Copolymerization Behavior of Unbridged Indenyl Metallocenes: Substituent Effects on the Degree of Comonomer Incorporation

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ABSTRACT: The copolymerization of ethylene and 1-hexene with a variety of unbridged indenylmetallocenes was investigated and compared to unbridged bis(indenyl)zirconium dichloride and bis(cyclopentadienyl)zirconium dichloride as well as *ansa*-bridged *rac*-ethylenebis(indenyl)zirconium dichloride ($EBIZrCl_2$). The unbridged bis(2-phenylindenyl)zirconium dichloride showed higher selectivity for the incorporation of 1-hexene than the bridged *rac*-ethylenebis(indenyl)zirconium dichloride and much higher 1-hexene incoporation than the unbridged bis(indenyl)zirconium dichloride and bis(cyclopentadienyl)zirconium dichloride. Both ligands appear to be important since the 1-hexene incorporation of the mixed ligand compound (cyclopentadienyl)(2-phenylindenyl)zirconium dichloride is much lower than that of bis(2-phenylindenyl)zirconium dichloride. For unbridged bis(indenyl)metallocenes, the nature of the substituent in the 2-position plays an important role in comonomer selectivity: bis(2-methylindenyl)zirconium dichloride and bis(2-phenylethynylindenyl)zirconium dichloride exhibit much higher 1-hexene incorporation than bis(indenyl)zirconium dichloride but lower than bis(2-phenylindenyl)zirconium dichloride.

Introduction

Ethylene copolymers of higher α-olefins such as 1-butene, 1-hexene, and 1-octene are industrially important materials. In 1996, worldwide production of ethylene/α-olefin copolymers exceeded 24 million metric tons[1] or approximately 30% of the market share of polymer products from ethylene. Control over the incorporation and distribution of α-olefins in ethylene/α-olefin copolymers is industrially important for the control of polymer properties such as melting point, glass transition temperature, tensile strength, flexibility, and processability.[2−11] In general, the short-chain branching introduced into polyolefins by α-olefin comonomers results in lower melting points, lower crystallinity, and lower density, making these polymer films more flexible and processable.

For both the production and study of ethylene/α-olefin copolymers, metallocenes offer several advantages over traditional Ziegler−Natta catalysts. In contrast to Ziegler−Natta catalysts, metallocene systems give narrow molecular weight distributions, high comonomer incorporation, and narrow compositional distributions.[12] In addition, the relationship between copolymerization behavior and catalyst structure is more readily investigated with metallocene catalysts and can provide insight into the mechanism of olefin polymerization.

Studies of metallocene-catalyzed copolymerization of ethylene with α-olefins ranging from C_3-C_{18} have been reported by several groups.[13−29] Incorporation of α-olefin comonomers has been studied as a function of ligand substitution pattern, interannular bridge, and metal. One common observation from these studies is that *ansa*-metallocenes with one- or two-membered bridges between the ligands incorporate α-olefin comonomers better than unbridged metallocenes.[21,22,29] Other studies have shown that benzannelation of bridged indenyl ligands increases reactivity toward α-olefins.[23]

In this paper, we show that certain classes of unbridged indenyl metallocenes, in particular the unbridged bis(2-phenylindenyl)zirconium dichloride, $(2\text{-PhInd})_2ZrCl_2$ (**1**), exhibit very high selectivity for hexene incorporation in ethylene/1-hexene copolymerizations when activated by methylaluminoxane (MAO). In a previous contribution, we observed that **1**/MAO shows high reactivity toward propylene in ethylene/propylene copolymerization.[30] In this paper we report a systematic study on the influence of cyclopentadienyl substitutents on the ethylene/1-hexene copolymerization behavior of a family of unbridged zirconocenes activated by MAO including: **1** as well as (cyclopentadienyl)(2-phenylindenyl)zirconium dichloride, $(Cp)(2\text{-PhInd})ZrCl_2$, **2**, bis(2-phenylethynylindenyl)zirconium dichloride, $(2\text{-PhEthInd})_2ZrCl_2$, **3**, and bis(2-methylindenyl)zirconium dichloride, $(2\text{-MeInd})_2ZrCl_2$, **7**. The copolymerization reactivity ratios, comonomer content, and comonomer distributions produced by these zirconocenes are discussed and compared to those observed with *rac*-ethylenebis(indenyl)zirconium dichloride, $EBIZrCl_2$, **4**, bis(indenyl)zirconium dichloride, Ind_2ZrCl_2, **5**, and bis(cyclopentadienyl)zirconium dichloride, Cp_2ZrCl_2, **6**.

