

The Influence of Aromatic Substituents on the Polymerization Behavior of Bridged Zirconocene Catalysts

Walter Spaleck,* Frank Küber, Andreas Winter, Jürgen Rohrmann, Bernd Bachmann, Martin Antberg, Volker Dolle, and Erich F. Paulus

Hoechst AG, 65926 Frankfurt am Main, Germany

Received August 19, 1993*

The synthesis of seven new bridged zirconocenes is described, which make isotactic polypropylene when used in polymerizations of propylene with methylaluminoxane as cocatalyst. Their polymerization behavior in propylene and ethylene polymerizations is examined and discussed. Aromatic substituents in appropriate positions of the zirconocene ligand frame result in catalysts with activities, stereospecificities, and polypropylene molecular weights much higher than those of any previously described metallocene system. By structure variations it is demonstrated that the effectiveness of these substitutions strongly depends on their position and on a nonincremental synergism with alkyl substituents on the ligand frame. The high activities of the systems can be explained well by electronic effects, whereas steric effects obviously play the more important role for the high stereospecificities and high molecular weights of the polymers.

Introduction

Since the discovery of the first soluble zirconocene-methylaluminoxane catalysts for the isotactic¹ and the syndiotactic² polymerization of propylene, an enormous amount of scientific work has been invested in both the optimization of the polymerization performance of these systems and the detailed explanation of their polymerization behavior. The explanation efforts focused on the question how the mode and degree of stereospecificity of these systems could be explained,³⁻¹⁵ fewer studies and considerations were directed to structure-performance relations concerning activities and ratios of chain propagation vs chain termination in different systems.^{11,13-16} Optimization targets were, of course, a higher activity and stereospecificity of the systems, and a lower tendency for chain termination, the latter resulting in a desired high

molecular weight of polymer. During these efforts, a large number of new bridged zirconocenes have been synthesized and polymerization-tested.^{10,11,14,17-20}

In this work we wanted to utilize all this previous information as functional increments, try to synthesize new optimized metallocenes for isotactic propylene polymerization and demonstrate their hopefully superior and unprecedented performance characteristics (activity, stereospecificity, molecular weight of the polymer). The candidate molecules are descendants of known structures with additive aromatic substituents. For a better understanding of the critical structural features of the high performance catalysts, we have synthesized further derivatives and tested them in propylene and ethylene polymerizations for comparison. These tests also included already described species. The results are integrated into the explanation patterns of the previous literature and illustrate the scope and limits of a "rational catalyst design" of metallocene catalysts at the present stage of understanding.

Results

General Approach. Metallocene catalysts for highly isotactic propylene polymerization should be bridged chiral zirconocenes exhibiting C_2 symmetry. Previously known examples are respective bis(indenyl)^{17,18} or substituted bis(cyclopentadienyl) systems.^{11,19} Their performance-relevant structural features are illustrated by Chart 1 and Table 1. The one-membered silicon bridge in **2a** seems to be preferable over the two-membered unsubstituted ethylene bridge in **1**, imposing higher rigidity and favorable electronic characteristics to the metallocene, thus inducing higher isotacticity and molecular weight of the polymer.²¹ In our previous work we further demonstrated, that a

* Abstract published in *Advance ACS Abstracts*, January 15, 1994.

(1) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* 1985, 97, 507; *Angew. Chem., Int. Ed. Engl.* 1985, 24, 507.

(2) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* 1988, 110, 6255.

(3) Pino, P.; Cioni, P.; Galimberti, M.; Wei, J.; Piccolrovazzi, N. In *Transition Metals and Organo-metals as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1988; p 269.

(4) Corradini, P.; Guerra, G.; Vacatello, M.; Villani, V. *Gazz. Chim. Ital.* 1988, 118, 173.

(5) Cavallo, L.; Corradini, P.; Guerra, G.; Vacatello, M. *Polymer* 1991, 32, 1329.

(6) Cavallo, L.; Guerra, G.; Vacatello, M.; Corradini, P. *Macromolecules* 1991, 24, 1784.

(7) Longo, P.; Proto, A.; Grassi, A.; Ammendola, P. *Macromolecules* 1991, 24, 4624.

(8) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* 1992, 114, 8687.

(9) Castonguay, L. A.; Rappé, A. K. *J. Am. Chem. Soc.* 1992, 114, 5832.

(10) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspelslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* 1991, 48/49, 253.

(11) Röhl, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem.* 1990, 102, 339; *Angew. Chem., Int. Ed. Engl.* 1990, 29, 279.

(12) Hortmann, K.; Brintzinger, H. H. *New J. Chem.* 1992, 16, 51.

(13) Burger, P.; Hortmann, K.; Brintzinger, H. H. *Makromol. Chem., Macromol. Symp.* 1993, 66, 127.

(14) Lee, I.-M.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* 1992, 11, 2115.

(15) Chien, J. C. W.; Sugimoto, R. *J. Polym. Sci., Polym. Chem. Ed.* 1991, 29, 459.

(16) Herfert, N.; Fink, G. *Makromol. Chem.* 1992, 193, 1359.

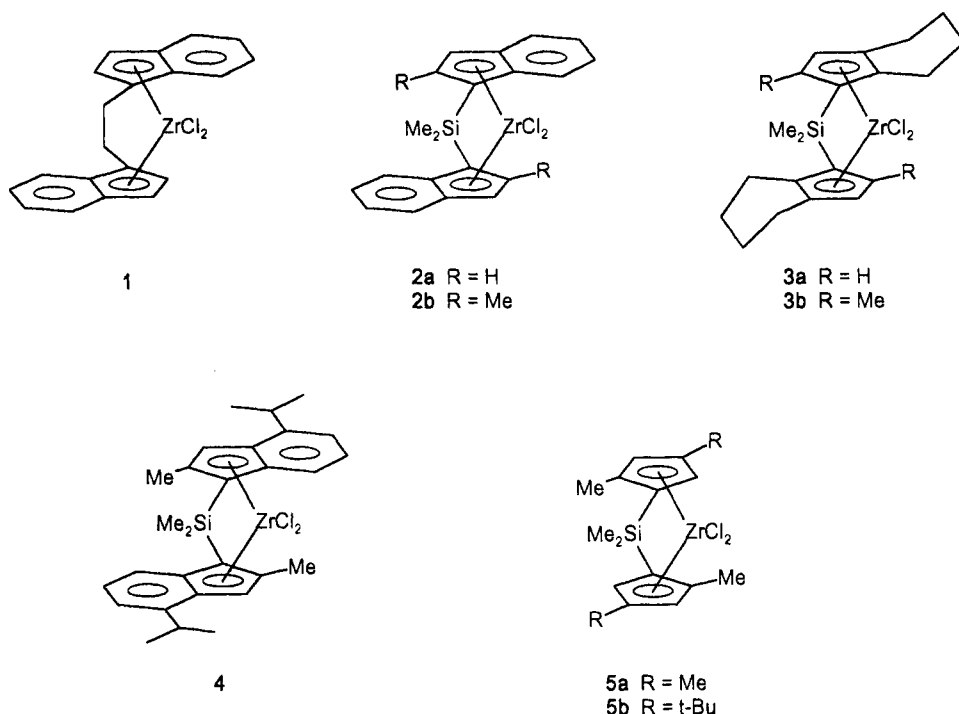
(17) Spaleck, W.; Antberg, M.; Dolle, V.; Klein, R.; Rohrmann, J.; Winter, A. *New J. Chem.* 1990, 14, 499.

(18) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem.* 1992, 104, 1373; *Angew. Chem., Int. Ed. Engl.* 1992, 31, 1347.

(19) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* 1989, 1853.

(20) Rieger, B. *J. Organomet. Chem.* 1992, 428, C33.

Chart 1

**Table 1. Polymerization of Liquid Propylene with Previously Described Zirconocene/Methylaluminumoxane Catalysts (70 °C, Zr:Al = 1:15 000)**

metallocene [amt (mg)]	polymer yield (g)	productivity		mp (°C)	mmmm (%)
		[kg of PP/ (mmol of Zr·h)]	$10^{-3}M_w$		
1 (2.09)	941	188	24	132	78.5
2a (2.39)	956	190	36	137	81.7
2b (2.46)	492	99	195	145	88.5
3a (2.41)	241	48	24	141	84.5
3b (2.48)	198	40	55	144	87.4
4 (2.80)	1220	245	213	150	88.6
5a (2.02)	485	97	31	149	89.2
5b (2.44)	49	10	19	155	94.3

combination of alkyl substitution in the position besides the bridge and an annelated aromatic six-membered ring on the cyclopentadienyl ring (i.e. an indenyl structure) induces a still higher molecular weight of the polymer (species 2b), and is in that respect superior to analogous tetrahydroindenyl and alkyl substituted cyclopentadienyl structures¹⁸ as 3b, 5a and 5b; finally, we could show that isopropyl substitution in the 4-position (species 4) further enhances catalyst performance, especially its stereospecificity, and that further enhancement of molecular weight might come from modification of the substituents in the bridge, as has been demonstrated by our previous work in isospecific and, more powerfully, in syndiospecific catalysts.^{17,22} The synthesis program derived from these considerations is shown in Scheme 1, the starting point for our optimization being species 4. Ways for optimization would be (1) annelation of a further aromatic ring, (2) useful modification of the substituent in the 4-position, and (3) introduction of aromatic substituents in the bridge. The 4,5-benzoidenyl structure 6a seemed to be a logical candidate for way 1, combining aromatic annelation with 4-substitution of the (former) indenyl six-membered ring;

structures 7a and 8 combine a 4-substituent larger than isopropyl with aromatic substitution as a promising version of way 2, and structure 7b adds to 7a with phenyl substitution in the bridge according to way 3. Structures 6b and 7c are variants of 6a and 7a with the omission of the 2-methyl group in their mother molecules and should thus demonstrate the isolated effect of the new increments "4,5-benzo" and "4-phenyl". Structure 9 (a mixture of isomers) puts the phenyl group in the respective 5- and 6-positions (instead of the 4-position in 7a) to test to what extent the position of substitution is critical.

