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Metallocenes for Ethene/Propene Copolymerizations with High Product of Reactivity Ratios

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ABSTRACT: Ethene/propene copolymerizations were performed with catalytic systems composed of a stereorigid racemic isospecific metallocene and polymethylalumoxane. A number of complexes were used as representatives of three different classes of metallocenes. *r*-$Me_2C(3$-*t*-Bu-$Cp)_2ZrCl_2$, *r*-$Me_2C(3$-*t*-Bu-$Ind)_2ZrCl_2$, *r*-$EBDMIZrCl_2$, *r*-$EBDMTHIZrCl_2$, and *r*-$Me_2Si(2$-Me-4-Ph-$Ind)_2ZrCl_2$ were chosen as sterically hindered complexes. The parent metallocenes, *r*-$Me_2C(Ind)_2ZrCl_2$, *r*-$EBIZrCl_2$, and *r*-$Me_2Si(Ind)_2ZrCl_2$ were also employed as well as other compounds bearing different substituents on the indenyl ligands such as *r*-$Me_2C(3$-Me_3Si-$Ind)_2ZrCl_2$, *r*/*m*-$Me_2C(3$-Me-$Ind)_2ZrCl_2$, and *r*-$Me_2Si(2$-Me-$Ind)_2ZrCl_2$. The reactivity ratios of copolymerization (r_E and r_P) were determined and examined in the light of the metallocene structure. The complexes that were particularly demanding from the steric point of view were identified as suitable candidates for promoting copolymerizations with a high product of reactivity ratios, giving r_Er_P in a range from 1.7 to 3.0. The other two classes of metallocenes gave rise to r_Er_P clearly lower than 1. A more complex situation was observed as far as the reactivity ratios r_E and r_P are concerned. The enhancement of the steric hindrance brought about in most cases an increase of r_E but not a substantial decrease of r_P. In some cases, r_E was found to remain almost unchanged and r_P dramatically increased. A correlation between the reactivity ratios and the metallocene structure is attempted.

Introduction

Metallocene-based catalytic systems (MBC)[1] find their fundamental application in the field of ethene-based (co)polymers.[2] They are already applied on the industrial scale, with an increasing penetration of the market.

The scientific interest is motivated primarily by their single-center nature[1,3] and by the availability of a large variety of metallocene structures, as they prepare homogeneous products covering a wide range of (co)polymers microstructures and properties. In the field of ethene/propene copolymers,[4] many authors focused their attention on the intramolecular distribution of the comonomers and determined their reactivity ratios, r_E and r_P. There is no doubt that the most interesting result is the capability of MBC to prepare copolymers with either long homosequences[5] or with an almost alternate distribution[4d,e,6] of ethene and propene.

We have recently reported[5] on a clear example of an ethene/propene copolymerization characterized by a high product of reactivity ratios (r_Er_P), promoted by a metallocene-based catalytic system, *rac*-[isopropylidenebis(3-*tert*-butyl-1-cyclopentadienyl)]zirconium dichloride[7] (*r*-$Me_2C(3$-*t*-Bu-$Cp)_2ZrCl_2$). The copolymerizations were not affected by appreciable physical limitations, a wide range of relative concentration of the comonomers in the polymerization solution was explored, and an outstanding fitting of experimental data was achieved. A r_Er_P of 2.8 ± 0.4 was obtained from the statistical approach. It appeared worthwhile to us to further investigate these peculiar ethene/1-olefin copolymerizations with a high product of reactivity ratios, as few other data are reported in the literature.[4f,8] Instead of embarking on undue speculations, we decided to collect more experimental data, to investigate how a single-center catalyst can allow the formation of long homosequences of two different comonomers, such as ethene and the 1-olefin, in the same macromolecular chain, prepared through an insertion polymerization substantially free from physical limitations.

In this manuscript we report on ethene/propene (E/P) copolymerizations. The results of ethene copolymerizations with 1-olefins higher than propene (1-butene, 1-octene) will be presented in a further paper.[9]

Moving from the basic features of the metallocenes employed in our previous works, we have investigated many other candidates, privileging the ones that are stereorigid, racemic, and characterized by a surrounding of the transition-metal atom that is particularly demanding from the steric point of view. E/P copolymerizations were thus performed with the following metallocenes: *r*-$Me_2C(3$-*t*-Bu-$Cp)_2ZrCl_2$, *rac*-[isopropylidenebis(3-*tert*-butyl-1-indenyl)]zirconium dichloride[7,10] (*r*-$Me_2C(3$-*t*-Bu-$Ind)_2ZrCl_2$), *rac*-[ethylenebis(4,7-dimethyl-1-indenyl)]zirconium dichloride[11] (*r*-$EBDMIZrCl_2$), *rac*-[ethylenebis(4,7-dimethyl-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride[12] (*r*-$EBDMTHIZrCl_2$), and *rac*-[dimethylsilylenebis(2-methyl-4-phenyl-1-indenyl)]zirconium dichloride[13] (*r*-$Me_2Si(2$-Me-4-Ph-$Ind)_2ZrCl_2$).

To investigate the role played by the substituents of the metallocene ligands, copolymerizations were also performed with the following two families of compounds: first, the “parent” metallocenes without substituents on the indenyl ligands, such as *rac*-[isopropylidenebis(1-indenyl)]zirconium dichloride[14] (*r*-$Me_2C(Ind)_2ZrCl_2$), *rac*-[ethylenebis(1-indenyl)]zirconium dichloride[15] (*r*-$EBIZrCl_2$), and *rac*-[dimethylsilylenebis(1-indenyl)]zirconium dichloride[16] (*r*-$Me_2Si(Ind)_2ZrCl_2$), then, the metallocenes bearing different substituents on the π ligands, such as *rac*-[isopropylidenebis(3-trimethylsilyl-1-indenyl)]zirconium dichloride[7,10] (*r*-$Me_2C(3$-Me_3Si-$Ind)_2ZrCl_2$), *rac*/*meso*-[isopropylidenebis(3-methyl-1-

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Table 1. E/P Copolymerization with Racemic Stereorigid Sterically Hindered Metallocenes and MAO as the Catalytic System[a]

