Regiochemistry of the Styrene Insertion with CH_2-Bridged *ansa*-Zirconocene-Based Catalysts

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ABSTRACT: Methylenebis(indenyl)zirconium dichloride substituted in C(3), activated by methylalumoxane, is able to give polystyrene and ethylene−styrene copolymers. In this study hydrooligomers, whose structure, determined by ^{13}C NMR and GC-MS techniques, gives information about the regiochemistry and the stereochemistry of styrene insertion, have been purposefully prepared. The regiochemistry of the styrene insertion is related to the encumbrance of substituents in C(3). *rac*-[Methylene-(3-R-1-indenyl)$_2$]$ZrCl_2$ with R = H, CH_3, or CH_2CH_3 induces a prevailingly secondary styrene insertion into the zirconium−carbon bond. With increasing the substituent's steric hindrance (R = $CH(CH_3)_2$), regiochemistry inversion occurs and the primary insertion becomes prevailing. The analysis of ethylene−styrene copolymers obtained in the presence of the different catalysts allows confirming the correlation between regiochemistry and comonomers' reactivity. Besides, also the stereospecificity can be evaluated from the structure of the hydrotrimers, when the insertion is primary. Whereas the isospecificity in the absence of substituents (secondary insertion) and in the presence of the *tert*-butyl substituent (primary insertion) is well-known, a surprising syndiospecificity is observed when the indenyl ligand bears the isopropyl substituent in C(3).

Introduction

The traditional Ziegler−Natta[1] catalysts as well as several more recent homogeneous catalysts promote styrene polyinsertion to give stereoregular polymers.[2,3] Some aspects of the styrene behavior are peculiar with respect to that of olefinic monomers. Whereas styrene insertion with $\delta TiCl_3/Al(^{13}CH_3)_3$ seems to follow the general primary regiochemistry of 1-alkenes,[4] experimental evidence supports a secondary regiochemistry of insertion (that is, the formation of the zirconium−benzylydene bond) in the presence of most C_2 and C_s symmetry zirconocenes.[5]

Evidence of a secondary styrene regiochemistry has also been reported by Rodewald and Jordan[6] in the study of the styrene monoinsertion with cationic zirconocene compounds. The same regiochemical behavior was found in 1987 by Pellecchia et al.[7] both by analyzing chain end groups of a syndiotactic polystyrene (s-PS) sample prepared with $Ti(CH_2C_6H_5)_4/MAO/Al(^{13}CH_2CH_3)_3$ and by isolating low molecular weight s-PS samples where the presence of $-CH(C_6H_5)CH_3$ and $CH(C_6H_5)=CH-$ end groups in equal amounts indicates the secondary insertion in both the initiation and termination steps.[8]

Ethylene−styrene copolymers obtained with [(methyl)(phenyl)methylene(1-cyclopentadienyl)(9-fluorenyl)]-$ZrCl_2/MAO/Al(^{13}CH_3)_3$ showed the prevailing secondary insertion of the aromatic monomer at least in the initiation step.[5a] Moreover, a study on the microstructure of propene−ethylene−styrene copolymers, obtained with C_2 and C_s zirconocene-based catalysts, suggests the secondary styrene insertion also in the propagation steps.[5b]

In contrast with this picture, recently in our laboratory was observed the behavior of *rac*-[methylene(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$ activated by methylalumoxane (MAO) in the polymerization and copolymerization of styrene.[9] As a matter of fact, the polystyrene obtained at different polymerization temperatures has isotactic microstructure, and the chain ends arising from initiation and termination steps indicate a prevailingly primary insertion. The presence of 3-*tert*-butyl substituents in indenyl ligands was invoked as responsible for this unusual styrene regiochemistry. In the ethylene−styrene copolymerization the formation of blockwise structure instead of the alternating or "pseudorandom" structure, generally obtained with *ansa*-zirconocene-based catalysts, could be explained as consequence of this regiochemistry.

In the present paper we report on the regiochemical behavior of styrene in the presence of methylene-bridged catalysts with different substituents in C(3) of the indenyl ligands.

Moreover, ethylene−styrene copolymerizations were performed in the presence of the same catalysts in order to evaluate the possible correlation between regiochemistry and comonomers reactivity ratio.

Results and Discussion

Catalysts Syntheses. The *ansa*-zirconocene complexes *rac*-[methylene(3-R-1-indenyl)$_2$]$ZrCl_2$ (Chart 1) were prepared as reported in the literature[10] (R = H, $CH(CH_3)_2$, $C(CH_3)_3$) or following Scheme 1 in the case of not previously described compounds (R = CH_3, CH_2CH_3).