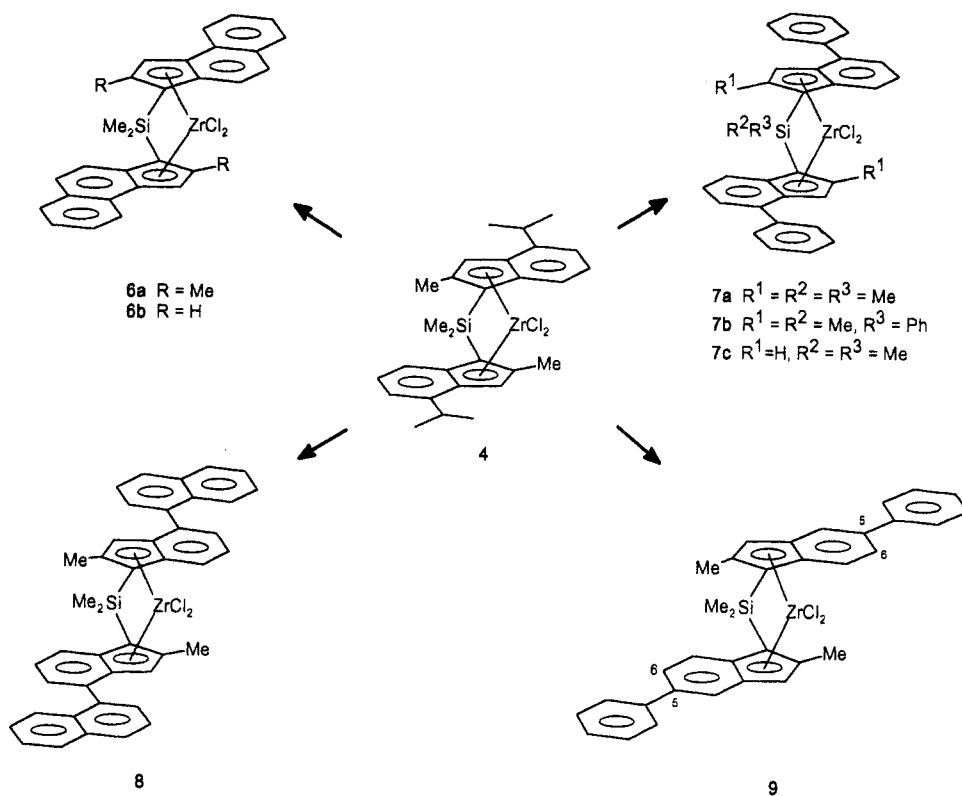
Preparation of the Indenes and Ligands. The indenes and ligands used in this study were prepared following the general synthetic pathway described for 7a-c (Scheme 2). Detailed descriptions of the synthetic methods are given in the Experimental Section. The appropriate benzyl halogenides used for the malonester synthesis are commercially available or were prepared by literature procedures. Following addition of the malonic ester, the saponification and decarboxylation were easily operable and gave the corresponding acid generally in good yields. Cyclization of the acid halogenides to the indanones using aluminum trichloride as the Friedel-Crafts catalyst worked, with one exception, in moderate yields. In the case of 2-methyl-4-(1-naphthyl)indanone, the intermediate in the synthesis of 8, the high reactivity of the naphthyl moiety (compared with phenyl) leads to various side reactions which lower the yield dramatically (only 13%). The reaction of the lithiated indene derivatives substituted in the 4-position results exclusively in ligands with the bridge in the 1-position of the indene. No other isomers could be observed. In the case of the ligand of 9, where we started from the 2-methyl-5-phenylindene, we got a mixture of isomers with the phenyl ring in the 6- or 5-position, obviously because of the lack of a bulky substituent having directing influence on the incoming bridge function. All attempts to separate the isomers by chromatography failed (vide infra).

Preparation of the Metallocenes 6a, 6b, 7a-c, 8, 9.

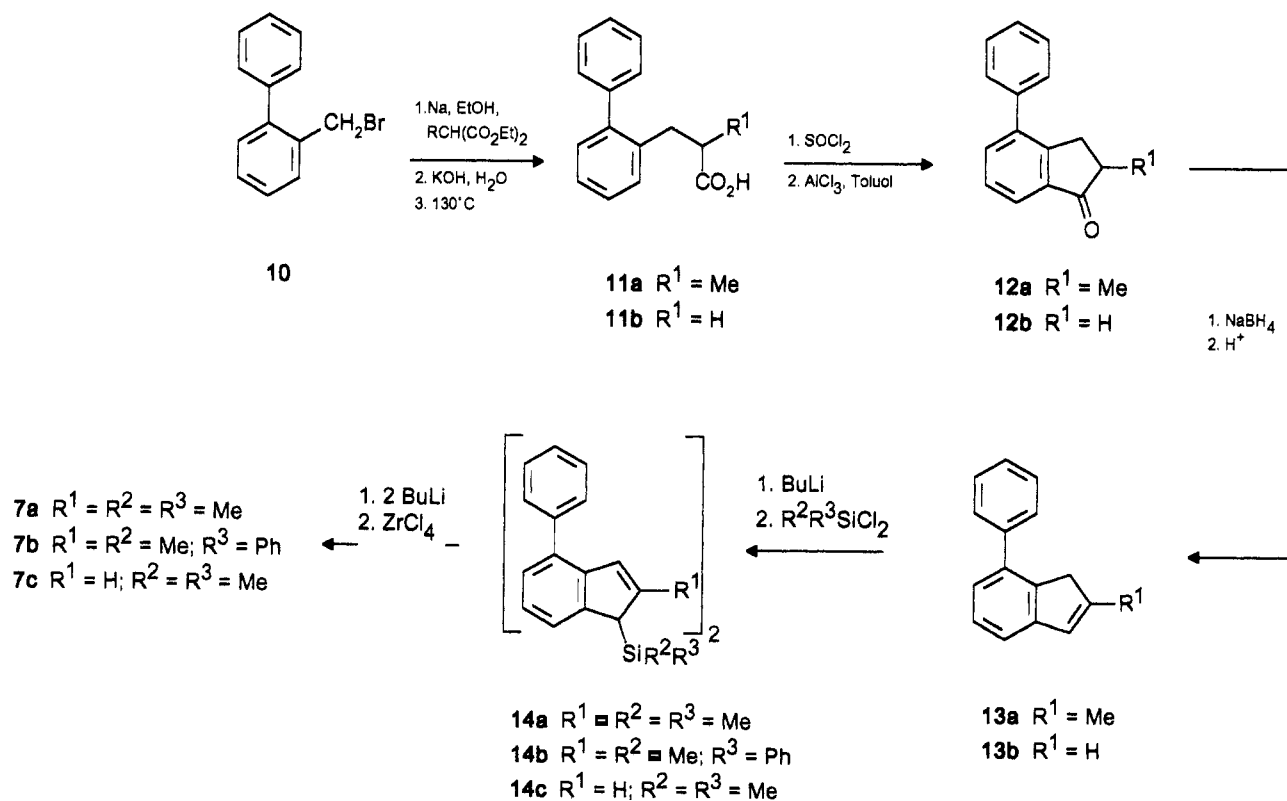
(21) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem.* 1989, 101, 1536; *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1511.

(22) Winter, A.; Rohrmann, J.; Antberg, M.; Dolle, V.; Spaleck, W. EP 387 690, 1989.

Scheme 1



Scheme 2



The silane bridged metallocenes were prepared using standard conditions (Scheme 2). In all cases, except for 9, it was possible to isolate the pure racemic forms by fractional crystallization or extraction. For the separation of the racemic and the meso form no standard procedure could be applied, every separation was individually optimized. Suitable crystals from 6a for X-ray diffraction were obtained by crystallization of the pure racemate from

dichloromethane at -30 °C. In the case of 9 we obtained a mixture of isomers with the phenyl ring in the 5- or 6-position of the indene moiety which could not be separated. In spite of the purification problem, the integration of 9 into the test program is justified by the polymerization data, which indicate either strong predominance of one isomer or identical behavior of both, the meso substance being quite inactive ($M_w/M_n < 2.5$ in

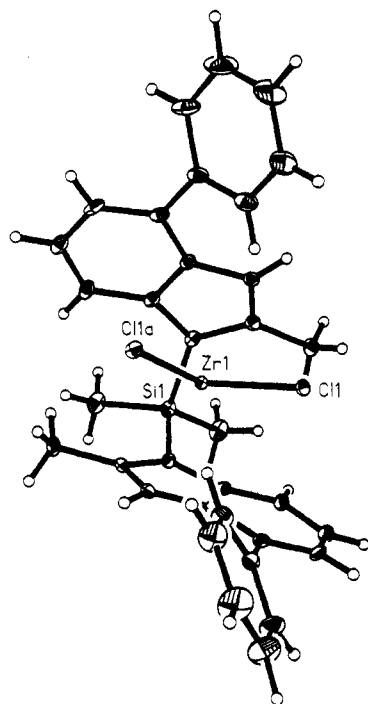


Figure 1. Molecular structure of 7a with 20% probability thermal ellipsoids depicted.

