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ansa-Zirconocene Polymerization Catalysts with Annelated Ring Ligands—Effects on Catalytic Activity and Polymer Chain Length[1]

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The dimethylsilyl-bridged zirconocene complexes $(CH_3)_2Si(benz[e]indenyl)_2ZrCl_2$ (I) and $(CH_3)_2Si(2\text{-methylbenz}[e]indenyl)_2ZrCl_2$ (II) have been synthesized; the structure of II was determined by X-ray diffraction. Complex I is about 4 times more active in polymerizing propene than its bis(indenyl) analog when activated with methylaluminoxane (MAO) under otherwise identical conditions. The resulting catalyst system polymerizes also the γ-branched olefins 3-methyl-1-butene and 3-methyl-1-pentene. Polymers produced with complex II have molecular weights about 4 times higher than those obtained with complex I under identical conditions. The α-methyl substituents of II appear to block those chain terminations which arise from β-H transfer directly to a coordinated monomer molecule.

Introduction

For practical applications of metallocene-based olefin polymerization catalysts, further improvements in their catalytic activities and in the molecular weights of their polyolefin products would be desirable. Previous studies on the activation of complexes of this type by methylaluminoxane (MAO) have shown that increased catalytic activities are associated with the presence of the aromatic six-membered rings in [ethylenebis(indenyl)]zirconium dichloride, as compared to its hydrogenated congener [ethylenebis(tetrahydroindenyl)]zirconium dichloride,[2–4] and that introduction of a phenyl substituent in the β-positions of a dimethylsilyl-bridged zirconocene complex induces a similar increase in catalytic activity.[5] As the essential structure elements of both bis(indenyl) and β-phenyl-substituted complexes are combined in *ansa*-zirconocene derivatives with benz[*e*]indenyl ligands, we have undertaken a study on the catalytic properties of complexes of this type.

Results and Discussion

The dimethylsilyl-bridged benz[*e*]indenyl complex I and its α-methyl-substituted homolog II were prepared in their pure racemic forms, as described in the Experimental Part. The structure of II was determined by X-ray diffraction. Its coordination geometry at the Zr center (Table 1, Figure 1) is practically indistinguishable from that of the bis(indenyl) complexes III or IV, previously studied by Spaleck and collaborators.[6] An analogous coordination geometry is to be assumed, therefore, also for complex I; the resulting structural model is represented in Figure 1, together with the structures of complexes II–IV.

Table 1. Selected Distances (Å) and Angles (deg) for Complex II

Zr–Cl	2.423(2)	Cl–Zr–Cl′	99.2(1)
Zr–CR[a]	2.247	Cr–Zr–CR′[a]	127.9
Zr–C	2.474–2.648	C(1)–Si–C(1)′	94.8(3)
		PL–PL′[b]	60.8

[a] CR and CR′: centroids of the Zr-bound C_5 rings. [b] PL and PL′: mean planes of these C_5 rings.

To investigate the effects of the additional benzannelation on the catalytic properties of complexes I and II, we have conducted catalytic polymerizations of propene with these complexes, activated with MAO in toluene solution, in comparison with their bis(indenyl) congeners III and IV. Under the conditions used (see Experimental Section), we find the activity of complex I in the

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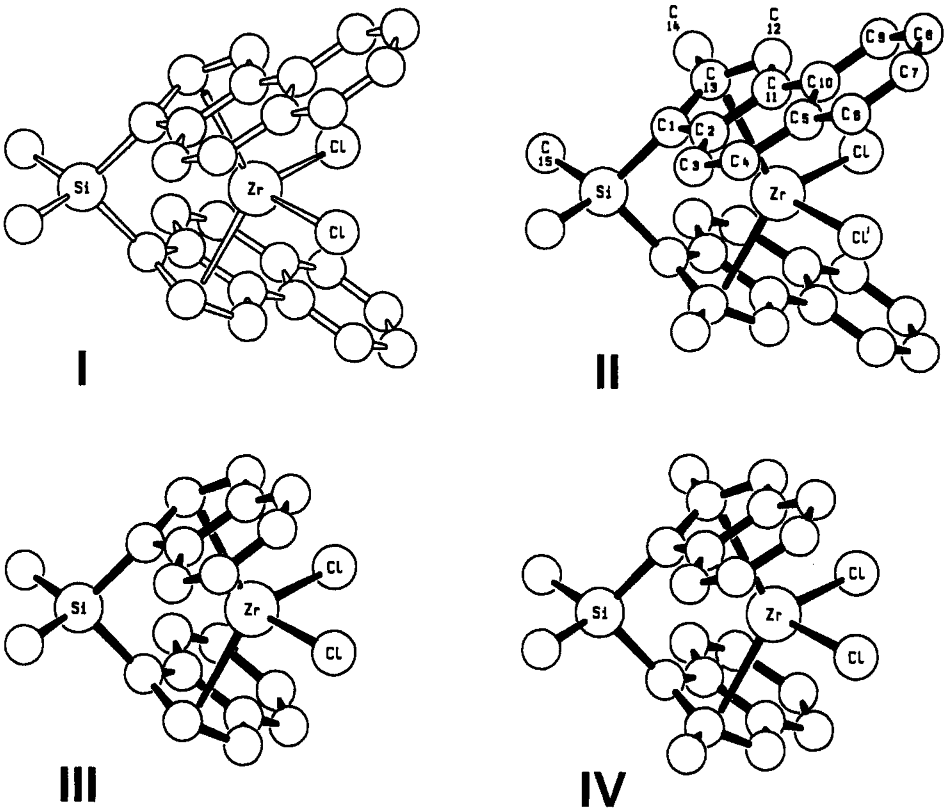