The indenyllithium salt was alkylated through reaction with the suitable alkyl bromide. The reaction with formalin (37% solution) and sodium ethoxide in dimethylformamide yielded a solution from which the ligand was purified through a chromatography column. Zirconocene dichlorides were prepared by reacting the dilithiated ligand precursors with Me_3SnCl and then with $ZrCl_4$ in toluene.[10b,11] The complexes were purified by crystallization from toluene. In the aromatic solvent the *racemic* form is, in all the cases, less soluble than the *meso* one.

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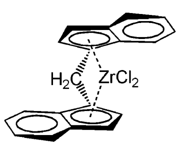
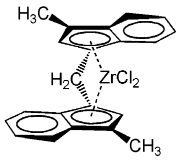
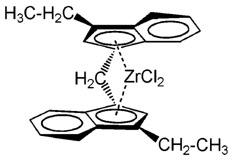
Chart 1



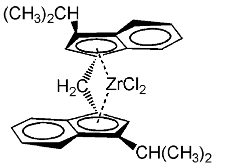
rac-[Methylene(1-indenyl)$_2$]ZrCl$_2$
(1)



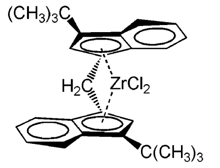
rac-[Methylene(3-methyl-1-indenyl)$_2$]ZrCl$_2$
(2)



rac-[Methylene(3-ethyl-1-indenyl)$_2$]ZrCl$_2$
(3)

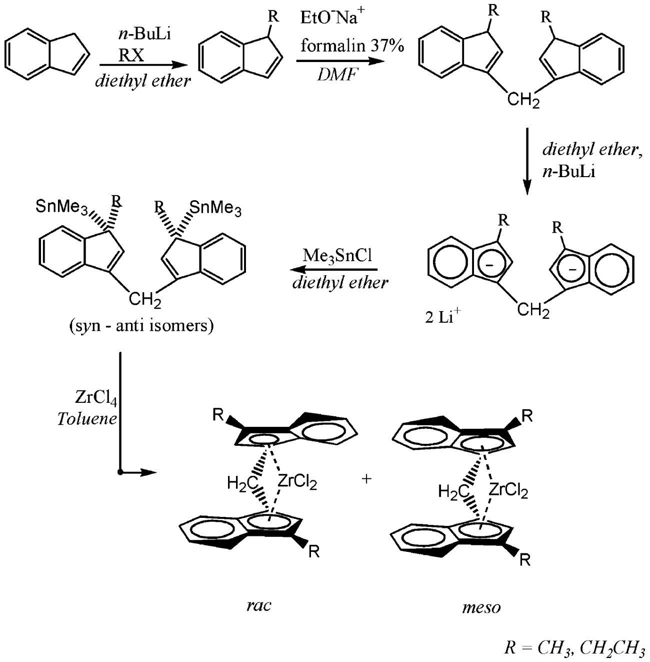


rac-[Methylene(3-propyl-1-indenyl)$_2$]ZrCl$_2$
(4)



rac-[Methylene(3-*t*-But-1-indenyl)$_2$]ZrCl$_2$
(5)

Scheme 1



Styrene Hydrooligomerization. Aimed at clarifying the regiochemistry of the styrene insertion, we have carried out a series of polymerizations of styrene in the presence of hydrogen (1 atm). The structure of hydrogenated oligomers obtained with the different complexes activated by MAO was analyzed by ^{13}C NMR and GC-MS techniques. This approach allows recognizing the regiochemistry of both the monomer insertion into the zirconium−hydrogen bond and the following insertions into the zirconium−carbon bond. ^{13}C NMR spectra of hydrooligomers produced at 20 °C, with catalysts precursors **1**−**5** (spectra a−e), are shown in Figure 1. A very similar hydrooligomeric composition is obtained at 60 °C.

Upon inspection of the aliphatic region of spectrum a, the most intense peaks at 31.36 and 36.06 ppm are due to carbon 2 and 1 of the 1,4-diphenylbutane, whereas the less intense signals at 29.57, 34.01, 36.15, 36.86, 38.76, and 45.66 ppm can be attributed to 1,3,6-triphenylhexane, in accordance with the literature data.[12] The GC-MS, with $M^+ = 210$ for the more abundant compound and $M^+ = 314$ for the less abundant one, are in agreement with this assignment. These structures of hydrodimer and hydrotrimer account for the styrene primary insertion into the zirconium−hydrogen bond followed by secondary insertions into the zirconium−carbon bond.