metallocene	run	Zr (μmol)	ethene/propene[b] (mol/mol) gas phase	liquid phase	yield (g)	activity (g pol/g Zr)	$(E)_{copolym}$[c] (mol %)	IV[d] (dL/g)	monomer conversion (%)
r-$Me_2C(3$-*t*-Bu-$Cp)_2ZrCl_2$	1	1.5	2.22	0.53	0.5	3 450	92.5	0.7	1.9
	2	3.5	1.60	0.38	1.0	3 200	87.1	0.3	3.0
	3	3.6	1.13	0.27	0.9	2 750	85.8	n.d.[e]	3.0
	4	1.2	0.99	0.23	1.0	9 150	84.7	0.5	3.7
	5	3.5	0.43	0.099	0.6	1 900	66.4	0.6	1.9
	6	2.5	0.37	0.087	0.7	3 200	69.1	0.2	2.4
	7	3.7	0.22	0.053	2.0	5 950	38.3	0.3	5.6
	8	3.6	0.099	0.020	1.7	5 200	19.8	0.08	4.3
r-$Me_2C(3$-*t*-Bu-$Ind)_2ZrCl_2$	9	1.2	2.28	0.54	0.9	8 700	89.5	n.d.[e]	3.4
	10	1.5	1.16	0.27	1.9	13 900	71.8	0.5	6.7
	11	1.5	0.29	0.069	2.0	14 650	37.0	n.d.[e]	6.3
r-$EBDMIZrCl_2$	12	1.3	5.90	1.48	0.3	2 600	94.0	2.5	1.2
	13	1.5	2.50	0.59	1.0	7 300	90.5	1.8	3.8
	14	0.8	1.00	0.24	1.8	24 700	76.3	n.d.[e]	6.7
	15	1.2	0.51	0.12	0.5	4 400	65.8	0.8	1.7
	16	1.5	0.21	0.049	0.3	2 000	44.9	n.d.[e]	1.5
r-$EBDMTHIZrCl_2$	17	1.5	0.16	0.038	1.2	9 000	63.6	n.d.[e]	4.0
r-$Me_2Si(2$-Me-4-Ph-$Ind)_2ZrCl_2$	18	1.3	5.90	1.48	0.8	6 750	75.5	1.5	2.9
	19	1.6	2.22	0.53	0.7	4 800	53.4	0.8	2.3
	20	1.1	2.04	0.48	0.1	1 400	49.7	n.d.[e]	<1.0
	21	1.5	1.04	0.25	1.6	11 700	37.1	n.d.[e]	5.0
	22	2.5	0.67	0.16	2.0	8 800	19.1	0.6	5.9

[a] Polymerization conditions: toluene = 100 mL, Al/Zr = 1000 (mol/mol), T = 50 °C, total pressure = 1.1 atm, flow rate of (E + P) mixture = 1.5 L/min, and polymerization time = 15 min. [b] Feed ratio. [c] From ^{13}C NMR analysis. [d] Intrinsic viscosity. [e] Not determined.

indenyl)]zirconium dichloride[7] (*r*/*m*-$Me_2C(3$-Me-$Ind)_2$-$ZrCl_2$), and *rac*-[dimethylsilylenebis(2-methyl-1-indenyl)]zirconium dichloride[17] (*r*-$Me_2Si(2$-Me-$Ind)_2ZrCl_2$).

Experimental data as well as their statistical elaboration are reported together with a tentative interpretation of the results.

Results

Polymerization Method. E/P copolymerizations were performed in solution and in the presence of polymethylalumoxane[18] (MAO) as the cocatalyst, adopting the experimental methods already discussed in previous manuscripts,[4h,i,19] suitable to avoid an appreciable effect of the physical aspects on the copolymerization results. In particular, the high ratio between the monomers fed into the reaction system and those converted in the copolymer, the low concentration of the polymer in solution, the use of a good solvent, and the relatively high polymerization temperature allow one to assume the concentration of the comonomers in the polymerization bath as constant and to calculate it through thermodynamic methods. Moreover, the isomeric purity of the metallocenes used in this work was carefully checked by means of ^1H NMR (see Experimental Section).

Stereorigid, Racemic Sterically Hindered Metallocenes as the Catalyst Precursors. In Table 1, data of the E/P copolymerizations performed with the metallocenes *r*-$Me_2C(3$-*t*-Bu-$Cp)_2ZrCl_2$, *r*-$Me_2C(3$-*t*-Bu-$Ind)_2ZrCl_2$, *r*-$EBDMIZrCl_2$, *r*-$EBDMTHIZrCl_2$, and *r*-$Me_2Si(2$-Me-4-Ph-$Ind)_2ZrCl_2$ are reported.

Detailed data and comments about *r*-$Me_2C(3$-*t*-Bu-$Cp)_2ZrCl_2$ were the basis of the previous manuscript[5] on this subject. Further tests are here reported to allow a direct comparison with the other metallocenes as well as to implement the information on this complex.

Tests were not reproduced to confirm the catalytic activity.

Moreover, the use of different amounts of zirconocenes (tuned to have a low polymer productivity) does not allow a correct comparison of copolymerization tests.

As a consequence, one can only observe that most catalytic activities are of the same order of magnitude and that *r*-$Me_2C(3$-*t*-Bu-$Cp)_2ZrCl_2$ has a slightly lower productivity.

The intrinsic viscosity of copolymers having similar chemical composition was measured. For an ethene content ranging from about 65 to about 75 mol %, all of the metallocenes give rise to similar molecular masses.

The copolymer microstructure was investigated through ^{13}C NMR analysis. Triad distributions of all the samples of Table 1 are shown in Table 2.

The presence of 2,1 propene insertions was observed in copolymers more rich in propene from any of the metallocenes,[22] except *r*-$Me_2C(3$-*t*-Bu-$Ind)_2ZrCl_2$. In particular, the high amount of even methylene sequences[21] observed in sample 17 from *r*-$EBDMTHIZrCl_2$ (3.4 mol % for a propene content of only 36.4 mol %) can affect the quantitative determination of the comonomers distribution. This suggested to us not to use copolymers from this metallocene for a careful determination of r_1 and r_2, and thus a series of copolymerizations was not performed. In the case of copolymers from the other metallocenes, the maximum amount of even methylene sequences[21] was observed in sample 16 from *r*-$EBDMIZrCl_2$ and was about 3.2 mol % for a propene content of 55.1 mol %. Hence, they were disregarded in the elaboration of the NMR data.

Triads of Table 2 were elaborated with a method, already reported in a previous publication,[5] that allows one to identify the statistical model suitable for describing the copolymerizations as well as for deriving the reactivity ratios between the comonomers.[23] It is worthwhile to briefly summarize a few basic concepts that are at the basis of the statistical method and of the following discussion. When the insertion of a comonomer is found to be influenced by the last inserted unit (ultimate

Table 2. ^{13}C NMR Characterization of E/P Copolymers Prepared with Racemic Stereorigid Sterically Hindered Metallocenes and MAO as the Catalytic System