Figure 1. Molecular structure of complex **II**, determined by X-ray diffraction, and structural model for complex **I**, derived from the structure of **II**. For comparison, the molecular structures of **III** and **IV**, as given in ref 6, are also represented.

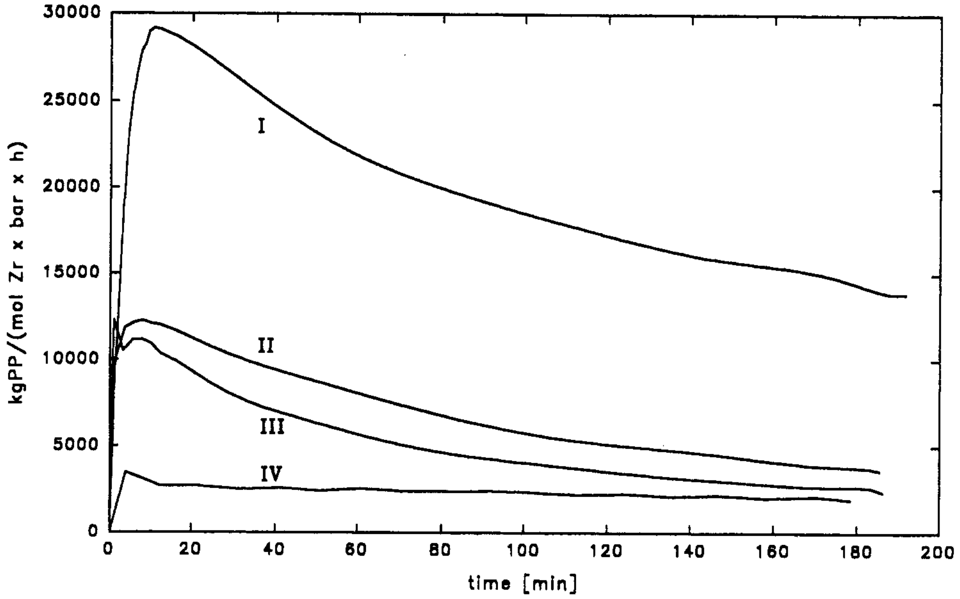

Figure 2. Activities of complexes **I**–**IV**, 2×10^{-6} M in a 2×10^{-2} M solution of MAO ($M \approx 1000$) in toluene, at 40 °C and 2 bar of propene pressure, for the polymerization of propene, with dependence on reaction time.

polymerization of propene to be 3–4 times higher than that for its bis(indenyl) analog **III** (Figure 2). The catalyst system **I**/MAO is deactivated at an unusually low rate. While low deactivation rates are typical for bis(indenyl)zirconium complexes (as opposed to alkyl-substituted bis(cyclopentadienyl) complexes,[7] the time required for deactivation to one-half of the initial activity—ca. 3 h for complex **I**—is about 3 times longer yet than that for the bis(indenyl) complex **III**.

The rate of deactivation in related reaction systems has been found to be second-order in the concentration of the active catalyst species.[7,8] Deactivation thus appears to proceed by an intermediate formation of binuclear zirconocene cations.[9,10] From Figure 1 it is apparent that the protruding ligand framework of the benzannelated