Spectra b and c are very similar but for the prevalence of the 1,3,6-triphenylhexane trimer, so suggesting again the secondary styrene insertion into the zirconium−carbon bond. On the contrary, the intense signals at 22.66, 34.09, 39.66, and 40.14 ppm in spectra d and e are assigned to 1,3-diphenylbutane and account possibly for the primary styrene insertion into the zirconium−hydrogen bond followed by further primary insertion into the zirconium−carbon bond (Scheme 2). The corresponding trimer 1,3,5-triphenylhexane bearing two asymmetric carbons is also detected in the spectrum.

In principle, the structure of 1,3-diphenylbutane could also account for the secondary styrene insertion into the zirconium−hydrogen bond followed by secondary insertion into the zirconium−carbon bond. However, this regiochemical hypothesis can be disregarded; in fact, either with no or very large substituents in C(3) [i.e., R = H, C(CH$_3$)$_3$] the styrene insertion into the zirconium−hydrogen bond is primary. It seems reasonable to extend to catalyst precursor **4** the regiochemical behavior of styrene for the insertion into the zirconium−hydrogen bond and consequently to infer the primary regiochemistry for the insertion into the zirconium−carbon bond.

Through GC-MS analysis, the relative abundance of dimers and trimers produced by each catalytic system has been calculated and reported in Table 1.

One can observe that in the presence of *rac*-[methylene(3-R-1-indenyl)$_2$]ZrCl$_2$ with R = H, CH$_3$, or CH$_2$CH$_3$ prevails secondary styrene insertion into the zirconium−carbon bond. Increasing the substituent steric hindrance (R = CH(CH$_3$)$_2$), a regiochemistry inversion occurs and the primary insertion is preferred with respect to the secondary one.

The previously reported regiochemical behavior of styrene in the case of system **5** (R = C(CH$_3$)$_3$) was attributed to the 3-*tert*-butyl substituents.[9] The results we report in the present paper confirm the hypothesis that styrene regiochemistry is dependent on alkyl substitutions on π ligands and fix the minimum steric hindrance of substituents able to induce the primary insertion and consequently the regiochemistry inversion.

Data reported in Table 2 show the relative amount of trimers and the ratio between the diastereoisomers