metallocene	sample[a] no.	f[b] (mol/mol)	$(E)_{copolym}$[c] (mol %)	PPP	PPE	EPE	PEP	PEE	EEE	isoindex[d] (%)	regioirreg.[e] (%)
r-$Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$	1	0.53	92.5	0.0000	0.0254	0.0492	0.0077	0.1057	0.8120	n.d.[f]	n.d.[f]
	2	0.38	87.1	0.0129	0.0510	0.0649	0.0107	0.1575	0.7031	100	n.d.[f]
	3	0.27	85.8	0.0132	0.0626	0.0658	0.0099	0.1813	0.6672	100	n.d.[f]
	4	0.23	84.7	0.0142	0.0684	0.0700	0.0203	0.1904	0.6366	100	n.d.[f]
	5	0.099	66.4	0.0793	0.1758	0.0807	0.0428	0.2551	0.3663	100	n.d.[f]
	6	0.087	69.1	0.0739	0.1575	0.0772	0.0385	0.2589	0.3940	100	n.d.[f]
	7	0.053	38.3	0.3045	0.2678	0.0446	0.0899	0.1925	0.1007	100	n.d.[f]
	8	0.020	19.8	0.5488	0.2371	0.0158	0.0842	0.0906	0.0234	100	0.90
r-$Me_2C(3\text{-}t\text{-}Bu\text{-}Ind)_2ZrCl_2$	9	0.54	89.5	0.0000	0.0303	0.0747	0.0134	0.1701	0.7116	n.d.[f]	n.d.[f]
	10	0.27	71.8	0.0413	0.1176	0.1232	0.0446	0.2637	0.4096	100	n.d.[f]
	11	0.069	37.0	0.3599	0.2003	0.0697	0.0982	0.1806	0.0912	100	none
r-$EBDMIZrCl_2$	12	1.48	94.0	0.0000	0.0000	0.0608	0.0000	0.1441	0.7951	n.d.[f]	n.d.[f]
	13	0.59	90.5	0.0067	0.0319	0.0563	0.0058	0.1419	0.7575	n.d.[f]	n.d.[f]
	14	0.24	76.3	0.0469	0.1080	0.0823	0.0333	0.2321	0.4974	n.d.[f]	n.d.[f]
	15	0.12	65.8	0.0985	0.1652	0.0782	0.0588	0.2736	0.3257	100	n.d.[f]
	16	0.049	44.9	0.2418	0.2303	0.0788	0.0939	0.2152	0.1399	100	3.15
r-$EBDMTHIZrCl_2$	17	0.038	63.6	0.1338	0.1799	0.0500	0.0231	0.2110	0.4022	100	3.38
r-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$	18	1.48	75.5	0.0361	0.0997	0.1091	0.0400	0.2252	0.4899	100	n.d.[f]
	19	0.53	53.4	0.1507	0.2119	0.1032	0.1005	0.2340	0.1996	100	n.d.[f]
	20	0.48	49.7	0.1791	0.2227	0.1006	0.1116	0.2214	0.1647	100	n.d.[f]
	21	0.25	37.1	0.3685	0.2433	0.0572	0.1098	0.1509	0.0702	100	n.d.[f]
	22	0.16	19.1	0.5788	0.2051	0.0255	0.1038	0.0699	0.0169	100	traces

[a] The numbers of the samples are those of the corresponding runs. [b] E/P feed ratio (mol/mol) in liquid phase. [c] From triad distribution as E = 100(PEP + EEP + EEE). [d] Calculated as $T_{\beta\beta}(mm)/[T_{\beta\beta}(mm) + T_{\beta\beta}(mr + rr)]$ (for nomenclature, see Experimental Section). [e] Calculated according to Randall[20] as $[100(^1/_2S_{\alpha\beta} + {}^1/_2S_{\beta\gamma})/(S_{\alpha\alpha} + {}^1/_2S_{\alpha\beta} + S_{\beta\beta} + {}^1/_2S_{\beta\gamma} + S_{\gamma\gamma} + {}^1/_2S_{\gamma\delta})]$ from 100.13 MHz ^{13}C NMR spectrum.[21] [f] Not determined.

Table 3. Reactivity Ratios for E/P Copolymerizations with Racemic Stereorigid Sterically Hindered Metallocenes and MAO as the Catalytic System

metallocene	$r_1 \pm \delta r_1$	$r_2 \pm \delta r_2$	$r_1r_2 \pm \delta(r_1r_2)$[a]	LS_{tot}
r-$Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$	28.3 ± 1.6	0.105 ± 0.008	3.0 ± 0.4	0.025
r-$Me_2C(3\text{-}t\text{-}Bu\text{-}Ind)_2ZrCl_2$	14.0 ± 1.3	0.19 ± 0.03	2.7 ± 0.7	0.010
r-$EBDMIZrCl_2$	18.0 ± 1.9	0.094 ± 0.016	1.7 ± 0.5	0.029
r-$EBDMTHIZrCl_2$	95.5[b]	0.063[b]	6.3	n.d.[c]
r-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$	2.84 ± 0.19	0.74 ± 0.04	2.1 ± 0.3	0.0091

[a] $\delta(r_1r_2) = r_1\delta r_2 + r_2\delta r_1$. [b] Estimated from diads distribution and bath composition (according to Kakugo et al.[25]). [c] Not determinable.

effect), a first-order Markovian statistical model[24] is adopted and values are obtained for the following reactivity ratios:

$$r_1 = k_{11}/k_{12}$$

$$r_2 = k_{22}/k_{21}$$

where k_{ij} is the rate constant of the reaction for the addition of the monomer j to a growing chain bearing the comonomer i as the last inserted one. In particular, 1 and 2 indicate ethene and the 1-olefin, respectively.

A first-order Markovian model was found to be the most suitable one to describe the copolymerizations promoted by all of the four metallocenes, as already reported for *r*-$Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$. The calculated values of r_1, r_2 and r_1r_2 are collected in Table 3, together with the confidence intervals from the least squares at the minimum point.

They appear to be a reliable basis for the discussion proposed hereinafter. The r_1 and r_2 values shown in Table 3 for *r*-$Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$ were calculated by using the data from the three new copolymerizations and by neglecting the tests with the highest comonomers conversion of the previous manuscript (runs 5 and 7 from Galimberti et al.[5]). They are very similar to those previously reported: r_1 moves from 25.6 ± 1.5 to 28.3 ± 1.6, r_2 from 0.110 ± 0.008 to 0.105 ± 0.008, and r_1r_2 from 2.8 ± 0.4 to 3.0 ± 0.4.

The E/P copolymerizations presented so far are thus characterized by a product of reactivity ratios higher than 1, indicating that these metallocenes favor the presence along the same macromolecular chain of homosequences of both ethene and propene.

The high values of r_1r_2 do not arise from unusually high values of r_1, with the exception of *r*-$EBDMTHIZrCl_2$.[26] As a matter of fact, E/P copolymerizations characterized by a high value of r_1 can be found in the literature dedicated to metallocenes.[19,27] An examination of the data of Table 3 obtained by using the statistical method shows that *r*-$Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$ gives rise to the highest r_1, and the values of *r*-$Me_2C(3\text{-}t\text{-}Bu\text{-}Ind)_2ZrCl_2$ and *r*-$EBDMIZrCl_2$ fall in a middle range, whereas *r*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ shows a particularly low value of r_1. In addition, the values of r_2 fall within the range defined by the literature data.[19,27] Again, *r*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ behaves differently from the other three metallocenes, as it gives rise to a remarkably higher r_2 value, among the highest so far reported in the literature, whereas the other values are very similar to each other.

These results confirm the correct selection of stereorigid, racemic, and sterically hindered isospecific metallocenes for promoting E/P copolymerizations with high r_1r_2.

