs. [b] Total pressure: correction for vapor pressure of toluene $p(C_2H_4) = p - 0.12$ (atm).

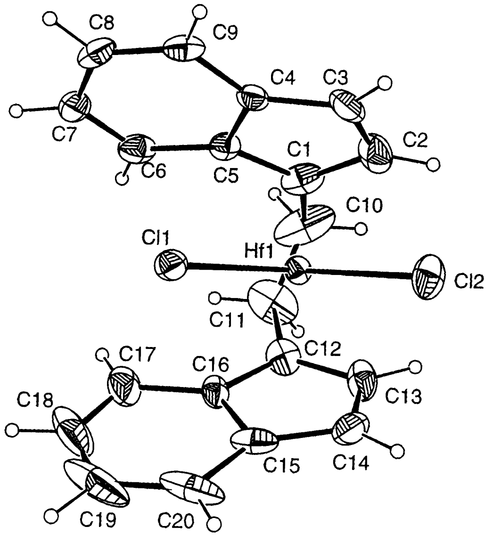


Figure 3. X-ray molecular structure of *meso*-EBIHfCl$_2$. Thermal ellipsoids are drawn at the 20% probability level.

Table 6. Selected Geometric Parameters for *meso*-EBIHfCl$_2$ and *meso*-EBIZrCl$_2$[a]

meso-EBIHfCl$_2$		*meso*-EBIZrCl$_2$	
Hf(1)−Cl(1)	2.379(2)	Zr(1)−Cl(1)	2.3968(8)
Hf(1)−Cl(2)	2.427(2)	Zr(1)−Cl(2)	2.4551(8)
Hf(1)−Cp	2.214	Zr(1)−Cp	
Hf(1)−Cp′	2.209	Zr(1)−Cp′	
Cl(1)−Hf(1)−Cl(2)	96.74(9)	Cl(1)−Zr(1)−Cl(2)	97.62(3)
Cp−Hf−Cp′	126.9	Cp−Zr−Cp′	126.2(1)
Cp−Hf−Cl(1)	105.5	Cp−Zr−Cl(1)	106.0(1)
Cp−Hf−Cl(2)	107.5	Cp−Zr−Cl(2)	107.8(1)
Cp′−Hf−Cl(1)	108.3	Cp′−Zr−Cl(1)	107.0(1)
Cp′−Hf−Cl(2)	107.7	Cp′−Zr−Cl(2)	108.6(1)
Rmsd(In)	0.031		
Rmsd(In′)	0.021		
In/In′	61.9(3)	In$\wedge$In′	62.3(1)

[a] Bond lengths are expressed in Å and angles in deg. Cp and Cp′ define the ring centroid respectively for C(1)−C5 and C(12)−C(16) five-atom carbon rings. In and In′ indicate the least-squares planes respectively between the C(1)−C(9) and C(12)−C(20) indenyl moieties.

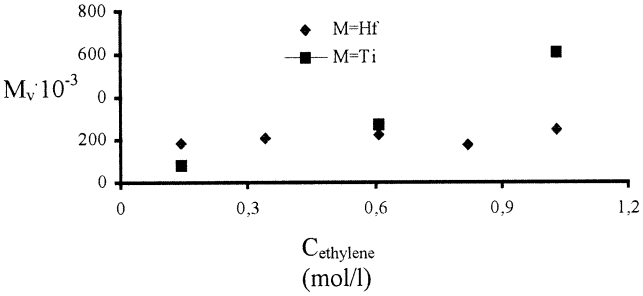


Figure 4. Viscosimetric molecular weights of polyethylene produced by *meso*-EBIMCl$_2$/MAO as a function of monomer concentration.

out via the reaction between HfCl$_4$ and the *syn*-3-trimethylsilyl derivative of the ethylenebis(1-indenyl) ligand, according to the procedure described by Nifant'ev et al.[15] Such a synthetic route was unsuccessful for the titanium analogue, for which we adopted the chromatographic method described by Brintzinger et al.[16] to separate the meso−racemic mixture. The ethylene polymerization in the presence of the above complexes activated by methylalumoxane produces polyethylene with high melting temperature (>130 °C) in whose ^{13}C NMR spectra the pattern of resonances of the branches are not detectable (Table 5). One can safely state that in the presence of these two catalytic systems the usual linear polyethylene is obtained as expected for the most metallocene catalysts. These results, however, contrast sharply with the formation of ethyl branches in the ethylene polymerization carried out in the presence of *meso*-zirconocene-based catalysts previously reported. The different behavior among these meso group 4 metallocenes is surprising all the more that their geometric features are very similar, in particular with regard to the zirconium and the hafnium one.