Table 2. Comparison of Typical Structural Parameters of Known Zirconocenes with 7a

	2a	2b	7a
Zr-Cl (Å)	2.4314(2)	2.419 ^a	2.419(1)
Cl-Zr-Cl (deg)	98.76(1)	99.06	96.8(1)
Zr-Cp ^b (Å)	2.2413(1)	2.244 ^a	2.243(4)
Zr-C(Cp) min (Å)	2.470(1)	2.462(3)	2.478(3)
Zr-C(Cp) max (Å)	2.659(1)	2.663(5)	2.640(4)
Cp-Zr-Cp (deg)	127.81(1)	128.11(1)	128.5(3)
E1-E2 ^c (deg)	61.94	61.39	59.2

^a Average. ^b Center of the Cp rings. ^c Interplanar angle of the indenyls.

all polymerizations, no double melting point and content of atactic PP <6% in propylene polymerizations).

X-ray Analysis of 7a. The results are given in Figure 1 and Table 7 (see Experimental Section). The two phenyl rings in the 4- and 4'-positions do not change the structural parameters of the bis(indenyl) core significantly. Table 2 shows a structural comparison between 2a,²¹ 2b,¹⁸ and 7a. The relatively large angle between the phenyl and the indenyl ring systems is expected to diminish the mesomeric effect.

This dihedral angle of the phenyl ring and the indenyl plane is 44.8°; the bond length to the indenyl ring is 1.474 Å. These parameters are in the range of those for α -substituted biphenyls. In biphenyl because of electronic interactions the two phenyl rings are coplanar and the bond length between them is 1.493 Å,²³ where for α -substituted biphenyls as a function of the steric interaction between the α -substituents, a twisted orientation is typically observed (e.g. 1-(biphen-2-yl)-5-methoxy-3-tosylbenzo[c]thiophene: 55.5° and 1.492 Å).²⁴

Polymerization of Propylene Using Compounds 6–9. The newly synthesized metallocenes 6–9 were tested with methylaluminoxane as cocatalyst (Al:Zr 1:15 000) in polymerizations of liquid propylene at 70 °C, to demonstrate

Table 3. Polymerization of Liquid Propylene with New Zirconocene/Methylaluminoxane Catalysts, Compared with Two Previous Systems (70 °C, Zr:Al = 1:15 000)

metallocene [amt (mg)]	polymer yield (g)	productivity [kg of PP/(mmol of Zr·h)]	$10^{-3}M_w$	mp (°C)	mmmm (%)
6a (2.88)	2020	403	330	146	88.7
6b (2.74)	1370	274	27	138	80.5
7a (2.20)	2640	755	729	157	95.2
7b (2.40)	1920	553	778	157	95.1
7c (3.00)	240	48	42	148	86.5
8 (2.18)	2620	875	920	161	99.1
9 (3.14)	314	63	188	139	78.1
For Comparison					
2a (2.09)	956	190	36	138	81.7
4 (2.80)	1220	245	213	150	88.6

Table 4. Slurry Polymerization of Propylene (5 bars) with Selected New and Previously Described Systems (70 °C, Zr:Al = 1:15 000)

metallocene [amt (mg)]	polymer yield (g)	productivity [kg of PP/(mmol of Zr·h)]	$10^{-3}M_w$	mp (°C)
6a (0.461)	155	194	100	145
7a (0.503)	146	182	210	156
9 (0.503)	11	11	55	138
For Comparison				
2a (0.359)	28	35	30	134
2b (0.381)	34	42	82	142
4 (0.448)	108	134	80	150

Table 5. Slurry Polymerization of Propylene (2 bars) with Selected New and Previously Described Systems (70 °C, Zr:Al = 1:15 000)

metallocene [amt (mg)]	polymer yield (g)	productivity [kg of PP/(mmol of Zr·h)]	$10^{-3}M_w$	mp (°C)
6a (0.461)	74	92	55	142
7a (0.503)	89	111	110	155
For Comparison				
2a (0.359)	11	14	25	133
4 (0.381)	34	49	35	148

their performance under optimum conditions. The results are summarized in Table 3 and can be compared with the polymerization data of previously known systems, as summarized in Table 1. Selected new and previously described systems were further tested in a high boiling hydrocarbon as diluent (70 °C, methylaluminoxane, Zr:Al = 1:15 000) at lower monomer concentrations (5 and 2 bars of propylene, respectively), with the intention of differentiating between the influences of metallocene structure on the one hand and polymerization conditions on the other (for results see Tables 4 and 5). As can be seen from the tables, the polymerization behavior of the new metallocenes covers a wide range of activities, polymer molecular weights, and melting points, naphthyl-substituted system 8 reaching the highest numbers in all of the properties. In detail, the activities of the aromatically substituted systems 6a, 7a, and 8 in liquid propylene polymerizations are 50–200% higher than that of the alkyl-substituted reference system 4, the difference from the nonsubstituted analogue 2 is even much larger. Slight changes in substitution patterns have detrimental effects on these activity performances, as replacement of the methyl group by hydrogen in the position next to the bridge (6b and 7c) or changing the position of the phenyl group on the six-membered ring (9). The strong dependence of polymerization behavior on the details of the substitution patterns is also shown in the melting points and molecular weights of the polymers, which reflect the stereospeci-

(23) Charbonneau, G.-P.; de Lugeard, Y. *Acta Crystallogr.* 1977, B33, 1586.

(24) Saito, T.; Ayukawa, H.; Sumizawa, N.; Shizuta, T.; Motoki, S.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. 1* 1991, 1405.

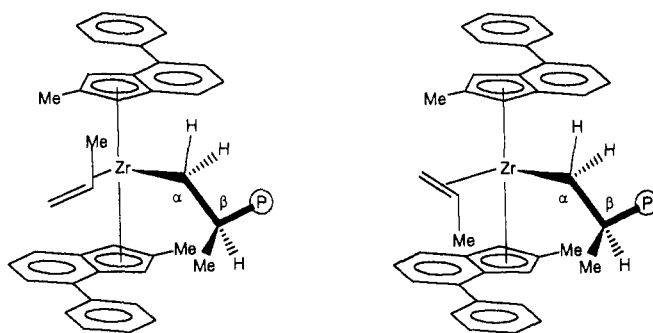
Table 6. Slurry Polymerization of Ethylene (5 bars) with Selected New and Previously Described Systems (70 °C, Zr:Al = 1:15 000)

metallocene [amt (mg)]	polymer yield (g)	productivity [kg of PE/ (mmol of Zr·h)]	10 ⁻³ M _w
6a (0.144)	154	617	532
6b (0.137)	128	512	238
7a (0.157)	230	922	786
7c (0.150)	14	58	230
8 (0.157)	110	510	540
9 (0.150)	18	75	266
For Comparison			
2a (0.120)	29	108	195
2b (0.123)	32	126	249
4 (0.140)	82	329	418

ficiencies and typical chain propagation/chain termination ratios of the different metallocenes. An aromatic substituent in the 4-position of the six-membered ring (**7a**, **7b**, **8**) causes a most substantial effect on the molecular weight, which is 4 times higher than with the isopropyl-substituted analogue **4**. Naphthyl substitution is slightly more effective than phenyl, and both are clearly above aromatic substitution by 4,5-benzoannulation (**6a**). Obviously, there are two conditions for the effect: (a) The substituent must be in the "right" position, or it will not be effective at all (cf. **9** with **7a** and non-4-substituted **2b**), and (b) an alkyl substituent in the 2-position next to the bridge is needed as a "synergist". Without the latter (H-substitution in **6b** and **7c**) the molecular weight of polymer is not higher than that with the completely unsubstituted system **2a**. This strict synergism between substitution in the 2- and 4-positions is only partly true for stereospecificity. It holds true in the comparison of benzoindenyl species **6a** and **6b**, whereas phenyl substitution in the 4-position retains part of the stereospecificity gain, compared with nonsubstituted **2a**, also in case the "methyl-synergist" is removed (**7c**). Concerning stereospecificity, only 2-alkyl, 4-aryl-substituted systems improve over the 2-alkyl, 4-isopropyl-substituted starting system **4**; the others fall back, **6b** and **9** even behind the solely 2-substituted system **2b**.

The low pressure propylene polymerizations in a hydrocarbon diluent (Tables 4 and 5) show that the stereospecificity of the catalysts is basically unaffected by monomer concentration,²⁵ whereas activity and polymer molecular weight show the strong dependence to be expected from the literature.^{25,26} On the other side, the large performance differences between the systems, as demonstrated in the bulk polymerizations, are not blurred, which indicates their structural origin. Slight alterations in the consecution of activities need special interpretation.