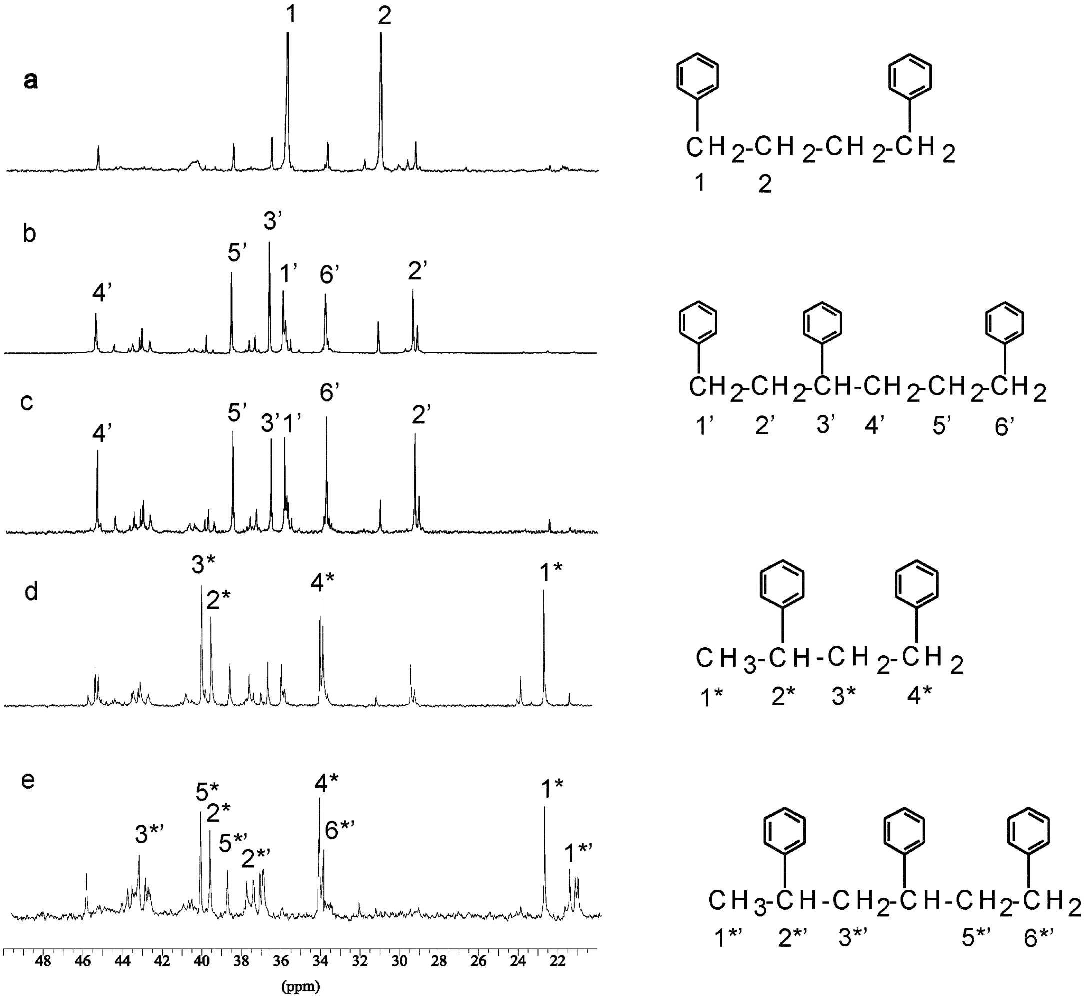


Figure 1. Aliphatic region of ^{13}C NMR spectra and chemical shift assignments of styrene hydrooligomers obtained in the presence of precursors **1**–**5** (spectra a–e) activated by MAO at 20 °C.

Table 1. Relative Amounts of Hydrodimer and Hydrotrimer Obtained at 20 °C and at 1 atm of Hydrogen Pressure with the Different Catalytic Systems

indenyl substituents in C(3)	1,4-dphb[a]	1,3-dphb[a]	1,3,6-tphe[b]	1,3,5-tphe[b]
H	99.4	0	0.6	0
CH_3	24	5.4	69.8	0.8
CH_2CH_3	17.8	16	64.1	2.1
$CH(CH_3)_2$	0.7	83.6	6.7	9.0
$C(CH_3)_3$	0.3	87.9	0.1	11.7

[a] Diphenylbutane. [b] Triphenylhexane.

Table 2. Relative Amounts of Stereochemical Isomers of Hydrotrimers Obtained at 20 °C and at 1 atm of Hydrogen Pressure with the Different Catalytic Systems

indenyl substituents in C(3)	1,3,6-tphe[a]	1,3,5-tphe[a]	iso/syndio
H	100	0	0
CH_3	98.9	1.1	0.8
CH_2CH_3	96.9	3.1	0.3
$CH(CH_3)_2$	42.6	57.4	0.2
$C(CH_3)_3$	0.5	99.5	27

[a] Triphenylhexane.

of 1,3,5-triphenylhexane.

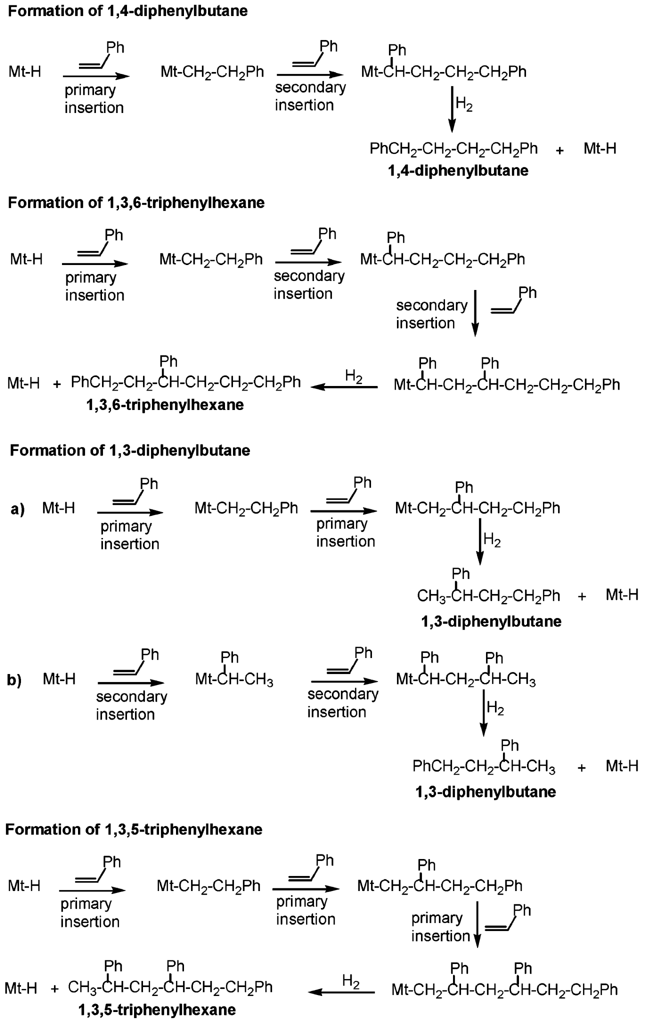
It is worth noting that increasing the steric hindrance on metallocene ligands, the relative amount of 1,3,5-triphenylhexane increases with respect to 1,3,6-triphenylhexane, according to the regiochemical trend.