The X-ray molecular structure of *meso*-ethylenebis(1-indenyl)hafnium dichloride is shown in Figure 3, and the corresponding selected interatomic distances and angles are reported in Table 6. The compound is isostructural and isomorphous with the Zr analogue[17] as a consequence of the 4f lanthanide contraction; the Hf−ring centroid distance and Hf−Cl bond length are shorter than the Zr compound. In Table 6 also the structural parameters of the Zr compound are listed for comparison. A conformational disorder problem, already observed in the Zr compound, together with the heavier atom effect explains the limited accuracy of the final structure.

The substantial structural identity between zirconium and hafnium complexes suggests that only the metal center should influence the reactive sequence that gives the branches. In this case electronic instead than geometric effects have to be invoked. The comparison with the analogue titanium complex is not possible due to the difficulty to obtain crystals suitable for X-ray analysis.

Experimental arguments for the rationalization of the different behavior can be drawn from the analysis of molecular weights of polyethylene obtained at different monomer concentration (Figure 4).

For the polymer produced with titanium complex one observes an increase of the molecular weight with increasing the monomer concentration, as can be expected if β-H transfer from the growing chain to the metal center is the dominant chain termination. Obviously, on the basis of the reported mechanism, such a chain termination cannot give rise to ethyl branches formation.

On the other hand, the monomer concentration has only a little influence on the molecular weight of polymers obtained in the presence of the hafnium-based catalyst. This fact suggests that the chain termination occurs mainly by β-H transfer to the coordinated monomer molecule, but more rarely than for the analogue zirconium-based catalyst, as shown by the comparison of the molecular weight of polymers produced by these two catalytic systems.

Conclusions

The results of this study seem to show that the meso structure of the metallocene catalyst precursor is not a sufficient feature to obtain branched polyethylene. In fact, the meso systems bearing alkyl or aromatic substituents in the indenyl ligands tested in the present work are not able to produce branched polyethylene. Moreover, *meso*-ethylenebis(1-indenyl)hafnium dichloride and *meso*-ethylenebis(1-indenyl)titanium dichloride unlike the analogue zirconium-based catalyst produce linear polyethylene. We have rationalized these findings, suggesting a decrease of the rate of β-H transfer to the coordinated monomer, which, in agreement to the proposed mechanism, is necessary to give the ethyl branches.

The cationic species *meso*-ethylenebis(1-indenyl)zirconium methyl, active in branched polyethylene production, has been generated through the reaction with different activator. The branches amount is substantially independent of the nature of the counterion. This fact suggests that the ion pair interaction strength does not have an influence on the chain growing isomerization.

Experimental Section

All manipulations involving air-sensitive reagents and materials were carried out under nitrogen or argon atmosphere using Schlenk or drybox techniques. Solvents were dried over Na−diphenylketyl (toluene, light petroleum ether, heptane, THF), over $LiAlH_4$ (diethyl ether), and over CaH_2 (dichloromethane) and distilled before use. Deuterated solvents were dried by storage over activated molecular sieves 4 Å. 1,2-Bis-(3-indenyl)ethane,[18] *syn*-[3-trimethylsilyl(1-indenyl)] ethane,[15] *meso*-C_2H_4(4,7-dimethyl-1-indenyl)$_2$$ZrCl_2$,[15] *meso*-$Me_2C$(3-^{i}Pr-1-indenyl)$_2$$ZrCl_2$,[19] Me_2Si(fluorenyl)$_2$$ZrCl_2$,[20] *meso*-$C_2H_4$(1-indenyl)$_2$$TiCl_2$,[16] $B(C_6F_5)_3$,[21] $[Ph_3C][B(C_6F_4Si^iPr_3)_4]$,[8a] and $[Ph_3C][B(C_6F_5)_4]$[22] were synthesized according to literature procedures; *meso*-Me_2Si(2-Me-benz[*e*]indenyl)$_2$$ZrCl_2$ was purchased from Mcat. MAO was purchased from Witco as a 10 wt % solution in toluene; before use, the volatile components were removed in a vacuum to yield a powdery solid. MMAO was purchased from Akzo Nobel as a 7 wt % solution in heptane and used as received. Polymerization grade ethylene was purchased from SON and further purified by bubbling through a 5 mol % xylene solution of Al^iBu_3.