Polymerization of Ethylene Using Compounds 6–9. Ethylene is a smaller monomer than propylene, and it lacks prochirality. Polymerization behavior of metallocene catalysts toward ethylene is thus believed to reflect more the electronic than the steric properties of the metallocene structure.^{27,28} We polymerized ethylene with a selection of the newly synthesized metallocenes (**6a,b**; **7a,c**; **8**; **9**) and of those previously described (**2a,b**; **4**), under the same

Chart 2

conditions as in the 5-bar propylene polymerizations. The results are summarized in Table 6. The activities basically follow the pattern of the propylene polymerizations, newly synthesized, aromatically substituted **6a**, **6b**, **7a**, and **8** having higher activities than previous systems, the structural variants **7c** and **9** lower ones. On the other hand, molecular weights of polymers do not show such distinctive differences as with the propylene monomer. **6a**, **7a**, and **8** again show the highest molecular weights, but their non-2-methyl-substituted analogues **6b** and **7c** are now on the same level as the solely 2-substituted **2b**, whereas in the case of propylene they are a factor of 3 or 5 below that level.

Discussion

In previous work about structure–performance relations of bridged metallocene polymerization catalysts, the aspect of stereospecificity has been examined and discussed most, as already pointed out (see Introduction). Compared with that, the ideas about the origin of differences in activity and molecular weight of polymers are much less clarified. We thus would like to discuss the stereospecificity data first and introduce with this some explanation patterns, which we will use again later.

(A) Stereospecificity. It is generally accepted that isotactic propylene polymerization with zirconocene catalysts takes place by a regioselective 1,2-insertion of the propylene monomer into the metal–carbon bond between the zirconium central atom and the first carbon atom of the polymer chain. For 1,2-insertion, the monomer can be coordinated in two prochiral positions, as depicted in Chart 2. One of these positions is energetically favored over the other, which results in stereospecific polymerization. The energetic difference between these two positions, or the corresponding transition states leading to 1,2-insertion, are believed to be mainly influenced by the steric position of the end of the growing chain, this chain end being positioned by the ligand frame of the active complex.^{8,4,8,9} According to recent theoretical work,^{8,9} this "indirect steric control" affects at least four consecutive carbon atoms of the chain end and is much more important than the direct influence of the complex ligands on the inserting monomer. It has been further proposed that high rigidity of the metallocene ligand frame and facility of an α -H-agostic interaction between the zirconium and one of the α -hydrogens of the chain might enhance stereospecificity.^{11,13}

The gain of stereospecificity by enlarging the groups in the 4,4'-positions from isopropyl (**4**) to phenyl (**7a**) and naphthyl (**8**) can easily be understood as optimizing indirect steric control. As this increase in size takes place

(25) N. Herfert, Dissertation, University of Düsseldorf, 1992.

(26) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Curtis, S.; Cheng, H. N. In *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Kodansha: Tokyo, 1990.

(27) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* 1990, 9, 3098.

(28) Kaminsky, W.; Engehausen, R.; Zoumis, K.; Spaleck, W.; Rohrmann, J. *Makromol. Chem.* 1992, 193, 1643.

far away from the coordinated monomer, it is plausible that it acts through steric influence on the chain, maybe even on further carbon atoms than the first four. This was not so evident with previously known examples of such optimizations as species **5b** vs **5a**. The optimum result with the naphthyl substitution might be due to the presumably high rotational barrier for the substituent which thus is accurately put into the most favorable position. In benzoindenyl species **6a**, on the other side, the steric impact of the isopropyl substituent in species **4** is cut down by "loss" of one methyl group and "fixation" of the other, the slight reduction of stereospecificity is thus expected. The methyl groups on the cyclopentadienyl rings in neighboring positions to the silicon bridge might interact with the methyl groups on the silicon and thus contribute to the rigidity of the ligand framework of **6a** and **7a** (and also of the previously published **2b** and **3b**). The considerable reduction of stereospecificity, which accompanies the replacement of the first mentioned methyl groups by hydrogen atoms in structures **6b** and **7c** is then a consequence of a loss in rigidity. The stereospecificity difference of mother structures **6a** and **7a** is retained in the pair **6b** and **7c**, underlining the strong stereoregulating effect of the big phenyl substituents in the 4,4'-positions. In species **9** these substituents are put in a position further away from the growing chain, the stereospecificity then is below that of a solely 2,2'-substituted system (**2b**). Maybe in this case not only the steric influence on the chain is lost but also a negative electronic influence on stereospecificity operates, as discussed by Collins¹⁴ for similar 5,6-dialkyl-substituted systems.

(B) Catalyst Activity and Molecular Weight of Polymer. Chain propagation and chain termination are competing reactions; thus the features of activity and molecular weight should be discussed together. The problem with this discussion is that the different influence factors cannot be separated on the basis of the momentarily existing knowledge and data. The activities in the tables are simply calculated from polymerization yields. Only if both compared catalysts have the same concentration of active centers under the chosen set of conditions can so-calculated activities be used for a comparison of propagation rates. This prerequisite is not trivial. A detailed examination of the polymerization behavior of two bridged zirconocene catalysts,^{16,25} the bis(indenyl) system **2a** (Table 1) and the syndiospecific ((2-cyclopentadienylisoprop-2-yl)fluorenyl)zirconium dichloride,² showed a strong dependence of activity on the zirconium:MAO ratio. The zirconium:MAO ratio for maximum activity (at lower ratios i.e. even higher MAO levels, a slow decrease of activity was found) was very different for two different zirconocenes and even different for different monomers. From these findings it can be concluded, that in the case of bridged zirconocene/MAO catalysts the number of active species is not a priori 100% of all zirconium atoms, but a function of several parameters, including the structure of the metallocene. According to the study cited, the rather extreme zirconium:aluminum ratio (1:15 000) applied here seemed to be advisable to ascertain at least a rough comparability of activity data; a more meaningful comparison would need detailed studies for each of the new systems.

Concerning now the influence of metallocene substitution patterns on activities, several and opposite factors have to be discussed. Hindrance of monomer access to

the coordination site by bulky substituents^{11,13,28} would slow down the propagation rate. Further it has been proposed that certain substituent patterns might bring the growing chain into conformations where an α -agostic interaction between one H-atom on the first carbon of the chain and the active zirconium is facilitated and thus the active center stabilized.¹¹ Electron donating alkyl or aryl substituents, on the other hand, could be expected to stabilize the active cationic species or facilitate its formation from the dichloro complex and thus enlarge the number of active sites or even make the coordination of the counterion less tight,¹⁴ thus enhancing the overall activity. For the high activities of systems **6a**, **6b**, **7a**, **7c**, and **8**, which are unprecedented by any earlier published bridged system, the electronic explanations can apply. They fit our observation that in comparative ethylene polymerizations (Table 6) the activity difference between these and less substituted analogues is equal or even higher. The similarity of activity effects in comparison of ethylene and propylene polymerization also holds true for the unexpectedly low activities of **7c** and **9** and proposes an electronic reason for these, although we can give no detailed explanation.

Concerning the influence of metallocene substitution patterns on polymer molecular weight, one must bear in mind the consequence of the competition between chain termination and chain propagation, which is nicely demonstrated by the effect of monomer concentration. Comparison of tables 3-5 shows that activity is a function of monomer concentration, i.e. propagation rates being low at low monomer concentrations. Assuming that β -hydrogen elimination is the important chain termination mechanism,²⁹ which means that the monomer is not involved in chain termination, it is expectable that lower monomer concentrations favor termination over propagation; i.e., molecular weights of polymers are reduced. This is actually observed.

As for the steric influence factor on chain termination in propylene polymerization it has been proposed that certain substitution patterns might favor conformations of the chain which make β -H interaction with the zirconium atom and thus chain termination difficult. Enhanced rigidity of the whole ligand framework would strengthen such an effect.^{11,13} On the other side, electron releasing substituents might lower the Lewis acidity on the active zirconium atom, thus reducing its tendency for hydrogen abstraction, i.e. chain termination.^{13,26}

The high polymer molecular weights reached with new systems **6a**, **7a**, **7b**, and **8** are unprecedented by any previously known metallocene system with propylene polymerization under the given conditions. They might be explained by both electronic and steric arguments. The steric arguments are favored by the observation that replacement of the methyl groups beside the bridge by hydrogen atom in **6b** and **7c** (which may result in decreased rigidity of framework) brings the molecular weight of the polymer down to the performance level of completely unsubstituted **2a**. That the combined influence of the 2-methyl substituents and the six-membered ring aromatic substituents is not incremental, but 100% synergistic, is hardly to be understood by a mere electronic argument. The preponderance of steric influence factors is also underlined by the observation that molecular weight differences are larger in comparative propylene than in

ethylene polymerizations. The comparatively low molecular weights with **7c** and **9**, however, may at least partly be a "trivial" activity effect: Lowering of the propagation rate compared to, e.g., **7a** with chain termination tendency being the same enlarges the termination:propagation ratio.

Concluding Remarks

Creative application of previous knowledge on structure-performance relations within stereospecific metallocene catalysts has resulted in dramatically optimized new systems and thus demonstrated the feasibility of a "rational catalyst design". The polymerization behavior can basically be understood by the explanation patterns found in the literature. On the other hand, polymerization kinetics measurements of selected systems and also further theoretical studies are highly desirable for a deeper understanding of the substituent influences. These experiments and studies should especially include the role of the methylaluminumoxane counterion or its possible better defined substitutes.^{30,31}

Experimental Section

All chemicals were reagent grade and purified as required. Hexane, tetrahydrofuran, toluene, and diethyl ether used in metallorganic reactions were all dried and deoxygenated by distillation from sodium-potassium alloy under argon. Dichloromethane was dried and deoxygenated by distillation from calcium hydride under argon. NMR spectra were obtained on a 100-MHz Bruker AM 100. Mass spectra were measured on a Finnigan MAT 95 Q, EI (70 eV), CI (isobutane).