Results

Seven metallocenes were studied for their ethylene/1-hexene copolymerization behavior (Figure 1). Ethylene/1-hexene copolymerizations with metallocenes **4**−**7** have been reported in the literature[22,25,28,31] but were reproduced under our conditions for comparison. Copolymerizations were carried out over a variety of comonomer feed ratios to obtain copolymers with a wide range of ethylene incorporation; the results are reported in Table 1. The experiments were carried out at low conversions to optimize the determination of the copolymerization parameters. These conditions are likely to lead to large uncertainties in the productivities obtained.

Metallocene **1** showed the highest molecular weights with distributions that were monomodal but broader than expected for a single-site metallocene catalyst ($M_w/M_n = 2.8-4.9$). Metallocene **2** also produced high molecular weight copolymer; however, this polymer had a very broad molecular weight distribution ($M_w/M_n = 7.0$) due to low molecular weight tailing. This may be an

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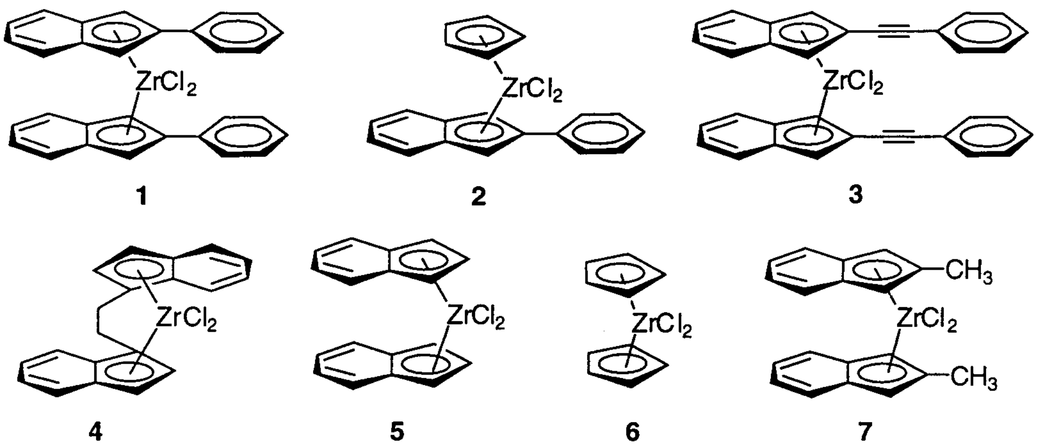

Figure 1. Metallocenes investigated for ethylene/hexene copolymerization.

Table 1. Ethylene/Hexene Copolymerization with Metallocene/MAO System

metallocene	run	[Zr] (μmol)	X_e/X_h[a]	yield (g)	prod[b] ($\times 10^3$)	(E)$_{copolymer}$ (mol %)	% hexene conversion	M_w ($\times 10^3$) (g/mol)	M_n ($\times 10^3$) (g/mol)	M_w/M_n
1	1	1.60	0.078	0.504	11.8	39.0	1.1	142	50.3	2.8
	2	0.80	0.119	0.460	19.2	51.4	0.8	628	172	3.7
	3	0.80	0.163	0.936	39.0	55.9	1.5	500	102	4.9
	4	0.49	0.214	0.700	53.8	61.8	1.0	1169	369	3.2
	5	0.49	0.266	1.211	93.2	66.8	1.5	1192	322	3.7
2	6	3.00	0.030	0.418	6.97	68.6	0.5			
	7	3.00	0.035	0.359	5.98	74.0	0.3			
	8	3.00	0.042	0.862	14.4	78.1	0.7			
	9	1.50	0.068	3.863	85.8	82.4	2.5			
	10	1.50	0.111	0.732	24.4	87.4	0.3	856	349	7.0
3	11	1.50	0.057	0.347	6.94	47.0	0.7			
	12	2.25	0.058	0.641	14.2	48.8	1.2			
	13	1.50	0.080	0.846	16.9	56.9	1.4			
	14	1.50	0.112	0.563	18.7	65.1	0.7	882	306	2.9
	15	1.50	0.163	0.692	34.6	78.0	0.6			
4	16	4.50	0.067	2.493	27.7	52.7	4.4			
	17	1.50	0.112	1.298	51.9	66.7	1.6	57.5	25.2	2.3
	18	4.50	0.171	1.828	40.6	76.6	1.6			
	19	1.00	0.214	1.662	62.3	77.4	1.4			
	20	0.75	0.275	0.349	17.4	80.8	0.2			
5	21	1.00	0.022	0.393	9.83	76.0	0.4			
	22	2.00	0.026	0.654	10.9	78.8	0.5	492	194	2.5
	23	1.00	0.030	0.260	19.5	82.9	0.2			
	24	1.25	0.034	0.842	25.3	84.0	0.5			
	25	1.00	0.040	0.680	51.0	89.2	0.3			
6	26	4.50	0.045	0.315	3.50	73.8	0.3	32.2	14.9	2.2
	27	4.50	0.080	1.046	7.75	79.4	0.8			
7	28	1.60	0.057	0.922	28.8	47.4	1.8			
	29	0.80	0.080	0.265	16.6	57.2	0.4			
	30	0.80	0.119	1.988	186	69.0	2.3	983	279	3.5
	31	0.80	0.165	1.091	68.2	77.3	0.9			