Synthesis of *meso*-C_2H_4(1-indenyl)$_2$$ZrCl_2$. 0.64 g (1.6 mmol) of *syn*-[3-trimethylsilyl(1-indenyl)] ethane was dissolved in 10 mL of CH_2Cl_2 and added to a suspension of 0.372 g (1.6 mmol) of $ZrCl_4$ in 15 mL of CH_2Cl_2. The mixture was heated until reflux for 6 h. The solvent was removed, and the residue was recrystallized from anhydrous THF (0.493 g, yield = 75%). The complex was identified by ^{1}H NMR.[17]

Synthesis of *meso*-C_2H_4(1-indenyl)$_2$$Zr(CH_3)_2$. 0.443 g (1.1 mmol) was suspended in 25 mL of diethyl ether. The reaction mixture was cooled at −78 °C, and 0.049 g of solid and ether-free CH_3Li was added. After 30 min the mixture was slowly warmed to room temperature and stirred for further 4 h. Then the solvent was removed under reduced pressure and the residue extracted with 30 mL of anhydrous toluene. Concentration of the extract followed by cooling to −20 °C gave 0.100 g (yield = 28%) of a pure yellow crystalline product, identified by ^{1}H NMR.

^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 7.33 (d, 2H), δ 7.08 (d, 2H), δ 6.95 (t, 2H), δ 6.88 (t, 2H), δ 6.46 (d, 2H), δ 5.71 (d, 2H), δ 3.06−3.01 (m, 2H), δ 2.64−2.60 (m, 2H), δ 0.14 (s, 3H), δ -2.18 (s, 3H).

Formation of Species *meso*-C_2H_4(1-indenyl)$_2$$ZrCH_3^+B(C_6F_5)_3CH_3^-$. In a NMR tube 1 equiv of solid $B(C_6F_5)_3$ was added to a benzene-d_6 solution of 10 mg of the dimethyl complex.

^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 7.16 (d, 2H), δ 6.77 (t, 3H), δ 6.64 (m, 3H), δ 5.99 (d, 2H), δ 5.89 (d, 2H), δ 2.72−2.67 (m, 2H), δ 2.55−2.50 (m, 2H), δ 0.41 (br, 3H), δ -1.81 (s, 3H).

Synthesis of *meso*-C_2H_4(1-indenyl)$_2$$HfCl_2$. 1 g of *syn*-[3-trimethylsilyl(1-indenyl)]ethane (2.5 mmol) was dissolved in 15 mL of toluene and added to a suspension of 0.9 g (2.8 mmol) of $HfCl_4$ in 10 mL of toluene. The red reaction mixture was kept at 60 °C overnight. The toluene was evaporated under reduced pressure, and the residue was dissolved in 40 mL of anhydrous THF. The yellow solution was concentrated in a vacuum to about 10 mL and stored at −20 °C. The pure complex was recovered as yellow-orange crystals (yield = 0.498 g, 42%) identified by ^{1}H NMR and characterized by X-ray diffraction.

^{1}H NMR (C_6D_6, 25 °C, 400 MHz): δ 7.35 (d, 2H), δ 7.01 (d, 2H), δ 6.86 (t, 2H), δ 6.73 (t, 2H), δ 6.51 (d, 2H), δ 5.80 (d, 2H), δ 3.33−3.27 (m, 2H), δ 2.90−2.85 (m, 2H).