Preparation of the Indenes. 2-(2-Phenylbenzyl)propionic Acid (11a). To 6.5 g (0.285 mol) of sodium in 160 mL of dry ethanol was added at room temperature 47 g (0.28 mol) of diethylmethylmalonate in 50 mL of dry ethanol. 2-phenylbenzyl bromide (**10**) (70 g, 0.285 mol) was added to the stirred reaction mixture at such a rate that the heat of reaction maintained the system at gentle reflux. Stirring at reflux was continued for 3 h. Then 150 mL of water and 56 g of potassium hydroxide were added at room temperature and the reaction mixture was heated to reflux for an additional 4 h. The solvents were distilled off, water was added until complete solution of the residue, and concentrated HCl was added to pH = 1. The precipitate was collected on a filter, dried, and heated for decarboxylation in a flask 1 h to 130 °C. The viscous, oily acid was used in the next step without further purification. Yield: 58 g, 85%, of **11a**. ¹H NMR (CDCl₃, 100 MHz): δ 11.7 (s, 1H, COOH), 7.1–7.5 (m, 9H, arom H), 2.3–3.2 (m, 3H, CH and CH₂), 0.9 (d, 3H, CH₃).

2-Methyl-4-phenylindan-1-one (12a). A mixture of 58 g (0.242 mol) of **11a** and 60 mL (0.83 mol) of thionyl chloride was stirred 18 h at room temperature. The excess of thionyl chloride was distilled off. To remove traces of thionyl chloride, 100 mL of dry toluene was added and removed in vacuo three times. The solution of the acid chloride in 200 mL of dry toluene was added at 10 °C to a stirred suspension of 48 g (0.363 mol) of aluminum trichloride in 800 mL of dry toluene over a period of 1 h. After heating to 80 °C for 1 h, the mixture was poured on 1000 g of ice, acidified with concentrated HCl to pH = 1, and extracted with 200 mL of diethyl ether three times. The combined organic layers were washed with a saturated aqueous solution of NaHCO₃ and brine. The solvents were removed under vacuo. The indanone **12a** was used in the next step without further purification. Yield: 50 g, 93%, of **12a**. ¹H NMR (CDCl₃, 100 MHz): δ 7.2–7.8 (m, 8H, arom H), 3.3 (dd, 1H, H-C(3)), 2.5–2.9 (m, 2H, H'-C(3) and H-C(2)), 1.3 (dd, 3H, CH₃).

(30) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* 1989, 111, 2728.

(31) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; La Pointe, R. F. *J. Am. Chem. Soc.* 1990, 112, 1289.

2-Methyl-7-phenylindene (13a). **12a** (50 g, 0.226 mol) in 300 mL of tetrahydrofuran/methanol (2:1) was treated at 0 °C with 12.8 g (0.34 mol) of sodium borohydride in portions. The reaction mixture was stirred at room temperature for 16 h. The mixture was poured on 300 g of ice, acidified with concentrated HCl to pH = 1 and extracted with 200 mL of diethyl ether three times. The combined organic layers were washed with brine and dried (MgSO₄). After removal of the solvent the residue was heated to reflux in 500 mL of toluene containing 2 g of *p*-toluenesulfonic acid monohydrate for 2 h. To remove the acidic catalyst the mixture was washed with a saturated aqueous solution of NaHCO₃. The indene **13a** was obtained after removal of the solvent and chromatography of the residue over silica gel (hexane/dichloromethane, 9:1) as a colorless oil. Yield: 42 g, 90%, of **13a**. ¹H NMR (CDCl₃, 100 MHz): δ 7.0–7.6 (m, 8H, arom H), 6.5 (m, 1H, H-C(3)), 3.4 (s, 2H, CH₂), 2.1 (d, 3H, CH₃).

3-(2-Biphenyl)propionic Acid (11b). Following the procedure described for **11a** (14 g (0.61 mol) of sodium, 400 mL of ethanol, 98 g (0.61 mol) of diethyl malonate in 50 mL of dry ethanol, 150 g (0.61 mol) of 2-phenylbenzyl bromide (**10**), and 102 g (1.83 mol) of potassium hydroxide) yielded the acid **11b** as a viscous, oily product. Yield: 112 g, 81%, of **11b**. ¹H NMR (CDCl₃, 100 MHz): δ 9.1 (s, 1H, COOH), 6.9–7.5 (m, 9H, arom H), 2.3–3.0 (m, 4H, 2 CH₂).

4-Phenylindan-1-one (12b). Following the procedure described for **12a** (102 g (0.45 mol) of **11b**, 37 mL (0.5 mol) of thionyl chloride, 72 g (0.54 mol) of aluminum trichloride, and 1000 mL of dry toluene) gave the indanone **12b** as an oily product. Yield: 90 g, 96%, of **12b**. ¹H NMR (CDCl₃, 100 MHz): δ 6.9–7.5 (m, 8H, arom H), 2.5–3.4 (m, 4H, 2 CH₂).

7-Phenylindene (13b). Following the procedure described for **13a** (86 g (0.41 mol) of **12b**, 300 mL of tetrahydrofuran/methanol (2:1), 23 g (0.62 mol) of sodium borohydride, 1000 mL of toluene, and 4.5 g of *p*-toluenesulfonic acid monohydrate) yielded the indene **13b** after removal of the solvent and distillation (0.1 Torr/96–108 °C) as a colorless oil. Yield: 33 g, 41%, of **13b**. ¹H NMR (CDCl₃, 100 MHz): δ 7.1–7.7 (m, 8H, arom H), 6.9, 6.5 (2m, 2H, CH), 3.5 (m, 2H, CH₂).

2-Methyl-3-(2-naphthyl)propionic Acid (15a). Following the procedure described for **11a** (5.2 g (0.224 mol) of sodium, 150 mL of dry ethanol, 39 g (0.224 mol) of diethyl methylmalonate, 50 g (0.224 mol) of 2-(bromomethyl)naphthalene (Aldrich), 40 g of KOH, and 200 mL of water) gave the acid **15a** as a beige-colored solid. Yield: 36 g, 76%, of **15a**. ¹H NMR (CDCl₃, 100 MHz): δ 8.3 (s, 1H, COOH), 7.0–7.8 (m, 7H, arom H), 2.7–3.3 (m, 3H, CH and CH₂), 1.1 (d, 3H, CH₃).

2-Methyl-6,7-benzoindan-1-one (16a). Following the procedure described for **12a** (21 g (98 mmol) of **15a**, 22 mL (0.3 mol) of thionyl chloride, and 26 g (0.2 mol) of aluminum trichloride) yielded indanone **16a** as a dark oily residue, which was purified by chromatography on silica gel (hexane/ethyl acetate, 9:3). Yield: 8.6 g, 45%, of **16a**. ¹H NMR (CDCl₃, 100 MHz): δ 7.2–7.8 (m, 6H, arom H), 3.3 (dd, 1H, H-C(3)), 2.5–2.9 (m, 2H, H'-C(3) and H-C(2)), 1.3 (d, 3H, CH₃).

2-Methyl-4,5-benzoindene (17a). Following the procedure described for **13a** (7.8 g (40 mmol) of **16a**, 250 mL of tetrahydrofuran/methanol (2:1), 2.2 g (60 mmol) of sodium borohydride, and 0.6 g of *p*-toluenesulfonic acid monohydrate) gave the indene **17a** after removal of the solvent and chromatography of the residue on silica gel (hexane/diisopropyl ether, 20:1) as a colorless oil. Yield: 4.7 g, 65%, of **17a**. ¹H NMR (CDCl₃, 360 MHz): δ 7.4–8.0 (m, 6H, arom H), 7.1 (m, 1H, H-C(3)), 3.4 (s, 2H, CH₂), 2.2 (d, 3H, CH₃).

3-(2-Naphthyl)propionic Acid (15b). Following the procedure described for **11a** (20.8 g (0.9 mol) of sodium, 600 mL of dry ethanol, 146 g (0.91 mol) of diethyl malonate, 200 g (0.9 mol) of 2-(bromomethyl)naphthalene (Aldrich), 152 g of KOH, and 200 mL of water) yielded the acid **15b** as a beige-colored solid. Yield: 163 g, 90%, of **15b**. Mp: 120–122 °C. ¹H NMR (CDCl₃, 100 MHz): δ 8.8 (s br, 1H, COOH), 7.2–7.9 (m, 7H, arom H), 2.7–3.2 (m, 4H, 2 CH₂).

6,7-Benzoindan-1-one (16b). Following the procedure de-

scribed for **12a** (141 g (0.7 mol) of **15b**, 78 mL (1.1 mol) of thionyl chloride, 104 g (0.77 mol) of aluminum trichloride) gave the indanone **16b** as a dark oily residue, which was purified by crystallization from hexane/ethyl acetate. Yield: 61 g, 47%, of **16b**. Mp: 78–80 °C. ¹H NMR (CDCl₃, 100 MHz): δ 9.2 and 7.4–8.1 (m, 6H, arom H), 3.2 and 2.8 (2 m, 4 H, 2 CH₂).