In addition, from the stereochemical point of view, the presence of 3-methyl substituents in C(3) of the indenyls leads to a similar amount of (R,R + S,S) isomers (which model an syndiotactic growing chain) and (R,S + S,R) isomers (which model a isotactic growing chain) of 1,3,5-triphenylhexane. The catalyst precursor is so aspecific in the styrene polymerization according to the reported behavior of C_2-symmetric bridged 3-methylindenyl catalysts in the propene polymerization.[13]

On the other hand with C_2-metallocenes bearing ethyl and isopropyl groups in carbon 3 prevail the (R,R + S,S) isomers, that is, syndiotactic stereocontrol. This fact can be justified by an asymmetric carbon induction on stereocontrol because the symmetry features of the catalysts cannot account for such a stereocontrol. By further increasing the steric hindrance of C(3) substituents on π ligands, with *tert*-butyl the catalyst site control is restored and a diastereoisomers mixture enriched in the (R,S + S,R) isomers is obtained.

Ethylene–Styrene Copolymerizations. Recently we reported[9] that the precursor **5** activated by MAO is able to produce block ethylene–styrene copolymers such structure probably being a consequence of the styrene primary insertion. To relate the microstructure of copolymers to the regiochemistry of styrene insertion, a series of ethylene–styrene copolymerizations were carried out in the presence of complexes **1**–**4** activated by MAO, at different temperatures and comonomer feed.

Scheme 2



In the ^{13}C NMR spectra of products obtained at 60 °C and with $[E]_{feed}/[S]_{feed} = 9.0 \times 10^{-2}$, signals assigned to atactic polystyrene sequences are present in addition to the copolymeric one. Attemps to fractionate the copolymerization products with boiling solvent failed, despite a large polydispersity index (about 10) characteristic of all the samples. So the contemporary presence of ethylene–styrene copolymer and atactic polystyrene cannot be disregarded.

However, a close inspection of ^{13}C NMR signals belonging to the copolymeric structure can purchase some information about the relative reactivity of ethylene vs styrene.

As shown in Table 3 increasing the bulkiness in C(3) (R = H, CH_3, CH_2CH_3) catalysts **1**–**3**, which induce a secondary styrene insertion, produces “pseudorandom” copolymers with a slightly decreasing amount of alternating styrene–ethylene–styrene (SES) sequences. At the same time the average length of methylene sequences increases. The absence of stereoregularity of copolymers obtained with precursors **2** and **3** (R = CH_3 and CH_2CH_3) is evident from ^{13}C NMR spectra where the $S_{\beta\beta}$ is split into two signals.

In the same experimental conditions, [SEE]/[SES][17] and $\bar{L}_{CH_2}$ values of copolymer obtained in the presence of precursor **4** (R = $CH(CH_3)_2$) indicate a decrease of relative reactivity of styrene. Also, if precursor **4** is scarcely prone to give styrene–ethylene alternating sequences, the resonances of the junction carbons cannot be detected and consequently cannot be inferred the formation of block copolymer. Probably the primary insertion of styrene is not so prevalent on the secondary one to induce an ethylene–styrene block copolymerization. This is also evident from data reported in Table 2: 1,3-diphenylbutane is prevalent on 1,4-diphenylbutane, but the two structural isomers of trimers are about in the same amount, so indicating the scarce regioselectively of the complex **4**.

Table 3. Relative Amount of Triads and Average Length of Methylene Sequences in the Ethylene–Styrene[a] Copolymers Obtained with the Different Catalyst Systems

indenyl substituents in C(3)	[SEE]/[SES][b]	$\bar{L}_{CH_2}$
H	0.14	3.3
CH_3	0.22	3.6
CH_2CH_3	0.31	4.2
$CH(CH_3)_2$	0.92	6.2
$C(CH_3)_3$	n.d.	12

[a] All the copolymerizations were carried out in the presence of MAO as cocatalyst, in 20 mL of toluene, *T* = 60 °C, *t* = 1 h, $[E]_{feed}/[S]_{feed} = 9.0 \times 10^{-2}$. [b] Calculated according to ref 17.

Finally, the copolymer obtained in the presence of system **5** (R = $C(CH_3)_3$) shows a strong increase of average length of methylene sequences and from the ^{13}C NMR spectrum as well as from GPC analysis is evidently a blockwise structure.