Ethylene Polymerization. The polymerization runs 1−6 and 10−16 were carried out in a 100 mL glass flask equipped with a magnetic stirrer. Toluene and MAO were added sequentially, the flask was evacuated and filled with ethylene, and finally 8 μmol of catalyst was added. For the polymerization runs 7−9 in a 100 mL glass flask were added toluene and triisobutylaluminum, the flask was saturated with ethylene, and 8 μmol of catalyst and 1 equiv of activator were added. The amounts of the solvents, the cocatalysts, the scavenger Al(i-Bu)$_3$, and the polymerization temperature are reported in the table notes. The polymerization runs 17−22 were carried out in a 250 mL, stirred, glass autoclave, which was thermostated at 50 °C and then charged with a toluene (80 mL) solution containing catalyst (8 μmol) and MAO dried. Ethylene was fed continuously in order to keep constant the pressure. The polymerization mixture was poured into acidified ethanol. The quenched polymer was recovered by filtration and dried under reduced pressure at 80 °C.

Polymer Analysis. ^{13}C NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz. The samples were prepared by dissolving 25 mg of polymer into 0.5 mL of 1,1,2,2-tetrachlorodideuterioethane. The spectra were recorded at 120 °C using hexamethyldisiloxane (HMDS) as an internal chemical shift reference.

Melting point were measured using a Du Pont 2920 DSC calorimeter with a heating rate of 10 °C/min^{-1}.

The samples for viscosimetric analysis were prepared dissolving 10 mg of polymer in 10 mL of decahydronaphthalene at 135 °C. The viscosity-average molecular weight was obtained using the Mark−Houwink equation $[\eta] = kM^{\alpha}$ with $k = 67.7 \times 10^{-5}$ dL/g and $\alpha = 0.67$.

X-ray Crystallography. A suitable crystal of *meso*-C_2H_4(1-indenyl)$_2$$HfCl_2$ (0.2 × 0.4 × 0.6 mm) was selected and sealed in a Lindemann capillary under a nitrogen atmosphere. Diffraction measurements were performed at room temperature on a Rigaku AFC7S diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.710\,69$ Å). An empirical absorption correction based on azimuthal scans of several reflections was applied.

The structure was solved by means of heavy atom method, expanded by Fourier techniques and refined on F^2 using all reflections by means of SHELX97.[23] Hydrogen atoms were positioned geometrically and refined using a riding model. Anisotropic thermal factors were used for all non-hydrogen atoms. A total of 208 refinable parameters were finally considered. Maximum and minimum residual density were respectively 2.91 and −1.50 eÅ^{-3}; these are both located very near to the Hf atom. Final disagreement indices: $R = 0.039$ for 2702 reflections with $F > 4\sigma_F$, $_wR_2 = 0.118$ for 4978 reflections.

The indenyl moiety is affected by disorder effects as results both from the large displacement parameters of the C atoms and the unreasonably short C10−C11 bond distance (1.34(2) Å). A structural model containing two possible ligand conformers has been refined with no successful result. A restrained least-squares procedure has been attempted, imposing that chemically equivalent bonds have equal bond distances within 0.01 standard deviations, but no sensible improvement has been obtained. Interestingly, the same disorder effects are observed in the Zr analogue, and the shapes of the thermal ellipsoids are similar.

Experimental details and full lists of atomic coordinates, anisotropic displacement parameters, bond lengths, and angles are provided as Supporting Information. ORTEP drawings performed by means of the program ORTEP32.[24]

Crystallographic Data. Formula: Hf Cl_2 C_{20} H_{16}, FW = 505.74, system: monoclinic, space group $P2_1/n$, $Z = 4$, a = 11.128(4) Å, b = 10.440(2) Å, c = 14.941(2) Å, β = 100.49(2)°, V = 1706.8(7) Å^3, D_x = 1.97 g cm^{-3}, μ_{calc} = 64.20 cm^{-1}.

For comparison, the crystallographic data of the Zr analogue[17] are a = 11.119(3) Å, b = 10.467(1) Å, c = 14.949(2) Å, β = 100.94(2)°, V = 1708(1) Å^3, space group $P2_1/n$, Z = 4, 4.

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Supporting Information Available: Tables of X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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