Parent Unsubstituted, Racemic Metallocenes as the Catalyst Precursors. As anticipated in the Introduction, to investigate the role played by the substitu-

Table 4. E/P Copolymerization with Racemic Stereorigid Metallocenes and MAO as the Catalytic System[a]

metallocene	run	Zr (μmol)	ethene/propene[b] (mol/mol) gas phase	ethene/propene[b] (mol/mol) liquid phase	yield (g)	activity (g pol/g Zr)	(E)$_{\text{copolym}}$[c] (mol %)	monomer conversion (%)
r-Me$_2$C(Ind)$_2$ZrCl$_2$	23	1.7	5.58	1.33	0.7	4 400	80.3	2.5
	24	1.7	2.59	0.61	0.04	250	65.4	<1
	25	3.5	1.29	0.30	1.9	6 050	50.0	6.2
	26	3.5	1.18	0.28	1.5	4 650	50.9	4.8
	27	3.5	0.55	0.13	2.3	7 350	30.2	6.7
r-EBIZrCl$_2$	28	0.5	2.33	0.55	0.5	11 000	86.9	1.9
	29	1.0	0.11	0.25	1.6	17 500	70.7	5.6
	30	3.0	0.41	0.096	1.0	3 550	55.5	3.2
	31	1.5	0.21	0.049	0.25	1 850	39.9	<1
r-Me$_2$Si(Ind)$_2$ZrCl$_2$	32	1.0	4.81	1.14	1.3	14 200	87.9	5.0
	33	1.4	2.47	0.58	1.5	11 750	76.4	5.5
	34	0.9	0.99	0.23	0.08	1 000	70.3	<1
	35	1.6	0.95	0.22	0.09	600	67.6	<1
	36	1.7	0.43	0.10	2.0	12 900	42.0	6.3
	37	2.5	0.23	0.054	0.04	200	33.4	<1
r-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$	38	1.0	2.21	0.52	0.6	6 150	78.5	2.2
	39	1.0	1.16	0.27	0.4	4 500	70.2	1.4
	40	1.0	0.60	0.14	0.5	5 050	55.8	1.5
	41	2.0	0.24	0.057	0.4	2 250	43.6	1.2
r/m-Me$_2$C(3-Me-Ind)$_2$ZrCl$_2$[d]	42	1.7	1.04	0.25	2.0	12 600	62.1	6.7
r-Me$_2$C(3-Me$_3$S-Ind)$_2$ZrCl$_2$	43	1.7	2.28	0.54	1.8	11 600	81.6	6.7
	44	1.7	0.99	0.23	1.6	10 200	71.3	5.6
	45	1.7	0.41	0.096	2.0	12 900	43.8	6.2

[a] Polymerization conditions: toluene = 100 mL, Al/Zr = 1000 (mol/mol), T = 50 °C, total pressure = 1.1 atm, flow rate of (E + P) mixture = 1.5 L/min, and polymerization time = 15 min. [b] Feed ratio (mol/mol). [c] From ^{13}C NMR analysis. [d] A *rac/meso* $^2/_1$ mixture was used.

Table 5. ^{13}C NMR Characterization of E/P Copolymers Prepared with Racemic Stereorigid Metallocene and MAO as the Catalytic System

metallocene	sample no.[a]	f[b] (mol/mol)	(E)$_{\text{copolym}}$[c] (mol %)	PPP	PPE	EPE	PEP	PEE	EEE	isoindex[d] (%)	regioirr.[e] (%)
r-Me$_2$C(Ind)$_2$ZrCl$_2$	23	1.33	80.3	0.0000	0.0304	0.1663	0.0431	0.2801	0.4801	n.d.[f]	n.d.[f]
	24	0.61	65.4	0.0232	0.1142	0.2084	0.1270	0.2988	0.2284	75.9	n.d.[f]
	25	0.30	50.0	0.0996	0.2392	0.1908	0.2085	0.1985	0.0635	77.5	n.d.[f]
	26	0.28	50.9	0.0996	0.1948	0.1962	0.2026	0.2274	0.0792	71.0	n.d.[f]
	27	0.13	30.2	0.3166	0.2677	0.1136	0.2030	0.0871	0.0120	76.5	1.33
r-EBIZrCl$_2$	28	0.55	86.9	0.0000	0.0160	0.1148	0.0181	0.2014	0.6497	n.d.[f]	n.d.[f]
	29	0.25	70.7	0.0199	0.0743	0.1988	0.0922	0.3121	0.3029	85.5	n.d.[f]
	30	0.096	55.5	0.0857	0.1624	0.1965	0.1738	0.2623	0.1193	83.0	0.86
	31	0.049	39.9	0.2224	0.2377	0.1406	0.1963	0.1608	0.0422	83.1	n.d.[f]
r-Me$_2$Si(Ind)$_2$ZrCl$_2$	32	1.14	87.9	0.0000	0.0125	0.1085	0.0193	0.2128	0.6468	n.d.[f]	n.d.[f]
	33	0.58	76.4	0.0000	0.0396	0.1967	0.0544	0.3043	0.4051	n.d.[f]	n.d.[f]
	34	0.23	70.3	0.0179	0.0792	0.2003	0.1077	0.3179	0.2770	n.d.[f]	n.d.[f]
	35	0.22	67.6	0.0412	0.0952	0.1879	0.1006	0.2947	0.2803	82.9	n.d.[f]
	36	0.10	42.0	0.1909	0.2170	0.1725	0.2167	0.1625	0.0404	87.8	n.d.[f]
	37	0.054	33.4	0.3039	0.2361	0.1263	0.2080	0.1023	0.0234	89.6	0.53
r-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$	38	0.52	78.5	0.0000	0.0399	0.1748	0.0555	0.2893	0.4404	n.d.[f]	n.d.[f]
	39	0.27	70.2	0.0084	0.0709	0.2188	0.0935	0.3279	0.2805	n.d.[f]	n.d.[f]
	40	0.14	55.8	0.0540	0.1443	0.2434	0.1976	0.2532	0.1074	100	n.d.[f]
	41	0.057	43.6	0.1543	0.2189	0.1911	0.2337	0.1599	0.0421	100	none
r/m-Me$_2$C(3-Me-Ind)$_2$ZrCl$_2$[g]	42	0.25	62.1	0.0142	0.1050	0.2599	0.1351	0.3043	0.1814	n.d.[f]	none
r-Me$_2$C(3-Me$_3$Si-Ind)$_2$ZrCl$_2$	43	0.54	81.6	0.0000	0.0362	0.1480	0.0296	0.2703	0.5159	n.d.[f]	n.d.[f]
	44	0.23	71.3	0.0145	0.0794	0.1927	0.0800	0.3166	0.3169	69.7	n.d.[f]
	45	0.096	43.8	0.1595	0.2360	0.1662	0.1841	0.1881	0.0662	64.5	none

[a] The numbers of the samples are those of the corresponding runs. [b] E/P feed ratio (mol/mol) in liquid phase. [c] From triad distribution as E = PEP + EEP + EEE. [d] Calculated as $T_{\beta\beta}(\text{mm})/[T_{\beta\beta}(\text{mm}) + T_{\beta\beta}(\text{mr} + \text{rr})]$ (for nomenclature, see Experimental Section). [e] Calculated according to Randall[20] as $[100(^1/_2S_{\alpha\beta} + {}^1/_2S_{\beta\gamma})/(S_{\alpha\alpha} + {}^1/_2S_{\alpha\beta} + S_{\beta\beta} + {}^1/_2S_{\beta\gamma} + S_{\gamma\gamma} + {}^1/_2S_{\gamma\delta})]$ from 100.13 MHz ^{13}C NMR spectrum[21]. [f] Not determined. [g] A *rac/meso* $^2/_1$ mixture was used.

ents of the π ligands in determining the reactivity ratios of E/P copolymerizations, the parent metallocenes without substituents on the indenyl ligands were studied under the same experimental conditions. r-Me$_2$C(Ind)$_2$ZrCl$_2$, r-EBIZrCl$_2$, and r-Me$_2$Si(Ind)$_2$ZrCl$_2$ were compared with r-Me$_2$C(3-t-Bu-Ind)$_2$ZrCl$_2$, r-EBDMIZrCl$_2$, and r-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$, respectively. Results of copolymerizations are reported in Table 4, and triad distributions from ^{13}C NMR analysis are in Table 5.