[a] Monomer feed ratio: X_e = mole fraction of ethylene, X_h = mole fraction of hexene. [b] Productivity = kg of polymer/(mol of Zr h).

indication that the catalyst is decomposing during polymerization. Metallocenes **3** and **7** gave high molecular weight polymers and molecular weight distributions of 2.9 and 3.5, respectively, while complexes **4**–**6** produced copolymers with lower molecular weights and narrower molecular weight distributions (M_w/M_n = 2.2–2.5).

Comonomer feed compositions were determined using an empirical equation reported by Spitz and co-workers.[32] Copolymer compositions and *n*-ad distributions calculated from ^{13}C NMR using the method of Cheng[33] are reported in Table 2. Comparison of copolymers of the same ethylene content prepared at different feed ratios by different metallocenes shows similar sequence distributions for each of the polymers. Reactivity ratios for each run were calculated from these experimental triad distributions according to the following two equations.[34]

$$r_e = \frac{(2[\mathrm{EEE}] + [\mathrm{EEH}])}{(2[\mathrm{EHE}] + [\mathrm{HHE}])\frac{X_e}{X_h}}$$

$$r_h = \frac{(2[\mathrm{HHH}] + [\mathrm{HHE}])\frac{X_e}{X_h}}{(2[\mathrm{EHE}] + [\mathrm{HHE}])}$$

The reactivity ratios were also calculated over all triads for all feed ratios simultaneously by optimizing the variation of the reaction probabilities P_{ij} (the probability that a monomer j will add to a polymer chain ending in monomer i) until the best fit between experimental triads and those calculated from the first-order Markov model was obtained. Reactivity ratios are calculated by this method with the following two equa-

Table 2. ^{13}C NMR Characterization of E/H Copolymers Prepared with Metallocene/MAO

		f	$(E)_{copolymer}$			triads[a]					
metallocene	run	(mol/mol)	(mol %)	HHH	HHE + EHH	EHE	HEH	HEE + EEH	EEE	r_e	r_h
1	1	0.078	39.0	0.196	0.253	0.161	0.162	0.156	0.069	6.5	0.088
	2	0.119	51.4	0.125	0.186	0.175	0.131	0.200	0.177	8.7	0.097
	3	0.163	55.9	0.079	0.160	0.202	0.120	0.244	0.191	6.8	0.092
	4	0.214	61.8	0.069	0.127	0.186	0.108	0.268	0.248	7.2	0.114
	5	0.265	66.8	0.041	0.105	0.186	0.070	0.279	0.331	7.4	0.105
2	6	0.030	68.6	0.028	0.072	0.213	0.081	0.267	0.325	62.3	0.008
	7	0.036	74.0	0.021	0.055	0.185	0.069	0.268	0.393	69.7	0.008
	8	0.042	78.1	0.000	0.052	0.167	0.049	0.257	0.467	74.1	0.006
	9	0.068	82.4	0.000	0.026	0.151	0.037	0.238	0.539	59.1	0.005
	10	0.111	87.4	0.000	0.012	0.114	0.018	0.152	0.698	58.3	0.006
3	11	0.057	47.0	0.152	0.198	0.180	0.118	0.228	0.125	15.2	0.051
	12	0.058	48.4	0.141	0.201	0.174	0.147	0.217	0.112	13.9	0.051
	13	0.080	56.9	0.063	0.159	0.209	0.115	0.253	0.192	13.9	0.039
	14	0.112	65.1	0.049	0.104	0.196	0.087	0.280	0.278	15.0	0.045
	15	0.163	78.0	0.000	0.048	0.172	0.051	0.307	0.439	18.5	0.020
4	16	0.067	52.7	0.094	0.140	0.239	0.169	0.234	0.115	11.3	0.035
	17	0.112	66.7	0.018	0.087	0.228	0.098	0.272	0.279	13.6	0.025
	18	0.171	76.6	0.004	0.093	0.192	0.078	0.288	0.331	11.7	0.036
	19	0.214	77.4	0.007	0.041	0.177	0.050	0.256	0.456	13.8	0.029
	20	0.275	80.8	0.000	0.022	0.170	0.019	0.229	0.551	13.4	0.017
5	21	0.022	76.0	0.013	0.044	0.183	0.053	0.255	0.442	123.7	0.004
	22	0.026	78.8	0.017	0.033	0.162	0.039	0.237	0.509	135.2	0.005
	23	0.030	82.9	0.056	0.016	0.098	0.015	0.213	0.459	180.5	0.016
	24	0.034	84.0	0.000	0.024	0.136	0.023	0.197	0.608	139.0	0.003
	25	0.040	89.2	0.000	0.000	0.108	0.000	0.184	0.639	167.5	0.000
6	26	0.045	73.8	0.000	0.030	0.232	0.112	0.295	0.331	42.8	0.003
	27	0.080	79.4	0.000	0.026	0.180	0.039	0.226	0.514	40.8	0.005
7	28	0.057	47.4	0.154	0.194	0.179	0.137	0.208	0.124	14.6	0.051
	29	0.080	57.2	0.090	0.152	0.186	0.112	0.240	0.212	15.9	0.050
	30	0.119	69.0	0.048	0.094	0.168	0.072	0.270	0.345	18.8	0.053
	31	0.165	77.3	0.026	0.049	0.152	0.048	0.247	0.477	20.7	0.047