Conclusions

Styrene hydrooligomers, produced in the presence of differently substituted C_2-symmetric *ansa*-zirconocenes activated by MAO, are a representation of the monomer initial insertion steps. In this work the structure of hydrooligomers has been studied to understand how substituent groups in C(3) of π ligands influence the regiochemical behavior of styrene toward the metal–carbon bond. Results show the styrene regiochemistry changes from secondary to primary as increasing the bulk in C(3): H < CH_3 < CH_2CH_3 < $CH(CH_3)_2$ < $C(CH_3)_3$. In particular, the isopropyl group is the smallest substituent capable to preferentially induce the primary styrene insertion. This regiochemistry becomes strongly prevalent in the presence of 3-*tert*-butyl-substituted zirconocene catalyst.

In a similar way, decreasing the tendency toward secondary insertion decreases the alternating enchainment of ethylene and styrene in copolymerization as shown by the relative amount of SES and SEE sequences.

A surprising result arises from the stereochemical analysis of the hydrooligomers containing couples of asymmetric carbons. With the ethyl substituent in C(3) and, even more, with the isopropyl substituent, a syndiotactic-like stereocontrol, possibly induced by the first asymmetric carbon, overcomes the isotactic-like stereocontrol expected from the C_2-symmetric catalytic center. On the contrary, with the *tert*-butyl substituent the site control is restored and the (R,S + S,R) hydrotrimers are obtained.

Experimental Part

Materials and General Procedures. All operations were performed under a nitrogen atmosphere by using Schlenk techniques. Solvents were dried over metallic sodium or $LiAlH_4$.

Ethylene was purchased from Società Ossigeno Napoli and used without further purification. Toluene (analytical grade reagent, Carlo Erba Reagenti) was refluxed over metallic sodium and distilled under a nitrogen atmosphere. Styrene (99% GC, Aldrich) was stirred over CaH_2 and distilled under reduced pressure of nitrogen. Methylalumoxane (MAO), provided by Witco as 30 wt % solution in toluene, was dried before use by removing in a vacuum the solvent. *rac*-[Methylene-(3-R-1-indenyl)$_2$]zirconium dichloride (R = H, $CH(CH_3)_2$, $C(CH_3)_3$) was synthesized according to the literature.[10]

Synthesis of Bis(1-methyl-3-indenyl)methane. 3.6 mL of formalin (37% solution, 48.6 mmol) was added dropwise to a mixture of methylindene[14] (13 g, 97 mmol) and sodium ethoxide (2.1 g, 31 mmol) in 140 mL of dimethylformamide. The reaction mixture was stirred 18 h at room temperature, then HCl 1 M (120 mL) was added, and the organic phase was extracted with petroleum ether (3 × 100 mL). The organic phases combined, anidrified with Na_2SO_4, were concentrated. The yellow oil obtained was purified over a chromatography column (eluent: petroleum ether) to yield 2.4 g of ligand (yield: 18%).

^{1}H NMR ($CDCl_3$): δ 7.49−7.25 (m, 8H, C_6H_4); 6.28 (d, 2H, C_5 ring =CH); 3.81 (s, 2H, CH_2); 3.08 (m, 2H, C_5 ring, CH); 1.40 (s, 6H, CH_3). MS: 272 (M^+)

Synthesis of Bis[3-methyl-3(trimethylstannyl)inden-1yl]methane. To a solution of bis(1-CH_3-3-indenyl)methane (2.4 g, 8.8 mmol) in 45 mL of diethyl ether was added dropwise, at −78 °C, 7 mL of *n*BuLi (2.5 M solution in hexane, 17.6 mmol). The mixture was stirred 1 h at −78 °C, and then it was allowed to warm at room temperature and stirred for 18 h. Then the solution was treated at −40 °C with 3.5 g of Me_3SnCl (18 mmol) in 5 mL of diethyl ether and stirred overnight. It was decanted and evaporated to obtain 3.9 g (6.5 mmol) of a yellow-orange oil (mixture of isomers)[10b,11] (yield: 74%).

^{1}H NMR ($CDCl_3$): δ 7.47−7.17 (m, 8H, C_6H_4); 6.35 (s, 2H, C_5 ring CH); 1.85 (s, 2H, CH_2 bridge); 1.58 (s, 6H, CH_3); −0.11 (s, 18H, $Sn(CH_3)_3$).