A first-order Markovian model was applied to fit the experimental data.[28] The values of r_1 and r_2, their products, and the confidence intervals from the least squares at the minimum point are in Table 6: the reliability of the values detected for the reactivity ratios is definitely satisfactory.

r-EBIZrCl$_2$ and r-Me$_2$Si(Ind)$_2$ZrCl$_2$ were already investigated by various authors, and data of r_1 and r_2, available in the literature, are collected in Table 7. Although they were calculated through different methods, most of them are substantially in line with the results presented in this manuscript.

Data of Table 6 show that stereorigid racemic metallocenes without substituents on the indenyl ligands give rise to relatively low products of reactivity ratios

Table 6. Reactivity Ratios for E/P Copolymerizations with Racemic Stereorigid Metallocenes and MAO as the Catalytic System

metallocene	$r_1 \pm \delta r_1$	$r_2 \pm \delta r_2$	$r_1r_2 \pm \delta(r_1r_2)$[a]	LS_{tot}
r-$Me_2C(Ind)_2ZrCl_2$	2.30 ± 0.19	0.21 ± 0.02	0.48 ± 0.09	0.019
r-$EBIZrCl_2$	9.3 ± 0.9	0.057 ± 0.010	0.53 ± 0.14	0.019
r-$Me_2Si(Ind)_2ZrCl_2$	5.8 ± 0.6	0.088 ± 0.015	0.51 ± 0.14	0.051
r-$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$	5.9 ± 0.4	0.045 ± 0.006	0.27 ± 0.05	0.010
r/m-$Me_2C(3\text{-}Me\text{-}Ind)_2ZrCl_2$[b]	n.d.[c]	n.d.[c]	0.20[d]	n.d.[c]
r-$Me_2C(3\text{-}Me_3Si\text{-}Ind)_2ZrCl_2$	7.6 ± 0.7	0.081 ± 0.017	0.62 ± 0.19	0.011

[a] $\delta(r_1r_2) = r_1\delta r_2 + r_2\delta r_1$. [b] A *rac/meso* $^2/_1$ mixture was used. [c] Not determined. [d] Calculated according to Carman et al.[30]

Table 7. Reactivity Ratios for E/P Copolymerizations with Stereorigid Metallocenes and MAO as the Catalytic System (from literature data)

metallocene	*T* (°C)	r_1	r_2	r_1r_2	ref
r-$EBIZrCl_2$	50	6.61	0.06	0.40	31
	50	2.57	0.39	1	8c
	40	5.34−8.86	0.09−0.13	0.60−0.71	8d
	25	6.26	0.11	0.69	31
	20	7.1	0.07	0.50	4f
	1	5.4	0.09	0.49	4f
	0	5.2	0.14	0.73	32
r-$EBTHIZrCl_2$	50	10.4	0.048	0.49	4h[a]
	50	2.9	0.28	0.81	8c
	40	10.6−12.8	0.072−0.097	0.76−0.97	33
r-$Me_2Si(Ind)_2ZrCl_2$	40	4.23	0.12	0.52	8d
	25	$r_{11} = 4.1$[b]	$r_{12} = 0.065$[b]		29
		$r_{21} = 3.9$[b]	$r_{22} = 0.153$[b]		
	20	1.31	0.36	0.47	4b
r-$Me_2Si(H_4Ind)_2ZrCl_2$	50	6.39	0.13	0.83	34
	20	12.4	0.08	0.99	4c
r-$Me_2C(H_4Ind)_2ZrCl_2$	50	4.95	0.14	0.72	34

[a] Values obtained applying the first-order Markovian model to triads published by Galimberti et al.[4h] for samples with a propene content from about 15 to about 50 mol %. [b] Second-order Markovian parameters.

in E/P copolymerizations, definitely lower than 1. By taking into account the values obtained with the hydrogenated homologues, *r*-$EBTHIZrCl_2$, *r*-$Me_2Si(H_4Ind)_2ZrCl_2$, and *r*-$Me_2C(H_4Ind)_2ZrCl_2$, collected in Table 7, this statement seems to have a general validity.

Moreover, the E/P copolymerizations promoted by these metallocenes are characterized by similar values of r_1 as well as of r_2, that are relatively low and pretty usual as compared to the values reported in the literature for metallocene-based copolymerizations.[19,27] A more detailed observation of the data of Table 6 and Table 7 showed that the metallocene with the isopropylidene bridge gives rise to a slightly lower r_1 and a slightly higher r_2.

In Figure 1, ^{13}C NMR spectra of samples 8 and 27, from *r*-$Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$ and *r*-$Me_2C(Ind)_2ZrCl_2$, respectively, selected as typical representatives of the two classes of metallocenes, are shown. In Figure 2, the (relative) concentration of EEE and PPP homotriads is plotted as a function of the ethene content for copolymers from the same metallocenes.

We have reported the curves of $Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$ to show that metallocenes that promote copolymerizations with high r_1r_2 allow the simultaneous presence of homosequences of both the comonomers, over a broad range of chemical composition.

E/P copolymerizations were carried out with *r*-$Me_2C(3\text{-}Me_3Si\text{-}Ind)_2ZrCl_2$ and a *rac/meso* mixture of $Me_2C(3\text{-}Me\text{-}Ind)_2ZrCl_2$ to investigate the influence on r_1 and r_2 of substituents other than the *tert*-butyl group in the 3 position of the indenyl ligands.

r-$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ was also studied in comparison with *r*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ and *r*-$Me_2Si(Ind)_2ZrCl_2$ to elucidate the role of substituents in positions 2 and 4 of the indenyl ligand, the methyl and the phenyl groups, respectively.

Copolymerization results, triad distributions of the copolymers and data for the reactivity ratios are in Tables 4, 5 and 6, respectively.

Similarly to the unsubstituted parent complexes, these metallocenes promote E/P copolymerizations described by a first-order Markovian model and characterized by r_1r_2 products lower than 1. In the case of $Me_2C(3\text{-}Me\text{-}Ind)_2ZrCl_2$, only a *rac/meso* mixture ($^2/_1$) was available. However, the low value obtained for the r_1r_2 product and the excess of the racemic isomer in the mixture allow one to assume that the *r*-$Me_2C(3\text{-}Me\text{-}Ind)_2ZrCl_2$ does not promote E/P copolymerizations with a high r_1r_2 product.

A general comparison among the reactivity ratios r_1 and r_2 of E/P copolymerizations promoted by either substituted or unsubstituted racemic metallocenes can be attempted by examining the data of Tables 3, 6, and 7, which are also presented in the bar chart of Figure 3.