[a] Triads do not sum to 1.00 for all runs. This reflects the experimental error in the calculation of triads from ^{13}C NMR.

Table 3. Reactivity Ratios for Ethylene/Hexene Copolymerizations

metallocene	N_{exp}[a]	X_e/X_h[b]	% E in polymer[c]	r_e[d,e]	r_h[d,e]	$r_e r_h$[d,f]	r_h/r_e ($\times 10^5$)
1	5	0.08–0.27	39–67	8 ± 1	0.09 ± 0.01	0.7 ± 0.1	1100
2	5	0.03–0.11	69–87	70 ± 10	0.006 ± 0.001	0.4 ± 0.1	9
3	5	0.06–0.16	47–78	17 ± 2	0.04 ± 0.01	0.7 ± 0.2	240
4	5	0.07–0.28	53–81	14 ± 2	0.027 ± 0.008	0.4 ± 0.1	190
5	5	0.02–0.04	76–89	149 ± 23	0.004 ± 0.006	0.5 ± 0.9	3
6	2	0.05–0.08	74–79	47 ± 7	0.003 ± 0.002	0.16 ± 0.09	6
7	4	0.06–0.16	47–77	19 ± 3.5	0.048 ± 0.003	0.9 ± 0.2	250

[a] Number of experiments used for determination of the average reactivity ratios. [b] Range of the ratios of mole fractions of ethylene and 1-hexene in the monomer feed. [c] Range of mol % E in the copolymers as determined by ^{13}C NMR. [d] Calculated by optimization of reaction probabilities from the triads over all N runs simultaneously (see ref 37). [e] Standard deviation calculated as $[(1/(N-1))\sum(r_{e,h(exp)} - r_{e,h(opt)})^2]^{1/2}$ where $r_{e,h(exp)}$ is the reactivity ratio calculated for the triads of an individual run and $r_{e,h(opt)}$ is the optimized reactivity ratio. [f] Standard deviation calculated as $(r_e r_h)[(\sigma r_e)^2 + (\sigma r_h)^2]^{1/2}$.

tions.[34]

$$r_e = \left(\frac{1}{P_{eh}} - 1\right)\frac{X_h}{X_e}$$

$$r_h = \left(\frac{1}{P_{he}} - 1\right)\frac{X_e}{X_h}$$

The optimized reactivity ratios are reported in Table 3.[35] All seven metallocenes showed a significantly higher reactivity toward ethylene as compared to 1-hexene. The product of reactivity ratios, $r_e r_h$, was between 0.16 and 0.9 in each case. As previously observed, the unbridged metallocenes bis(indenyl)zirconium dichloride (**5**) and bis(cyclopentadienyl)zirconium dichloride (**6**) exhibit very poor 1-hexene incorporation as manifested in high $r_e = 47-149$ and low $r_h = 0.003-0.004$. The ethylene/1-hexene copolymerization reactivity ratios determined for the bridged zirconocene EBIZrCl$_2$, **4**, under our conditions are consistent with literature values.[21] As previously observed, the bridged *rac*-ethylenebis(indenyl)zirconium dichloride (**4**) exhibited much higher 1-hexene incorporation than the unbridged bis(indenyl)zirconium dichloride (**5**), as manifested in the lower r_e and higher r_h values (Table 3). In contrast, substituting the two indene ligands of the unbridged metallocene **5** with phenyl groups in the 2-position gives the metallocene **1**, which shows comparable or slightly better 1-hexene incorporation compared to that of **4** (compare run 4 vs 19 in Table 1 and r_e r_h values in Table 3). The 1-hexene incorporation of the mixed-ligand metallocene **2** is also quite poor and comparable to that of Cp$_2$ZrCl$_2$ (**6**) (compare run 8 vs 26, Table 1; $r_e r_h$ values in Table 3).