4,5-Benzoindene (17b). Following the procedure described for **13a** (39 g (218 mmol) of **16b** in 250 mL of tetrahydrofuran/methanol (2:1), 6.2 g of sodium borohydride, 1 g of *p*-toluenesulfonic acid monohydrate) yielded the indene **17b** after removal of the solvent and chromatography over silica gel (hexane/methylene chloride, 9:1) as a colorless oil. Yield: 22.6 g, 62%, of **17b**. ¹H NMR (CDCl₃, 100 MHz): δ 7.4–8.2 (m, 7H, arom H and H–C(3)), 6.7 (dt, 1H, H–C(2)), 3.6 (t, 2H, CH₂).

2-(2-(1-Naphthyl)benzyl)propionic Acid (19). Following the procedure described for **11a** (9.9 g (0.43 mol) of sodium, 1000 mL of dry ethanol, 74 g (0.43 mol) of diethyl methylmalonate, 75 g (0.43 mol) of 2-(1-naphthyl)benzyl bromide (prepared by following the procedure described in ref 32), 85 g of KOH, and 250 mL of water) gave the acid **19** as a viscous, oily product. Yield: 96 g, 77%, of **19**. ¹H NMR (CDCl₃, 100 MHz): δ 10.0 (s br, 1H, COOH), 7.0–7.9 (m, 11H, arom H), 2.0–2.8 (m, 3H, CH and CH₂), 0.8 (dd, 3H, CH₃).

2-Methyl-6-(1-naphthyl)-1-indanone (20). Following the procedure described for **12a** (96 g (0.33 mol) of **19**, 36 mL (0.5 mol) of thionyl chloride, 44 g (0.33 mol) of aluminum trichloride, and 1000 mL of toluene) gave the indanone **20** after chromatography on silica gel (dichloromethane) as a yellow solid. Yield: 12 g, 13%, of **20**. ¹H NMR (CDCl₃, 100 MHz): δ 7.3–8.0 (m, 11H, arom H), 2.2–3.2 (m, 3H, 2H–C(3) and H–C(2)), 1.3 (d, 3H, CH₃).

2-Methyl-7-(1-naphthyl)indene (21). Following the procedure described for **13a** (12 g (45 mmol) of **20** in 150 mL of tetrahydrofuran/methanol (2:1), 1.3 g (34 mmol) of sodium borohydride, and 0.5 g of *p*-toluenesulfonic acid monohydrate) yielded the indene **21** after removal of the solvent and chromatography over silica gel (hexane) as a colorless solid. Yield: 10 g, 86%, of **21**. ¹H NMR (CDCl₃, 100 MHz): δ 7.0–8.0 (m, 10H, arom H), 6.6 (m, 1H, H–C(3)), 3.0 (s, 2H, CH₂), 2.0 (s, 3H, CH₃).

2-(4-Phenylbenzyl)propionic Acid (23). Following the procedure described for **11a** (11.5 g (0.50 mol) of sodium, 500 mL of dry ethanol, 87 g (0.50 mol) of diethylmethylmalonate 101 g (0.50 mol) of 4-phenylbenzyl chloride (Aldrich), 150 g of KOH, and 300 mL of water) yielded the acid as a viscous, oily product. Yield: 104 g, 87%, of **23**. ¹H NMR (CDCl₃, 100 MHz): δ 10.3 (s, 1H, COOH), 7.1–7.7 (m, 9H, arom H), 2.3–3.2 (m, 3H, CH and CH₂), 1.0 (d, 3H, CH₃).

2-Methyl-6-phenyl-1-indanone (24). Following the procedure described for **12a** (120 g (0.5 mol) of **23**, 73 mL (1 mol) of thionyl chloride, 73 g (0.55 mol) of aluminum trichloride) gave the indanone **24** after crystallization from diethyl ether as colorless crystals. Yield: 99 g, 89%, of **24**. ¹H NMR (CDCl₃, 100 MHz): δ 7.3–8.0 (m, 8H, arom H), 3.3 (dd, 1H, H–C(3)), 2.6–2.9 (m, 2H, H–C(3) and H–C(2)), 1.3 (dd, 3H, CH₃).

2-Methyl-5-phenylindene (25). Following the procedure described for **13a** (19 g (88 mmol) of **24** in 450 mL of tetrahydrofuran/methanol (2:1), 5.0 g (0.13 mol) of sodium borohydride, and 0.5 g of *p*-toluenesulfonic acid monohydrate) gave the indene **25** after removal of the solvent and chromatography over silica gel (hexane) as a colorless solid. Yield: 42 g, 90%, of **25**. Mp: 81–82 °C. ¹H NMR (CDCl₃, 100 MHz): δ 7.1–7.7 (m, 8H, arom H), 6.5 (m, 1H, H–C(3)), 3.3 (s, 2H, CH₂), 2.1 (s, 3H, CH₃).

Preparation of the Ligands. Dimethylbis(2-methyl-4-phenylindenyl)silane (14a). To a solution of 15 g (73 mmol) of **13a** in 200 mL of dry toluene and 10 mL of dry THF under an argon atmosphere was added at room temperature 29 mL (73 mmol) of a 2.5 M solution of butyllithium in hexane. After stirring at 80 °C for 1 h, the reaction mixture was cooled to 0 °C and 4.7 g (36.5 mmol) of dimethylsilane dichloride was added. The mixture was heated to 80 °C for 1 h, and after the reaction was

complete, 100 mL of water was added. The organic layer was separated, the solvent was removed in vacuo, and the residue was purified by chromatography over silica gel (hexane/CH₂Cl₂, 9:1). Yield: 12 g, 70%, of **14a**. ¹H NMR (CDCl₃, 100 MHz): δ 7.1–7.7 (m, 16H, arom H), 6.8 (m, 2H, H–C(3)), 3.8 (s, 2H, H–C(1)), 2.2 (s, 6H, CH₃), –0.2 (m, 6H, CH₃Si). Anal. Calcd for C₃₄H₃₂Si: C, 87.13; H, 6.88. Found: C, 86.98; H, 6.91.

Phenylmethylbis(2-methyl-4-phenylindenyl)silane (14b). Following the procedure described for **14a** (63.6 g (308 mmol) of **13a**, 400 mL of toluene, 20 mL of THF, 123 mL (308 mmol) of 2.5 M butyllithium in hexane, and 29.4 g (154 mmol) of phenylmethylsilane dichloride) yielded **14b** after chromatography over silica gel (hexane/dichloromethane, 5:1) as a colorless oil. Yield: 36.5 g, 44%, of **14b**. ¹H NMR (CDCl₃, 100 MHz): δ 7.0–8.0 (m, 21H, arom H), 6.8 (m, 2H, H–C(3)), 4.2 (m, 2H, H–C(1)), 2.0–2.4 (m, 6H, CH₃), –0.1 (m, 3H, CH₃Si). Anal. Calcd for C₃₈H₃₄Si: C, 88.25; H, 6.46. Found: C, 87.87; H, 6.39.

Dimethylbis(4-phenylindenyl)silane (14c). Following the procedure described for **14a** (10 g (50 mmol) of **13b**, 100 mL of toluene, 5 mL of THF, 20 mL (50 mmol) of 2.5 M butyllithium in hexane, and 3.2 g (25 mmol) of dimethylsilane dichloride) gave **14c** by crystallization from heptane. Yield: 6.7 g, 62%, of **14c**. ¹H NMR (CDCl₃, 100 MHz): δ 7.0–7.7 (m, 18H, arom H and H–C(3)), 6.8 (dd, 2H H–C(2)), 3.8 (m, 2H, H–C(1)), –0.2 (m, 6H, CH₃Si). Anal. Calcd for C₃₂H₂₈Si: C, 87.22; H, 6.40. Found: C, 87.45; H, 6.61.

Dimethylbis(2-methyl-4,5-benzoindenyl)silane (18a). A 2.5 M solution of butyllithium in hexane (10.2 mL, 26 mmol) was added at room temperature to a solution of 4.6 g (26 mmol) of **17a** in 50 mL of tetrahydrofuran. The mixture was heated to reflux for 1 h. The red solution was then added to a solution of 1.6 g (13 mmol) of dimethylsilane dichloride in 10 mL of tetrahydrofuran at room temperature over a period of 2 h. After complete addition the mixture was heated to reflux for 5 h. Water was added and the mixture was extracted several times with diethyl ether. The combined organic layers were dried (MgSO₄), and the solvent was removed under vacuo. After chromatography over silica gel (hexane/ethyl acetate 20:1) 0.5 g of unreacted starting material **17a** and the ligand **18a** could be isolated. For further purification **18a** was recrystallized from hexane. Yield: 1.7 g, 44% of **18a**. ¹H NMR (CDCl₃, 100 MHz): δ 7.3–8.2 (m, 12H, arom H), 7.2 (m, 2H, H–C(3)), 4.0 (s, 2H, H–C(1)), 2.4 (2d, 6H, CH₃), –0.2 (3s, 6H, CH₃Si). Anal. Calcd for C₃₀H₂₈Si: C, 86.49; H, 6.77. Found: C, 86.21; H, 6.81.