In the case of metallocenes of the type $Me_2C(3\text{-}X\text{-}Ind)_2ZrCl_2$, the substituted complexes (i.e., X ≠ H) give rise to higher r_1 values than do the parent unsubstituted homologue. The highest r_1 is observed for the metallocene substituted with the *tert*-butyl group. On the contrary, the r_2 values obtained with the metallocenes with either H or *t*-Bu as the X substituent are similar to each other.

An increase of both r_1 and r_2 was obtained by introducing two methyl groups in positions 4 and 7 of *r*-$EBIZrCl_2$ and *r*-$EBTHIZrCl_2$. By comparing the data of *r*-$EBDMIZrCl_2$ and *r*-$EBDMTHIZrCl_2$,[26] it seems that the hydrogenation of the phenyl ring brings about a further dramatic increase or r_1, whereas r_2 only slightly decreases.

The reactivity ratios obtained with *r*-$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ are very similar to those of the unsubstituted

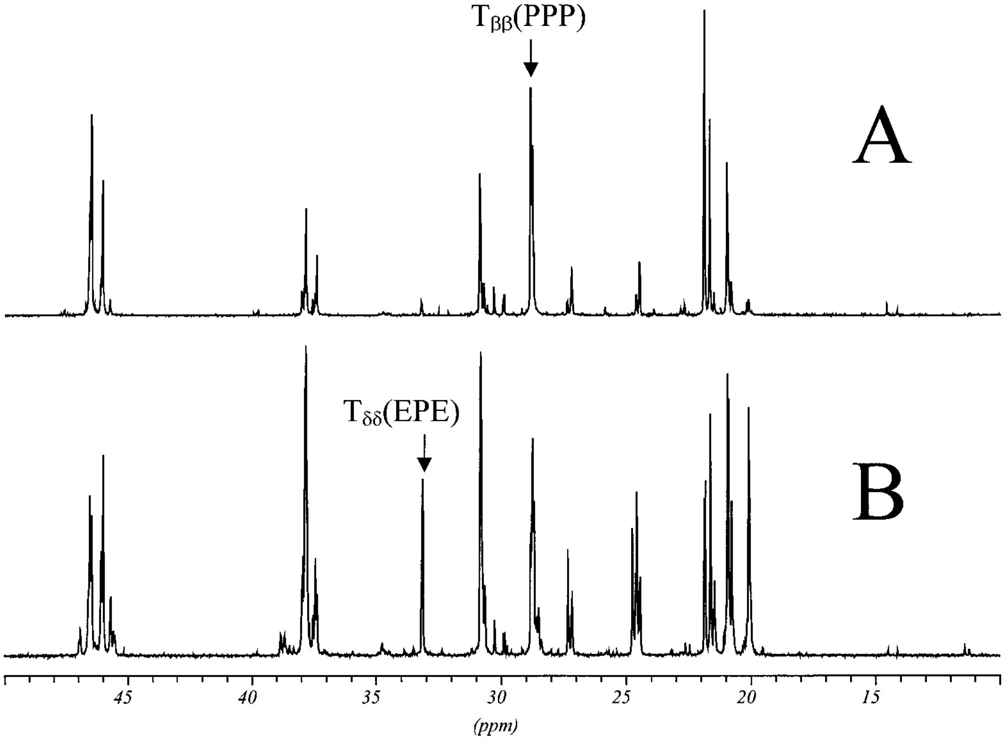

Figure 1. ^{13}C NMR spectra of sample 8 from *r*-Me$_2$C(3-*t*-Bu-Cp)$_2$ZrCl$_2$ (A) and sample 27 from *r*-Me$_2$C(Ind)$_2$ZrCl$_2$ (B).

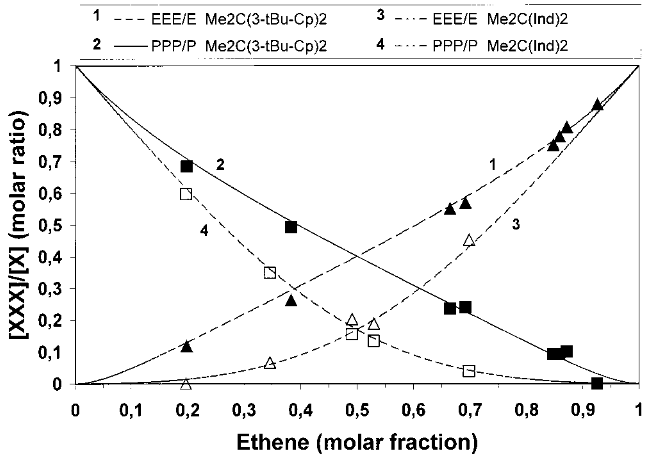

Figure 2. Relative concentration of homotriads, EEE/E and PPP/P, vs ethene content for copolymers from *r*-Me$_2$C(3-*t*-Bu-Cp)$_2$ZrCl$_2$ (curves 1 and 2) and *r*-Me$_2$C(Ind)$_2$ZrCl$_2$ (curves 3 and 4).

homologue. The introduction of a phenyl group in the 4 position has a minor effect on r_1, whereas it brings about a dramatic increase of r_2, of 1 order of magnitude.

Discussion

In a metallocene, the substituents on the π ligands bring about both electronic and steric effects. All of the substituents reported in this paper are electronic donating groups, although to a different extent. Their role played from the steric point of view depends not only on their bulkiness but also, for a given metallocene structure, on their position on the π ligands.

A general overview of the results show that in most cases the introduction of a substituent on the indenyl ligands causes an increase of r_1, which can be reasonably correlated with the enhanced steric demand of the metallocene.

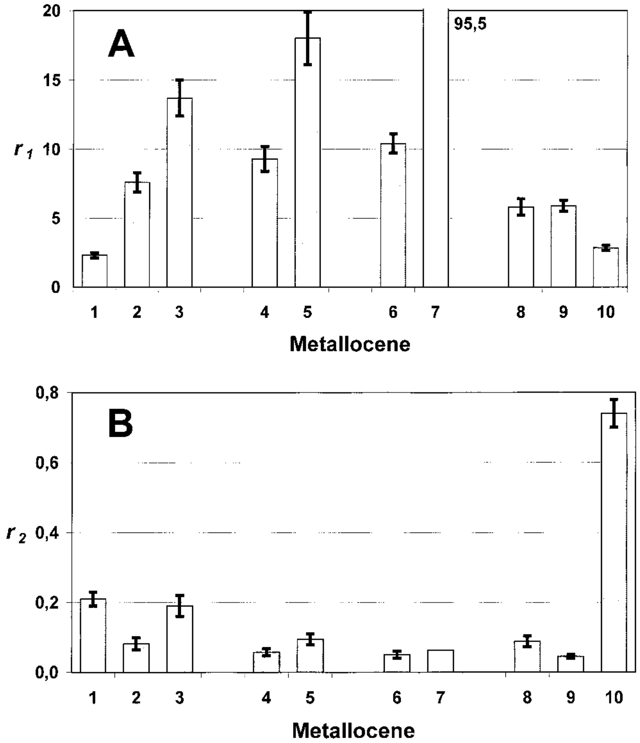

Figure 3. Reactivity ratios r_1 (A) and r_2 (B) of ethene/propene copolymerizations promoted by different families (see text) of stereorigid racemic isospecific metallocenes. (**1** = *r*-Me$_2$C(Ind)$_2$ZrCl$_2$, **2** = *r*-Me$_2$C(3-Me$_3$Si-Ind)$_2$ZrCl$_2$, **3** = *r*-Me$_2$C(3-*t*-Bu-Ind)$_2$ZrCl$_2$, **4** = *r*-EBIZrCl$_2$, **5** = *r*-EBDMIZrCl$_2$, **6** = *r*-EBTHIZrCl$_2$, **7** = *r*-EBDMTHIZrCl$_2$, **8** = *r*-Me$_2$Si(Ind)$_2$ZrCl$_2$, **9** = *r*-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$, and **10** = *r*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$).