For the unbridged indenyl series (**1**, **3**, **5**, **7**) introduction of a substituent on the 2-position has a significant effect on the ability to incorporate 1-hexene: metallocenes **3** and **7** incorporate 1-hexene much better than the unsubstituted **5** (compare runs 15, 22, and 31 of Table 1 or $r_e r_h$ values in Table 3) but not as well as the 2-phenyl-substituted metallocene **1** (run 2 vs 14 and 30, Table 1, or $r_e r_h$ values in Table 3).

Table 4. Selected Bonding Parameters for Metallocenes 1, 4, and 5

zirconocene	Zr−C (min−max) (Å)	Zr−Cl (av) (Å)	Cen−Zr−Cen (deg)	Cl−Zr−Cl (deg)	ref
1					
anti rotamer	2.465−2.622	2.433	131.3	95.44	44
syn rotamer	2.476−2.624	2.427	131.0	94.39	
4	2.438−2.624	2.388	125.3	99.09	51
5	2.478−2.616	2.440	128.3	94.71	52

Discussion

The incorporation of α-olefin comonomers is an important means of influencing the architecture and properties of ethylene/α-olefin copolymers. The use of metallocenes in these copolymerizations makes it possible to control both the degree of incorporation and to some extent the distribution of comonomers in the chain.[36−43] To design metallocenes rationally for these copolymerizations, it is useful to determine which structural features of metallocenes influence comonomer selectivity.

We have found that the unbridged metallocene, (2-PhInd)$_2$ZrCl$_2$, incorporates surprisingly high amounts of 1-hexene comonomer in ethylene/1-hexene copolymerizations. Previous studies comparing metallocenes such as Ind$_2$ZrCl$_2$ and Cp$_2$ZrCl$_2$ with *rac*-EBI have led to the suggestion that bridged metallocenes incorporate α-olefin comonomers more readily than unbridged metallocenes.[21,22] One explanation proposed for this phenomenon is that the larger coordination gap aperture of the bridged compounds allows the incoming α-olefin better accessibility to the zirconium center.[1,21,22] Our results with metallocenes **4**, **5**, and **6** are consistent with the literature observations that the bridged metallocene **4** incorporates 1-hexene more readily than the unbridged metallocenes **5** and **6**; however, systematic studies with the series of metallocenes **1**−**7** suggest that *the presence or absence of a bridging group may not be as important as the nature of the substituents for controlling the comonomer incorporation*.

The results of this study reveal that, among the metallocenes **1**−**7**, the unbridged (2-PhInd)$_2$ZrCl$_2$ (**1**) exhibits the highest tendency to incorporate 1-hexene. One crude measure of this selectivity is the ratio r_h/r_e (Table 3), which reveals that the reactivity toward 1-hexene follows the general trend **1** > **3**, **4**, **7** ≫ **2**, **5**, **6**. Thus, these results suggest that unbridged metallocenes can exhibit comonomer selectivity equal to or greater than that of analogous bridged metallocenes. As pointed out previously, introduction of a bridge has a significant influence on the ability to incorporate comonomer (compare **4** vs **5**); however, it is clear from this study that introduction of a 2-substituent can have an equal or even greater influence (compare **1** vs **5**).

Previous studies have invoked a structural argument to explain the better comonomer incorporation for the bridged metallocenes **4** relative to the unbridged **5**.[21,22] To assess the role of coordination geometry on the copolymerization behavior, selected structural parameters from the literature for **1**, **4**, and **5** are presented in Table 4. Two torsional isomers, *syn* and *anti* conformations, were found in the X-ray crystal structure of **1**;[44] parameters for both isomers are reported in Table 4. Analysis of the reported structural features for metallocenes **1**, **4**, and **5** reveals that bond lengths and angles for **1** are closer to those of **5** than to those of **4**. Steric arguments alone would predict, therefore, that the reactivity of **1** would be closer to **5** than **4**. The observation that **1** has much higher r_h and lower r_e than **5** implies that factors other than coordination gap aperture and ligand geometry are important for determining the reactivity of **1** toward α-olefins.