Dimethylbis(4,5-benzoindenyl)silane (18b). Following the procedure described for **14a** (10.5 g (63 mmol) of **17b**, 100 mL of toluene, 5 mL of THF, 25.2 mL (63 mmol) of 2.5 M butyllithium in hexane, and 4.1 g (31 mmol) of dimethylsilane dichloride) gave **18b** by chromatography over silica gel (hexane/dichloromethane, 5:1). Yield: 7.4 g, 60%, of **18b**. ¹H NMR (CDCl₃, 100 MHz): δ 7.3–7.2 (m, 6H, arom H), 6.9, 6.7 (2 dd, 4H, H–C(2) and H–C(3)), 3.9 (m, 2H, H–C(1)), 0.0, –0.2, –0.4 (3s, 6H, CH₃Si). Anal. Calcd for C₂₈H₂₄Si: C, 86.55; H, 6.23. Found: C, 86.37; H, 6.54.

Dimethylbis(2-methyl-4-(1-naphthyl)indenyl)silane (22). Following the procedure described for **14a** (9.9 g (38 mmol) of **21**, 75 mL of toluene, 5 mL of THF, 15 mL (38 mmol) of 2.5 M butyllithium in hexane, and 2.5 g (19 mmol) of dimethylsilane dichloride) yielded **22** after chromatography over silica gel (hexane/dichloromethane 5:1) as a colorless oil. Yield: 8.2 g, 75%, of **22**. ¹H NMR (CDCl₃, 100 MHz): δ 7.1–8.0 (m, 16H, arom H), 6.4 (m, 2H, H–C(3)), 4.1 (m, 2H, H–C(1)), 2.2 (m, 6H, CH₃), –0.1 (m, 6H, CH₃Si). Anal. Calcd for C₄₂H₃₈Si: C, 88.68; H, 6.38. Found: C, 88.31; H, 6.72.

Dimethylbis(2-methyl-5(6)-phenylindenyl)silane (26). Following the procedure described for **14a** (10.0 g (48 mmol) of **25**, 200 mL of toluene, 10 mL of dry THF, 19.6 mL (49 mmol) of a 2.5 M solution of butyllithium in hexane, and 3.1 g (24 mmol) of dimethylsilane dichloride) **26** was obtained after chromatography over silica gel (hexane/dichloromethane, 5:1) as a mixture of isomers, carrying the phenyl substituents in the 6- or 5-position of the bis(indenyl) system. The isomers could not be separated.

(32) Miyano, S.; Okada, S.; Suzuki, T.; Handa, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* 1989, 59, 2044.

Yield: 8.3 g, 73%, of **26**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.2–7.9 (m, 16H, arom H), 6.8 (s, 2H, H–C(3)), 3.8 (s, 2H, H–C(1)), 2.2 (d, 6H, CH_3), –0.2 (m, 6H, CH_3Si). Different elemental analysis gave erratic results.

Preparation of the Zirconocenes 7a–c, 6a, 6b, 8, 9. [Dimethylsilanediylbis(2-methyl-4-phenylindenyl)]zirconium Dichloride (7a). To a solution of 6 g (13 mmol) of **14a** in 100 mL of dry toluene under an argon atmosphere was added at room temperature 10.6 mL (26 mmol) of a 2.5 M solution of butyllithium in hexane. After stirring at reflux for 3 h the reaction mixture was cooled to -25°C and 3.2 g (13.6 mmol) of zirconium tetrachloride was added. The reaction mixture was allowed to warm to room temperature over a period of 2 h. The suspension was filtered over a G3-Schlenk frit, and the residue was washed with 50 mL of dry toluene. The solvent of the combined extracts was removed in vacuo. A 9.0-g quantity of the complex was obtained as a 1:1 mixture of the racemic and the meso forms. The pure racemate was obtained after fractional crystallization of the 1:1 mixture from dry dichloromethane. Yield: 2.74 g, 33%, of **7a**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.0–7.7 (m, 16H, arom H), 6.9 (s, 2H, H–C(3)), 2.2 (s, 6H, CH_3), 1.3 (s, 6H, CH_3Si). MS (EI): m/z 626 ($^{90}\text{Zr}^{35}\text{Cl}_2$). Anal. Calcd for $\text{C}_{34}\text{H}_{30}\text{SiZrCl}_2$: C, 64.94; H, 4.81. Found: C, 64.66; H, 5.05.

[Phenylmethylsilanediylbis(2-methyl-4-phenylindenyl)]zirconium Dichloride (7b). Following the procedure described for **7a** (24.6 g (46.4 mmol) of **14b**, 300 mL of toluene, 37 mL (92.8 mmol) of a 2.5 M solution of butyllithium in hexane, 10.8 g (46.4 mmol) of zirconium tetrachloride) gave the racemate by fractional crystallization of the rac/meso 1:2 mixture from dichloromethane/hexane at -30°C . Yield: 3.2 g, 10%, of **7b**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.9–8.2 (m, 17H, arom H), 6.9 (m, 2H, H–C(3)), 2.3, 2.0 (2s, 6H, CH_3), 1.3 (s, 3H, CH_3Si). MS (EI): m/z 688 ($^{90}\text{Zr}^{35}\text{Cl}_2$). Anal. Calcd for $\text{C}_{39}\text{H}_{32}\text{SiZrCl}_2$: C, 67.80; H, 4.67. Found: C, 67.49; H, 5.01.

[Dimethylsilanediylbis(4-phenylindenyl)]zirconium Dichloride (7c). To a solution of 6.6 g (16 mmol) of **14c** in 70 mL of dry diethyl ether under an argon atmosphere was added at room temperature 12 mL (32 mmol) of a 20% solution of butyllithium in toluene. The mixture was heated 3 h to reflux. The solvent was removed in vacuo; the residue was suspended in 60 mL of dry hexane and filtered over a G3-Schlenk frit. The dilithiosalt of **14c** was dried in vacuo (0.1 Torr, room temperature) for 4 h and then added to a stirred suspension of 3.6 g (16 mmol) of zirconium tetrachloride in 80 mL of dichloromethane at -78°C . The mixture was allowed to warm to room temperature overnight. The orange suspension was filtered over a G3-Schlenk frit, and the residue was extracted with 200-mL portions of dichloromethane. Concentration of the combined filtrates and crystallization from dichloromethane/hexane 1:1 yielded a 1:1 mixture of the racemic and the meso forms of the complex. The pure racemate was obtained after fractional crystallization of the 1:1 mixture from dry dichloromethane. Yield: 1.43 g, 15%, of **7c**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.0–7.8 (m, 18H, arom H and H–C(3)), 6.1 (d, 2H, H–C(2)), 1.1 (s, 6H, CH_3Si). MS (EI): m/z 598 ($^{90}\text{Zr}^{35}\text{Cl}_2$). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{SiZrCl}_2$: C, 63.98; H, 4.36. Found: C, 64.23; H, 4.24.

[Dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)]zirconium Dichloride (6a). Following the procedure described for **7c** (1.7 g (4 mmol) of **18a**, 20 mL of tetrahydrofuran, 4.0 mL (10.2 mmol) of a 2.5 M solution of butyllithium in hexane, 1.0 g (4 mmol) of zirconium tetrachloride, and 25 mL of dichloromethane) yielded the racemate by extraction of the rac/meso 1:1 mixture with toluene to remove the meso form of the complex. The residue was then extracted with 40 mL of dichloromethane. Concentration of the filtrate and crystallization at -30°C yielded the racemic form. Yield: 0.97 g, 42% of **6a**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.3–8.0 (m, 12H, arom H), 7.3 (s, 2H, H–C(3)), 2.4 (s, 6H, CH_3), 1.4 (s, 6H, CH_3Si). MS (EI): m/z 574 ($^{90}\text{Zr}^{35}\text{Cl}_2$). Anal. Calcd for $\text{C}_{30}\text{H}_{26}\text{SiZrCl}_2$: C, 62.48; H, 4.54. Found: C, 62.27; H, 4.44.

[Dimethylsilanediylbis(4,5-benzoindenyl)]zirconium Dichloride (6b). Following the procedure described for

Table 7. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (\AA^2) for **7a**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
C(01)	0.3386(3)	0.1752(2)	0.1337(5)	0.026(1)
C(02)	0.3104(3)	0.1472(1)	0.0145(5)	0.026(1)
C(03)	0.2107(3)	0.1410(2)	0.0170(5)	0.026(1)
C(04)	0.1469(3)	0.1128(2)	–0.0737(4)	0.030(1)
C(05)	0.0525(3)	0.1117(2)	–0.0356(5)	0.036(1)
C(06)	0.0198(3)	0.1368(2)	0.0854(5)	0.038(1)
C(07)	0.0790(3)	0.1652(2)	0.1698(6)	0.035(1)
C(08)	0.1773(3)	0.1679(2)	0.1390(5)	0.027(1)
C(09)	0.2579(3)	0.1913(1)	0.2116(3)	0.025(1)
C(10)	0.4422(3)	0.1851(2)	0.1694(6)	0.035(1)
C(11)	0.1808(3)	0.0866(2)	–0.1997(5)	0.036(1)
C(10)	0.1462(4)	0.0332(2)	–0.2373(6)	0.060(2)
C(13)	0.1740(5)	0.0075(3)	–0.3525(8)	0.091(2)
C(14)	0.2339(5)	0.0370(3)	–0.4415(7)	0.090(2)
C(15)	0.2717(4)	0.0898(2)	–0.4050(6)	0.066(2)
C(16)	0.2433(4)	0.1142(2)	–0.2860(4)	0.046(1)
C(17)	0.1472(3)	0.2460(2)	0.4532(4)	0.045(1)
Cl(1)	0.3775(1)	0.2550(1)	–0.1576(1)	0.030(1)
Cl(2)	0.4442(5)	0.0334(3)	0.2546(10)	0.273(2)
Cl(3)	0.4783(5)	0.0522(2)	–0.6246(9)	0.168(2)
Si(1)	0.2500	0.2500	0.3400(1)	0.028(1)
Zr(1)	0.2500	0.2500	0.0047	0.019(1)

^a Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

7c (7.4 g (19 mmol) of **18b**, 100 mL of diethyl ether, 15.2 mL (38 mmol) of a 2.5 M solution of butyllithium in hexane, 4.4 g (19 mmol) of zirconium tetrachloride, and 25 mL of dichloromethane) yielded the racemate by extraction of the rac/meso 1:1 mixture with tetrahydrofuran to remove lithium chloride and then dichloromethane to remove the meso form of **6b**. Yield: 1.9 g, 18%, of **6b**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.2–8.0 (m, 12H, arom H), 7.2 (d, 2H, H–C(3)), 6.4 (d, 2H, H–C(2)), 1.2 (s, 6H, CH_3Si). MS (EI): m/z 546 ($^{90}\text{Zr}^{35}\text{Cl}_2$). Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{SiZrCl}_2$: C, 61.29; H, 4.04. Found: C, 61.53; H, 4.19.