The comparison of the r_1 and r_2 values afforded by *r*-Me$_2$Si(Ind)$_2$ZrCl$_2$ and by the substituted homologues demonstrate on one side that the substitution in the 2 position of the indenyl ligand, at least with a methyl group, has a negligible influence on the reactivity ratios of copolymerization and underscore on the other side

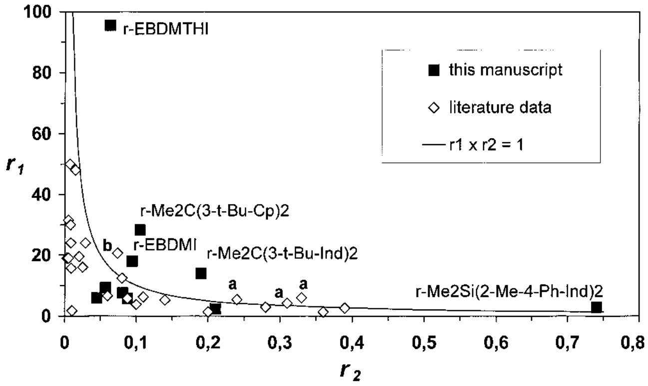

Figure 4. r_1 vs r_2 for ethene/propene copolymerizations from metallocene-based catalytic systems (see refs 19 and 27). For literature data, single values provided by the authors, for given polymerization conditions, are considered (for points a and b, see ref 35).

the role played by the phenyl group in position 4.

The high value of r_1r_2 obtained with both *r*-EBDMIZrCl$_2$ and with the hydrogenated homologue indicates that a difference of the electronic effects played by the methyl group on an aromatic or hydrogenated C-6 ring, if any, has no influence on the comonomer distribution.

The results achieved with the metallocenes substituted in position 4 of the indenyl ligands seem to indicate that this is a strategic position to promote an increase of r_1r_2, at least when the indenyl ligands have a dimethylsilylene or an ethylene bridge: even a methyl group can be effective. Moreover, an increase of not only r_1r_2 but also of r_2 can be observed by comparing *r*-EBIZrCl$_2$ with *r*-EBDMIZrCl$_2$ and *r*-EBTHIZrCl$_2$ with *r*-EBDMTHIZrCl$_2$.

In the case of metallocenes of the type *r*-Me$_2$C(3-X-Ind)$_2$ZrCl$_2$, only the bulky *tert*-butyl group is able to favor a high product of the reactivity ratios, whereas the intramolecular comonomer distributions promoted by the other two substituted metallocenes (X = Me and Me$_3$Si) and by the unsubstituted homologue are substantially similar. To explain the low r_1r_2 afforded by *r*-Me$_2$C(3-Me$_3$Si-Ind)$_2$ZrCl$_2$, the higher length of the C−Si bond, with respect to that of the C−C, can be taken into account. The higher flexibility of the C−Si bond is likely to result in a substantial reduction of the steric hindrance of the trimethylsilyl substituent, which is moved further apart from the catalytic center.[10]

The low effectiveness of the 3 position in metallocenes of the type *r*-Me$_2$C(3-X-Ind)$_2$ZrCl$_2$ could also be attributed to the larger dihedral angle between the indenyl planes allowed by the isopropylidene bridge (70−75°; see Resconi et al.[10]), with respect to those of dimethylsilylene (60.2°) and ethylene (60.4°), which would allow an easier accessibility of propene to the catalytic center.

The high r_1r_2 products presented in this manuscript are quite an unusual event in the field of E/P copolymerizations from single-center catalytic systems, as shown by the graph of Figure 4, where r_1 is plotted versus r_2 on the basis of the data available in the literature.[35]

It is worth observing that the stereorigid racemic sterically hindered metallocenes that are suitable candidates to promote E/P copolymerizations with $r_1r_2 > 1$ have different catalytic activities in the homopolymerization of ethene[38] and propene, prepare polypropenes with different degrees of regio- and stereoregularities,[39] and show a different reactivity for the 1-olefin.[40] The comonomer distribution in E/P copolymers seems thus to be the only common feature.

A working hypothesis for a qualitative interpretation of these experimental findings is proposed as follows.

As already anticipated elsewhere,[5,19] the formation of sequences of ethene and 1-olefin could be correlated with the energy involved in the whole process that leads to the insertion of the comonomer, the approach to the catalytic center, and the following insertion into the metal−carbon bond. It is evident from the r_1 and r_2 values that the ethene insertion is preferred when both ethene and propene are the last inserted units. However, the relative reactivity of propene versus ethene increases when propene is the last inserted unit. As a matter of fact, $r_1r_2 > 1$ implies that $k_{22}/k_{21} > k_{12}/k_{11}$. This means that, when moving from ethene to propene as the last inserted unit, the propene insertion is less disfavored, from the energetic point of view, with respect to the ethene one. We attribute this to the highly demanding steric situation brought about by the inserted 1-olefin.

The results reported above underscore the role played by the steric effects and privilege a tentative interpretation of the reactivity ratios based thereupon. Furthermore, indications can be drawn on the key positions of the π ligands for emphasizing the effect of the substituents on the reactivity ratios of copolymerization.

A correct interpretation of the results should however also take into account the role played by the electronic effects, that could to an extent be responsible, for example, for the different values of r_1 and r_2 detected in the series of the racemic substituted metallocenes. As a matter of fact, ethene and 1-olefin are definitely different from both the steric and the electronic point of view. Our research will proceed moving from this working hypotheses and, above all, collecting as much reliable experimental data as possible.

Experimental Section

General Procedures and Materials. All operations, from purification and storage of chemicals to manipulations of organometallic compounds and synthesis of polymers, were carried out under dry nitrogen atmosphere using the standard Schlenk techniques.

Toluene (Carlo Erba RPE), used as solvent, was deoxygenated by bubbling nitrogen, dried over CaCl$_2$, filtered, refluxed for 8 h over Al(isobutyl)$_3$, and distilled.

Polymerization grade ethene and propene gases were received from Montell Ferrara plants.

The E/P mixtures were prepared in a 5 L steel cylinder, filled with quantities of the two gases small enough to prevent their condensation. The composition of the gaseous mixture, in the cylinder, as inlet and outlet streams of the reactor, was controlled through GC analysis.