Synthesis of *rac*-$CH_2[(3\text{-}CH_3\text{-}1\text{-}Ind)_2]ZrCl_2$. A solution of 3.9 g (6.5 mmol) of bis[3-methyl-3(trimethylstannyl)inden-1yl]-methane in 10 mL of toluene was added dropwise to a suspension of 1.5 g (6.5 mmol) of $ZrCl_4$ in 22 mL of toluene. The mixture was stirred 18 h at room temperature, then stirred for 4 h at 100 °C, and finally cooled to 0 °C. 1.6 g (3.7 mmol) of a deep-red crystalline solid was filtered off and dried in a vacuum (yield: 42% based on ligand).

^{1}H NMR ($CDCl_3$): δ 7.17−7.28 (m, 8 H, C_6H_4); 5.64 (s, 2 H, C_5 ring); 4.75 (s, 2H, CH_2); 2.35 (s, 6H, CH_3). Anal. Calcd for $C_{21}H_{18}Cl_2Zr$: C, 58.32; H, 4.19. Found: C, 58.64; H, 4.55.

Synthesis of *rac*-$CH_2[(3\text{-}CH_3CH_2\text{-}1\text{-}Ind)_2]ZrCl_2$. The above-reported procedure was also employed for the synthesis of *rac*-$CH_2[(3\text{-}CH_3CH_2\text{-}1\text{-}Ind)_2]ZrCl_2$. The pure compound was obtained by precipitation from toluene (yield: 20% based on ligand).

Bis(1-ethyl-3-indenyl)methane. ^{1}H NMR ($CDCl_3$): δ 7.47−7.23 (m, 8 H, C_6H_4); 6.21 (d, 2 H, C_5 ring, =CH); 3.75 (s, 2H, CH_2 bridge); 3.05 (m, 2H, C_5 ring, CH); 1.55 (m, 4H, CH_2); 0.91 (s, 6H, CH_3). MS: 300 (M^+).

Bis[3-ethyl-3(trimethylstannyl)inden-1yl]methane. ^{1}H NMR ($CDCl_3$): δ 7.48−7.16 (m, 8 H, C_6H_4); 6.36 (s, 2 H, C_5 ring, CH); 2.25 (s, 2H, CH_2 bridge); 1.56 (m, 4H, CH_2); 0.87 (t, 6H, CH_3); −0.11 (s, 18H, $Sn(CH_3)_3$).

rac-$CH_2[(3\text{-}CH_3CH_2\text{-}1\text{-}Ind)_2]ZrCl_2$. ^{1}H NMR ($CDCl_3$): δ 7.18−7.48 (m, 8 H, C_6H_4); 5.67 (s, 2 H, C_5 ring); 4.75 (s, 2H, CH_2); 2.70 (m, 4H); 1.17 (t, 6H). Anal. Calcd for $C_{23}H_{22}Cl_2Zr$: C, 59.98; H, 4.81. Found: C, 60.04; H, 4.99.

Styrene Hydrooligomerization. Styrene hydrooligomerizations were carried out in a 100 mL glass flask charged under a nitrogen atmosphere with toluene (20 mL) and MAO (8 mmol). The mixture, magnetically stirred, was thermostated at 20 or 60 °C, and then 2 mL of a 4 mM toluene solution of the catalyst was added (Al/Zr in mol = 1000). The inert atmosphere was removed and replaced with hydrogen, and then 10 mL of styrene was injected. The flask was fed with hydrogen over the reaction time. The hydrooligomerization was stopped after 2 h, adding acidified methanol. The oligomers were recovered by treating the solution with acidified water, then by washing with water until neutrality, and drying the organic layer in a vacuum.

1,4-Diphenylbutane. ^{13}C NMR ($CDCl_3$): δ 31.36 (C2), 36.06 (C1), the aromatic C atoms resonated between 125.8 and 142.8. MS: 210 (M^+). Mp = 49−52 °C.

1,3-Diphenylbutane. ^{13}C NMR ($CDCl_3$): δ 22.66 (C1), 34.09 (C4), 39.66 (C2), 40.14 (C3), the aromatic C atoms resonated between 125.2 and 145.7. MS: 210 (M^+). Bp = 67−70 °C (0.01 Torr).

1,3,6-Triphenylhexane. ^{13}C NMR ($CDCl_3$): δ 29.57 (C2), 34.01 (C6), 36.15 (C1), 36.86 (C3), 38.76 (C5), 45.66 (C4), the aromatic C atoms resonated between 126.2 and 145.6. MS: 314 (M^+). Bp = 109−116 °C (0.1 Torr).