[Dimethylsilanediylbis(2-methyl-4-(1-naphthyl)indenyl)]zirconium Dichloride (8). Following the procedure described for **7c** (8.2 g (14.4 mmol) of **22**, 50 mL of diethyl ether, 11.5 mL (28.8 mmol) of 2.5 M solution of butyllithium in hexane, 3.4 g (14.4 mmol) of zirconium tetrachloride, and 60 mL of dichloromethane) gave the racemate by crystallization of the rac/meso 1:1 mixture from dichloromethane. Yield: 1.2 g, 11%, of **8**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.0–8.0 (m, 20H, arom H), 6.5 (s, 2H, H–C(3)), 2.2 (s, 6H, CH_3), 1.3 (s, 6H, CH_3Si). MS (EI): m/z 726 ($^{90}\text{Zr}^{35}\text{Cl}_2$). Anal. Calcd for $\text{C}_{42}\text{H}_{34}\text{SiZrCl}_2$: C, 69.20; H, 4.70. Found: C, 69.00; H, 4.81.

[Dimethylsilanediylbis(2-methyl-5(6)-phenylindenyl)]zirconium Dichloride (9). Following the procedure described for **7a** (3.1 g (6.7 mmol) of **26**, 40 mL of toluene, 5.6 mL (14 mmol) of 2.5 M solution of butyllithium in hexane, and 1.6 g (6.7 mmol) of zirconium tetrachloride) yielded the racemate of **9** after extraction with 250 mL of toluene and crystallization from the concentrated, combined filtrates at 0°C as a mixture of the 5- and 6-phenyl isomers. Any attempt to separate these isomers by crystallization from several solvents failed. Yield: 0.54 g, 13%, of **9**. $^1\text{H NMR}$ (CDCl_3 , 100 MHz): δ 7.0–7.8 (m, 16H, arom H), 6.8 (s, 2H, H–C(3)), 2.3 (s, 6H, CH_3), 1.3 (s, 6H, CH_3Si). MS (EI): m/z 626 ($^{90}\text{Zr}^{35}\text{Cl}_2$). Different elemental analysis gave erratic results.

Zirconocenes Previously Described. The previously described zirconocenes according to Table 1 were synthesized by methods in the cited literature.

X-ray Structure Analysis of 7a. Single crystals of **7a** were obtained by crystallization from dichloromethane. A crystal of $0.4 \times 0.4 \times 0.25 \text{ mm}^3$ was sealed in a Lindemann glass capillary. 25 reflections with $\theta > 10^\circ$ were used to determine the cell constants $a = 14.158(1) \text{ \AA}$, $b = 23.642(2) \text{ \AA}$, $c = 9.903(1) \text{ \AA}$. Other data: orthorhombic, $Ccc2$, $Z = 4$, $V = 3314.8(9) \text{ \AA}^3$, $\text{C}_{34}\text{H}_{30}\text{Cl}_2\text{SiZr} \cdot 0.5\text{CH}_2\text{Cl}_2$, $M_r = 699.7$, $D_x = 1.402 \text{ Mg/m}^3$. Reflections ($-18 \leq h \leq 8$, $0 \leq k \leq 31$, $0 \leq l \leq 13$) with $|F| > 1\sigma(F)$ (3409 reflections

measured, 2115 out of 2161 unique reflections, $R(I)_{\text{int}} = 0.01$) were used for the structure analysis: computer controlled diffractometer (Siemens), Mo K α radiation, $\mu = 0.712 \text{ mm}^{-1}$, $T = 193 \text{ K}$. Direct methods were employed for solving the phase problem,³³ and refinement of the structure parameters was by least-squares methods (minimization of $(|F_o| - |F_c|)^2$; weighting scheme, $w = 1/\sigma^2(F)$ according to the counting statistics; 191 parameters; coordinates of the H-atoms calculated; $S = 2.79$; $R = 0.034$, $R_w = 0.027$; 10 largest peaks in the difference map, 0.57 ... 0.25 electrons/Å³). All calculations were done by a microVAX II with the SHELXTL-PLUS programs.³³ Tables of the anisotropic thermal coefficients, bond lengths, bond angles, torsion angles, and H-atom coordinates are available as supplementary material.

Polymerization Procedures. Polymerization grade ethylene and propylene were used; propylene was further purified by passage through columns of 10-Å molecular sieves. A solution of methylaluminoxane in toluene (10.1 wt % MAO, cryoscopic $M_w = 950$) purchased from Witco GmbH was directly applied. EXXSOL 100/120, a saturated hydrocarbon diluent (bp 100–120 °C), purchased from ESSO GmbH, was used for ethylene and propylene suspension polymerizations (vide infra) after purification with 10-Å molecular sieves.

Polymerizations of Liquid Propylene. A dry 16-L, thermostatable steel reactor was charged with nitrogen and 10 L of liquid propylene at 30 °C. Then 30 mL of the solution of methylaluminoxane in toluene (vide supra, 45 mmol Al) was added to the stirred reactor. Simultaneously, 5 μmol of metallocene (runs with 7a, 7b and 8: 3 μmol) was dissolved in an identical solution of methylaluminoxane in toluene (20 mL, 30 mmol) and allowed to react for 15 min at 25 °C. The colored solution was then added to the reactor. The reactor was heated to 70 °C within 3 min and kept at this temperature for 1 h. The reaction was stopped by the addition of 2-propanol (10 mL) and cooled, the pressure was released, and the product was taken out and dried in vacuum. The yield was determined by weighing. This procedure was applied to previously known metallocenes 1–5 and to newly synthesized 6–9. With systems yielding products with rather low molecular weights, such as 1a, 2a, 6b, 7c, free flowing polymer powders were obtained, and no reactor fouling

appeared. With the others, besides powder, agglomerates were found and the reactor wall was more or less coated with product. In these cases, reproducibility of polymerization yields was no better than $\pm 20\%$.

Suspension Polymerizations of Propylene. A dry 1.5-L, thermostatable steel reactor was charged with nitrogen and 750 mL of EXXSOL 100/120 at 30 °C. Then 5 mL of the solution of methylaluminoxane in toluene (7.5 mmol Al) was added, and the stirred reactor was pressurized with 5 bars of propylene (second series: 2 bars of propylene). Metallocene (0.8 μmol) was reacted with 3 mL (4.5 mmol of Al) of methylaluminoxane solution, as above, and introduced to the reactor, and the reactor temperature was raised to 70 °C. A pressure of 5 bars (2 bars) was kept by continuously feeding propylene for 1 h and then stopped as above. The obtained polymer was stirred in a 20 vol % ethanolic hydrochloric acid solution overnight, washed with water and ethanol, dried in vacuum, and weighed for yield determination.

Suspension Polymerizations of Ethylene. The procedure of the respective propylene polymerizations was applied. Due to higher catalyst activities with ethylene and in order to keep the Zr:Al ratio of 1:15 000 constant, quantities of metallocene and cocatalyst were changed: 0.25 μmol of metallocene and overall 2.5 mL of methylaluminoxane solution.

Polymer Analyses. Molecular masses were determined by gel permeation chromatography on a Waters 150 C instrument (solutions in 1,2-dichlorobenzene at 135 °C); molecular mass distributions M_w/M_n were < 3 in any case. Melting points were determined with a Perkin-Elmer DSC-4 system at a heating rate of 20 °C/min. The results of the second scan are reported. ¹³C NMR measurements were performed on a Bruker WP 300 instrument at 110 °C (the polymer dissolved in hexachlorobutadiene/ $\text{CDCl}_2\text{CDCl}_2$). The percentage of isotactic pentades was calculated from the integration of the spectra according to the literature.

Supplementary Material Available: Tables of experimental data, bond lengths and angles, torsion angles, thermal parameters, and H atom coordinates and figures of the structure with atom labels and the crystal packing diagram (12 pages). Ordering information is given on any current masthead page.

OM930579S

(33) Sheldrick, G. M. SHELXTL-PLUS, an Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. University of Göttingen, 1990.