To further investigate the influence of the 2-phenyl substituent on comonomer reactivity, ethylene/1-hexene copolymerizations were carried out with the mixed ligand zirconocene **2**. The reactivity of **2** toward 1-hexene is more similar to the unsubstituted compound **6** than to **1**, which seems to indicate that the high reactivity of **1** toward 1-hexene arises from the additive effect of having both indenes substituted with a 2-phenyl group.

For the unbridged indenyl metallocenes, the presence and nature of the 2-substituent on the indene have a significant effect on the ability to incorporate comonomer. In this study, we have shown that the 2-substituted indenyl complexes **1**, **3**, and **7** all incorporate 1-hexene more readily than the unsubstituted complex **5**. Similar observations were reported for a variety of 2-alkyl-substituted unbridged indenylmetallocenes[45] as well as for **7** and bis(2-benzylindenyl)zirconium dichloride,[28] both of which showed unusually high comonomer incorporation. Consistent with the data from Yoon,[28] we find that **7** gives much better 1-hexene incorporation than **5**, but under our conditions, we calculate copolymerization parameters for **7** ($r_e = 19$, $r_h = 0.048$ compared to $r_e = 4.53$, $r_h = 0.15$[28])[46] that are roughly comparable to that of **4** and **3**.

The higher comonomer incorporation of the 2-phenyl-substituted **1** relative to the 2-methyl-substituted **7** (run 2 vs 30 and 3 vs 31 and Table 3) prompted us to speculate that the high comonomer incorporation may require a conjugated substituent in the 2-position. Consequently, we synthesized **3** and studied its copolymerization behavior.[47] Zirconocene **3** retains the extended conjugation of **1** but spaces the phenyl group farther from the coordination site of the catalyst. Ethylene/1-hexene copolymerization with **3** showed 1-hexene reactivity lower than that of **1**, comparable to that of **7**, but much higher than that of **5**. While steric arguments might predict that spacing the phenyl group farther from the coordination site would increase reactivity toward 1-hexene, the observed reactivity ratios suggest that *having the phenyl group closer to the coordination site increases the selectivity for 1-hexene*. Moreover, the similar copolymerization behavior of **3** and **7** suggests that any substituent larger than hydrogen is sufficient to improve the 1-hexene incorporation relative to **5**.

Although we do not fully understand the high comonomer incorporation by the unbridged metallocenes **1**, **3**, and **7**, one possible explanation is that the substituent in the 2-position affects the conformational dynamics for the activated unbridged metallocene. For unbridged metallocenes, conformational dynamics may be influenced by factors including identity of the counterion,[48] steric effects of the coordinated polymer chain, and substituents on the ligands. For the unbridged metallocene with no indenyl substituents, Ind$_2$ZrCl$_2$, many