1,3,5-Triphenylhexane. ^{13}C NMR ($CDCl_3$): δ 21.38 (C1), 33.96 (C6), 37.51 (C2), 38.70 (C5), 43.26 (C3), the aromatic C atoms resonated between 125.9 and 147.9. MS: 314 (M^+). Bp 115−125 °C (0.01 Torr).

Example of Hydrooligomerization. In a 100 mL glass flask were added, in a nitrogen atmosphere, 20 mL of toluene and 0.46 g (8.0 mmol) of MAO. The mixture was magnetically stirred and thermostated at 20 °C, and then 2 mL of a 4 mM toluene solution of *rac*-$CH_2[(3\text{-}CH_3CH_2\text{-}1\text{-}Ind)_2]ZrCl_2$ (11 mg in 6.0 mL of toluene) was added (Al/Zr in mol = 1000). The inert atmosphere was removed and replaced with hydrogen, and then 10 mL of styrene was injected. The flask was fed with hydrogen over the reaction time. The hydrooligomerization was stopped after 2 h, adding acidified methanol. The oligomers were recovered by treating the solution with acidified water, then by washing with water until neutrality, and drying the organic layer in a vacuum (yield: 500 mg).

Ethylene−Styrene Copolymerizations. Ethylene−styrene copolymerizations were carried out in a 100 mL glass flask charged under a nitrogen atmosphere sequentially with styrene (10 mL) and MAO (11 mmol). The mixture was magnetically stirred, and the glass flask was thermostated at the desired temperature. The inert atmosphere was removed and replaced with ethylene feed, and 3 mL of a 3.6 mM toluene solution of the zirconocene compound was introduced (Al/Zr in mol = 1000). The flask was fed with an ethylene−argon mixture over the polymerization time. The steadiness of gaseous mixture composition was monitored via gas chromatography. The reaction was stopped after 2 h, and the copolymer was coagulated by pouring the reaction mixture into acidified methanol, filtered, washed with additional methanol, and dried in a vacuum.

The ethylene concentration in the liquid phase was calculated by using the Lewis and Luke's equation conjoined with the fugacity function chart of ethylene as reported in the literature.[15]

Example of Copolymerization. In a 100 mL glass flask were added, under a nitrogen atmosphere, 10 mL of styrene and 0.64 g of MAO (11 mmol), then the mixture was magnetically stirred, and the glass flask was thermostated at 60 °C. The inert atmosphere was removed and replaced with an ethylene−argon feed (0.06 atm of ethylene partial pressure), and 3 mL of a 3.6 mM toluene solution of *rac*-$CH_2[(3\text{-}CH_3CH_2\text{-}1\text{-}Ind)_2]ZrCl_2$ (10 mg in 6 mL of toluene) was introduced. The steadiness of gaseous mixture composition was monitored via gas chromatography. The reaction was stopped after 2 h, and the copolymer was coagulated by pouring the reaction mixture into acidified methanol, filtered, washed with additional methanol, and dried in a vacuum (yield: 850 mg)

^{13}C NMR Analysis. The ^{13}C NMR spectra of the hydrooligomers were recorded on an AV 400 Bruker operating at 100 MHz in the Fourier mode at 293 K. The samples (5 mg) were dissolved in 0.5 mL of $CDCl_3$ into a tube with 5 mm o.d. Tetramethylsilane (TMS) was used as internal chemical shift reference. The assignment has been carried out through the additivity rules[16] and through comparison with the literature data.[12]

The ^{13}C NMR spectra of copolymers were recorded in the same way but dissolving 30 mg of sample in 0.5 mL of $CDCl_3$. Tetramethylsilane (TMS) was used as internal chemical shift reference. The relative amount of triads in the ethylene−styrene copolymers has been evaluated from the NMR spectra as reported in the literature.[17] Likewise, the average length of methylene sequences can be evaluated by means of the following equation:

$$\bar{L}_{\mathrm{CH_2}} = 0.5(A_{25.4} + A_{27.8} + A_{29.9} + A_{35.0} + A_{37.0})/(A_{35.0} + A_{37.0})$$

GPC Analysis. GPC of the copolymers was recorded on a PSS SDV gel permeation chromatography with three polystyrene divinylbenzene gel columns (100, 10^4, 10^6 Å pore size), a WGE refraction index detector using $CHCl_3$ as eluent at 25 °C, a flow rate of 1 mL/min, and standard polystyrene samples for calibration. The M_w values were in the range between 1.8×10^4 and 1.2×10^5; the polydispersity index was around 10 for all the samples.

GC-MS Analysis. GC-MS measurements of the mixture of hydrooligomers were recorded on a GC Trace 2000 SERIES connected to a Finnigan Thermoquest GLQ Plus 2000 spectometer operating with an ion trap detector.

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