MAO (Witco, 10% w/w in toluene) was used without further purification.

r-Me$_2$C(3-*t*-Bu-Cp)$_2$ZrCl$_2$,[41] *r*-Me$_2$C(3-*t*-Bu-Ind)$_2$ZrCl$_2$,[10,41] *r*-EBDMIZrCl$_2$,[11c] *r*-EBDMTHIZrCl$_2$,[12] *r*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$,[13] *r*-Me$_2$C(Ind)$_2$ZrCl$_2$,[41] *r*-Me$_2$Si(Ind)$_2$ZrCl$_2$,[16] *r*/*m*-Me$_2$C(3-Me-Ind)$_2$ZrCl$_2$,[41] *r*-Me$_2$C(3-Me$_3$Si-Ind)$_2$ZrCl$_2$,[10,41] and *r*-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$[13] were synthesized following the respective reported procedures.

r-EBIZrCl$_2$ was purchased from Witco.

Determination of the Concentration of the Polymerization Solutions. The vapor−liquid equilibrium for E/P/toluene mixtures was calculated from the Redlich−Kwong−Soave equations.[42] This set of thermodynamic equations was selected among those available in Aspen Plus (commercialized by Aspen Technology Inc., Release 9) on the basis of a comparison with the experimental results. The concentrations of the comonomers were hence calculated.

Copolymerizations. The copolymerizations were carried out at 50 °C in a 250 mL glass reactor equipped with a mechanical stirrer, a thermometer, and a pipe for monomer feeding and were kept in a thermostatic bath. First, 100 mL of toluene and the desired amount of MAO solution (Al/Zr = 1000 mol/mol) were introduced into the nitrogen-purged reactor. At the polymerization temperature, the nitrogen was removed and replaced with the monomer mixture, with a flow rate of 1.5 L/min. When the equilibrium pressure (80 mmHg of overpressure) was reached, the amount of the catalyst, dissolved in 5 mL of toluene in the presence of a small amount of MAO (Al/Zr = 10 mol/mol), was added to start the polymerization. During the reaction, the temperature was kept within ±0.2 °C. After 15 min, the polymerization was quenched by adding 1 mL of methanol, and the copolymer was precipitated with 300 mL of methanol acidified with HCl, filtered, washed, and dried in vacuo at 50 °C.

Analysis of Reagents and Products. *GC Analysis.* The E/P mixtures were analyzed using a Carlo Erba 4300 gas chromatograph, equipped with a 4 m, 6 × 4 mm, packed column in Aluminum, with silicon oil "C" at 20% on Celite 22 60−80 mesh as the stationary phase. A thermal conductivity detector was used.

NMR Analysis of Metallocenes. The isomeric purity of the metallocenes was checked by ^{1}H NMR using a DPX-200 Bruker spectrometer operating at 200.13 MHz in the Fourier transform mode at room temperature. The samples were prepared under dry nitrogen atmosphere, by dissolution of 5 mg of compound in 0.5 mL of $CDCl_3$ or CD_2Cl_2. The peak of the residue undeuterated solvent (7.25 and 5.32 ppm for $CDCl_3$ and CD_2Cl_2 respectively) was used as the reference. Each spectrum was acquired with a 15° pulse and 2 s of delay between pulses. About 32 transients were stored in 16K data points using a spectral window of 2000 Hz.

NMR Analysis of Copolymers. The chemical composition and the microstructure of the copolymers were investigated by ^{13}C NMR analysis. The spectra were recorded on a DPX-200 Bruker spectrometer operating at 50.32 MHz in the Fourier transform mode at 120 °C. The peak of the $S_{\delta\delta}$ carbon at 29.9 ppm (nomenclature according to Carman et al.[30]) was used as reference. The samples were prepared by dissolution of 40 mg of copolymer in 0.5 mL of 1,1,2,2-tetrachloroethane-d_2 at 120 °C. Each spectrum was acquired with a 90° pulse, 12 s of delay between pulses, and CPD (waltz16) to remove ^{1}H−^{13}C coupling. About 5000 transients were stored in 32K data points using a spectral window of 3000 Hz.

To determine the regioirregularities content, some samples were also analyzed using a DPX-400 Bruker spectrometer operating at 100.61 MHz. About 2000 transients were stored in 32K data points using a spectral window of 6000 Hz.

The molar mm% was calculated through the following equation:

$$\text{mm\%} = 100 \times T_{\beta\beta}(\text{mm})/[T_{\beta\beta}(\text{mm}) + T_{\beta\beta}(\text{mr} + \text{rr})]$$

Triad distribution was calculated according to that given in Kakugo et al.,[25] applying the method reported by Galimberti et al.[5]

Intrinsic Viscosity (IV). IV of copolymers was determined in tetrahydronaphthalene at 135 °C.

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References and Notes

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(22) In the previous publication[5] on *r*-$Me_2C(3\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$, we reported that "not even for PPP content as high as 55 mol % was it possible to detect the presence of stereoerrors" and that "the copolymers can be regarded as *bi*polymers composed of ethene and propene with regioregular propene units inserted in a single macromolecular chain with the same enantioface". Data of Table 2 show that regioerrors can be detected in samples having at least 80 mol % as propene content. However, their very low amount (0.9 mol %) allows to consider as substantially correct the definition of these copolymers as *bi*polymers.

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(27) For a collection of r_1 and r_2 available in the literature, see: refs 5j, 5x, and 6a in ref 5.

(28) It was already reported, by Fink[29] and by us,[4h,6b] that metallocenes of the $XInd_2MR_2$ type (X = ethene, Me_2Si, Me_2C), with either aromatic or hydrogenated C-6 rings fused on the Cp group, promote E/P copolymerizations that can be better described by a second-order Markovian model. *r*-EBI$ZrCl_2$, *r*-$Me_2Si(Ind)_2ZrCl_2$, and *r*-$Me_2C(Ind)_2ZrCl_2$ are among these metallocenes. However, the difference with the results given by a first-order Markovian model is small enough to consider the r_1 and r_2 shown in Table 6 correct for describing the behavior of the copolymerization and suitable for the scope of this paper.

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(35) Examples of E/P copolymerizations with $r_1r_2 > 1$ from single-center metallocene-based catalytic systems were reported by Chien and He,[8c] who obtained $r_1r_2 = 1.52$ with Cp_2HfCl_2/MAO (point b in Figure 4), by Lehtinen and Löfgren,[8d] who found $r_1r_2 = 2.51-2.75$ with Ind_2ZrCl_2/MAO, and by Kravkenko and Waymouth,[4f] who published $r_1r_2 = 1.3$ from (2-Ph-Ind)$_2ZrCl_2$/MAO and $r_1r_2 = 1.3-1.9$ from $\{2\text{-}[(CF_3)_2\text{-}Ph]\text{-}Ind\}_2ZrCl_2$/MAO (points a in Figure 4). However, we have not been able to reproduce these results by performing the E/P copolymerizations with the same catalytic systems, when available. We have already reported[5] that with Cp_2HfCl_2/MAO we found $r_1r_2 = 0.55$. With Ind_2ZrCl_2 we detected $r_1r_2 = 0.8$.[36] As a matter of fact, Lehtinen and Löfgren stated that "the block structure of the copolymer might appear from two or more active centres in the catalyst". With (2-Ph-Ind)$_2ZrCl_2$, we observed, in both solution and slurry, r_1r_2 values lower than 1.[37]

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