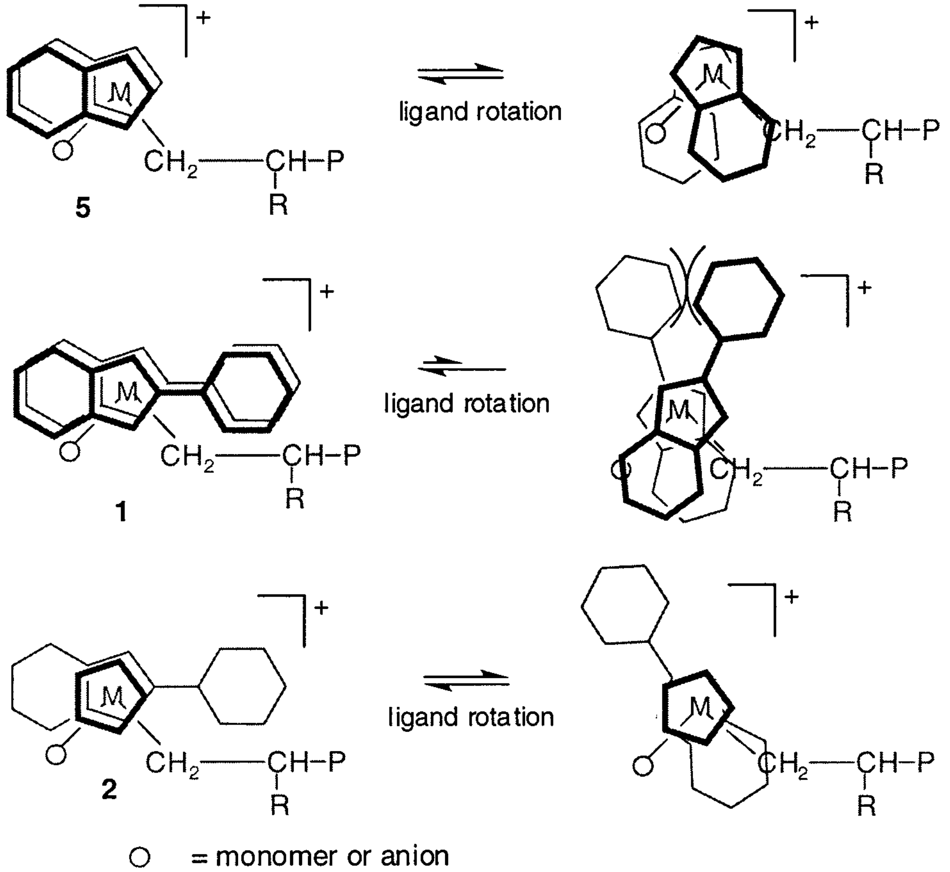

Figure 2. Possible rotamers of unbridged indenylmetallocenes.

conformations for the indenyl ligands of the active cation are imaginable, including those in which the indenyl ligands project out directly over the metal coordination site (Figure 2). Placing a large phenyl group in the 2-position of both indene ligands, such as in metallocene **1**, may sterically restrict conformations in which the indenyl groups block the metal coordination sites, thus making these sites more open for coordination of the larger comonomer. For metallocene **2**, the presence of a 2-phenyl substituent on only one ligand again makes accessible conformations with blocked coordination sites.

While conformational effects may in part explain the high comonomer reactivity by metallocene **1**, we suspect that having arenes near the metal coordination site also plays a role in comonomer coordination. This factor might explain the higher comonomer incorporation of **1** vs **3** and **7** as well as the higher comonomer incorporations observed for benzannelated bridged zirconocenes in ethylene/1-hexene copolymerization.[23]

Conclusions

$(2\text{-PhInd})_2ZrCl_2$ shows higher reactivity toward 1-hexene in ethylene/1-hexene copolymerization than the unbridged metallocenes Ind_2ZrCl_2 and Cp_2ZrCl_2 as well as the bridged *rac*-$EBIZrCl_2$. Substitution in the 2-position of unbridged bis(indenyl)zirconium dichloride complexes, in general, leads to higher comonomer incorporation as seen by high 1-hexene incorporation with $(2\text{-PhInd})_2ZrCl_2$, $(2\text{-MeInd})_2ZrCl_2$, and $(2\text{-PhEthInd})_2ZrCl_2$. The effect of the 2-phenyl substituent appears to be additive as demonstrated by the lower 1-hexene reactivity of $(Cp)(2\text{-PhInd})ZrCl_2$. Spacing the phenyl groups farther from the indene ligand, as in $(2\text{-PhEthInd})_2ZrCl_2$, results in slightly decreased 1-hexene reactivity. These reactivity differences may be at least partially explained by the phenyl groups decreasing the accessibility of conformations in which the metal coordination sites are blocked by the indene ligands. Further copolymerization studies with these metallocenes are underway.

Experimental Section

Materials. Standard Schlenk techniques and a Vacuum Atmospheres drybox were used in handling air- and moisture-sensitive compounds. The catalyst precursors bis(cyclopentadienyl)zirconium dichloride, **6**, and bis(indenyl)zirconium dichloride, **5**, were supplied by Witco. Bis(indenyl)zirconium dichloride was sublimed prior to use. *rac*-Ethylenebis(indenyl)zirconium dichloride, **4**, was supplied by Witco and recrystallized prior to use. Bis(2-phenylindenyl)zirconium dichloride,[44] **1**, and (cyclopentadienyl)(2-phenylindenyl)zirconium dichloride,[49] **2**, were prepared according to literature procedures. Bis(2-methylindenyl)zirconium dichloride, **7**, was prepared analogous to **1** and characterized by comparison to a literature procedure.[50] Polymerization grade ethylene (supplied by Matheson) and toluene were purified by passage through columns containing Q5 and alumina. Modified methylaluminoxane (MMAO type 4) was supplied as a toluene solution by Akzo Nobel and dried under vacuum to remove solvent and residual trimethylaluminum prior to use. 1-Hexene (97%) was dried over CaH_2, distilled, and degassed prior to use.

2-Phenylethynylindene. Phenylacetylene (1.86 g, 18.21 mmol) dissolved in diethyl ether (50 mL) was added to a solution of phenyllithium (1.8 M in cyclohexane−diethyl ether 70:30, 10.12 mL, 18.21 mmol) in diethyl ether (50 mL) at −78 °C. After warming to 22 °C and stirring for 1 h, 2-indanone (1.92 g, 18.21 mmol) was dissolved in diethyl ether (50 mL) and added dropwise at −78 °C. The reaction was warmed to 22 °C and stirred overnight. The reaction mixture was quenched with ice and washed with aqueous NH_4Cl. The aqueous layer was extracted with diethyl ether and dried. The residue was dissolved in toluene (50 mL) and refluxed with *p*-toluenesulfonic acid monohydrate (0.35 g, 1.82 mmol) for 4 h. After cooling to 22 °C the reaction was washed twice with aqueous $KHCO_3$, and the aqueous layer was extracted with diethyl ether. The combined organics were dried over magnesium sulfate, filtered, and concentrated on a solvent evaporator. Recrystallization from methanol gave the pure product. Yield: 2.75 g (70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.64 (s, 2H), 7.17 (s, 1H), 7.22−7.31 (m, 2H), 7.32−7.37 (m, 3H), 7.41 (d, 1H, $J = 7.4$ Hz), 7.45 (d, 1H, $J = 7.3$ Hz), 7.51−7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 42.7, 86.7, 94.1, 121.4, 123.3, 123.6, 125.7, 126.8, 127.3, 128.2, 128.3, 131.5, 137.3. 143.0, 144.1.

Bis(2-phenylethynylindenyl)zirconium Dichloride (3). *n*-Butyllithium (2.5 M in hexane, 1.67 mL, 4.17 mmol) was added dropwise at 0 °C to a solution of 2-phenylethynylindene (1.00 g, 4.63 mmol) in diethyl ether. The mixture was warmed to 22 °C and stirred for 1 h. All volatiles were removed in vacuo. Zirconium tetrachloride (0.49 g, 2.08 mmol) was added to the lithium salt in the drybox, the flask was cooled to −78 °C, and methylene chloride (50 mL) was slowly added. After stirring overnight at 22 °C, the solution was filtered through Celite. The solvent was removed in vacuo, and the crude product was recrystallized from toluene to give yellow/green crystals. Yield: 0.88 g (32%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.74 (s, 2H), 7.22−7.24 (m, 2H), 7.38−7.41 (m, 3H), 7.48−7.5 (m, 2H), 7.58−7.61 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 83.5, 95.6, 109.1, 113.6, 122.3, 124.7, 126.9, 127.5, 128.1, 131.8. Elemental C, H analysis for $C_{34}H_{22}Cl_2Zr$. Anal. Found (Calcd): C, 68.57 (68.9); H, 3.39 (3.74).

Ethylene−Hexene Copolymerization Procedure. All polymerizations were carried out in a 300 mL stainless steel Parr reactor. MAO (100 mg) was suspended in 35 mL of 1-hexene in the drybox and loaded into a 150 mL double-ended injection tube. The Parr reactor was evacuated on a vacuum line and then refilled and flushed three times with 130 psig of ethylene. The MAO/1-hexene solution was injected into the reactor and allowed to equilibrate under the appropriate ethylene overpressure for at least 30 min. A metallocene dichloride stock solution was prepared by dissolving 5−10 mg in 25 mL of toluene in the drybox. The desired amount of stock solution (typically 10−100 μL) was diluted to 5 mL with 1-hexene and loaded into a 25 mL double-ended injection tube. The polymerization was started by disconnecting the ethylene feed, venting the reactor by 10 psig, and injecting the metallocene dichloride solution under ethylene pressure. The ethylene feed was then reconnected to the reactor. The polymerization temperature was maintained constant via an ethylene glycol/water cooling loop. After the desired reaction time, the ethylene feed was disconnected, and 15 mL of methanol was injected via a single-ended injection tube pressurized with argon. The reactor was vented, and the contents of the reactor were poured into acidified methanol and stirred overnight. Copolymers were filtered, washed with additional methanol, and dried for at least 6 h in a 40 °C vacuum oven.

Polymer Characterization. Number- and weight-average molecular weights (M_n, M_w) were obtained using a Waters 150C high-temperature GPC at 139 °C in 1,2,4-trichlorobenzene with two Polymer Laboratories PL GEL mixed-B columns at a flow rate of 1 mL/min. High-density polyethylene standards were used. ^{13}C NMR spectra were recorded at 75.4 MHz on a Varian UI 300 spectrometer at 100 °C using 10 mm sample tubes. Samples were prepared by dissolving 150 mg of polymer in a 90:10 solution of 1,2-dichlorobenzene:d_6-benzene containing approximately 5 mg of chromium(III) acetylacetonate to reduce T_1. Spectra were recorded using pulse repetition intervals of 5 s and gated proton decoupling.

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References and Notes

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