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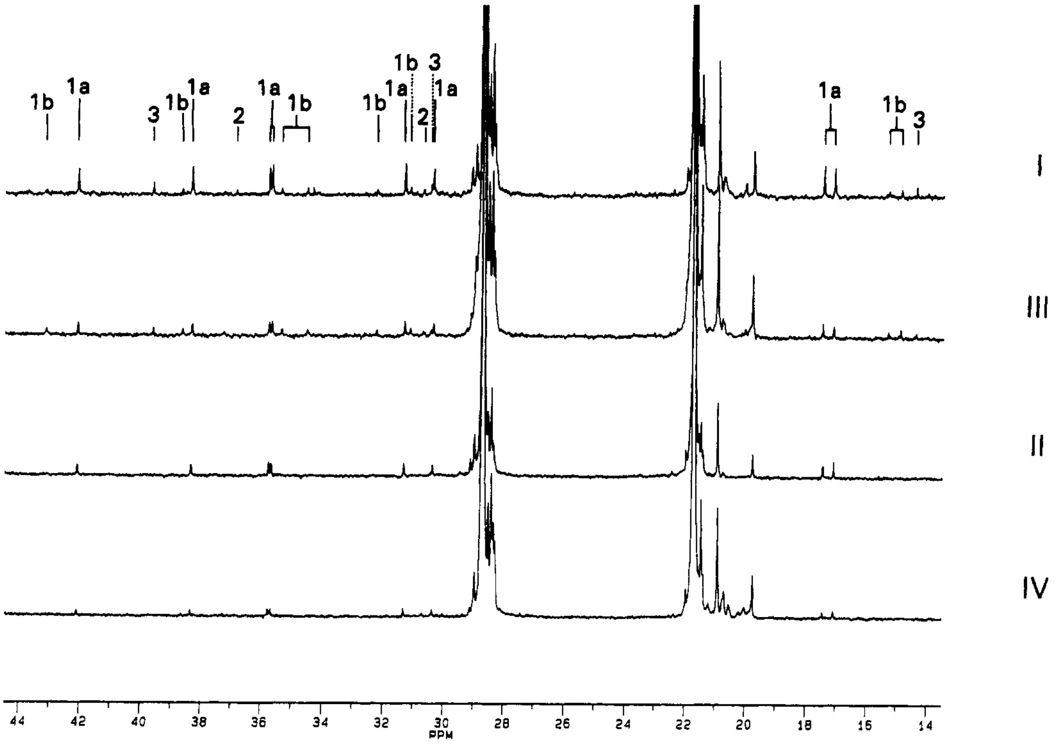

Figure 3. ^{13}C NMR spectra of polypropene obtained with complexes **I–IV**, activated with MAO at a propene pressure of 2 bar (cf. Table 2). Misinsertion signals: **1a**, m-2,1-units; **1b**, r-2,1-units; **2**, 3,1-units; **3**, *n*-propyl end groups.

Table 2. Propene Polymerization with $Me_2SiL_2ZrCl_2$/MAO at 50 °C ([Zr] = 1.25 μmol/L; [Al]/[Zr] = 15 800)

catalyst	L	p^a (bar)	$c(C_3H_6)^b$ (mol/L)	t^c (min)	productivity [kg of PP/(mol of [Zr]·h·bar)]	$M_w{}^d$	$M_w/M_n{}^d$	T_{mp} (°C)	mmmm (%)	2,1-units (%)
I	BenzInd	1	0.31	150	5200	29 800	1.67	139	88	0.5
I	BenzInd	2	0.66	120	12300	35 100	1.60	140	88	0.8
I	BenzInd	3	1.02	60	17800	38 600	1.67	141	88	0.6
I	BenzInd	7	2.43	20	41100	39 600	1.64	142	90	0.7
II	2-MeBenzInd	1	0.31	240	1700	80 500	1.52	150	92	0.3
II	2-MeBenzInd	2	0.66	120	4500	137 100	1.56	151	92	0.4
II	2-MeBenzInd	3	1.02	120	3900	182 200	1.61	151	93	0.2
II	2-MeBenzInd	5	1.72	12	29000	247 700	1.71	152	93	0.3
III	Ind	2	0.66	180	7000	61 900	1.67	142	89	0.4
IV	2-MeInd	2	0.66	240	4600	135 000	1.64	150	90	0.2

[a] Total pressure; correction for vapor pressure of toluene yields propene pressure $p(C_3H_6) = p - 0.12$ (bar). [b] Calculated as $c(C_3H_6) = p(C_3H_6) \times 0.353$ (cf. ref 7b). [c] Polymerization times have been chosen so as to yield ca. 15–50 g of polymer for catalyst I and ca. 5–15 g for catalyst II. [d] Determined by GPC.

complexes will hinder any bulky reaction partner from approaching the Zr center of these complexes. Their decreased rate of deactivation might thus result from a steric hindrance of the mutual approach of their Zr centers by their large ligand frameworks. This protrusion might likewise make close contacts of the presumably bulky $XMAO^-$ counteranion with the cationic Zr center of these complexes sterically unfavorable. It remains to be determined whether the formation of the olefin-separated ion pairs required for chain growth is indeed enhanced in these complexes at the expense of the normally preponderant, "dormant" tight ion pairs.[11]

^{13}C NMR spectra of polypropenes produced with each of the four complexes **I–IV** reveal a high degree of stereoregularity, with mmmm pentad probabilities of ca. 90%, and a finite incidence of 2,1 regioirregular (tail-to-tail and head-to-head) insertion units (Figure 3, Table 2).[12–17] With other catalysts, a substantial decrease in catalytic activity has been found to be caused by occasional regioirregular insertions, since olefin insertion into the resulting bulky, secondary Zr–alkyl units occurs at greatly decreased rates.[18,19] In these cases, a rearrangement of

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(17) The α-methyl substituted complexes **II** and **IV** produce only about half as many 2,1-misinsertions as their unsubstituted counterparts **I** and **III**, each of the bis(indenyl) complexes being distinctly more regioregular than its bis(benzindenyl) analog. While complexes **II** and **IV** give rise to m-configurated 2,1-units only, some r-configurated 2,1-units are also found in polymers formed with the unsubstituted complexes **I** and **III**. Melting points of the polypropene products appear to decrease substantially with increasing 2,1-misinsertion contents.

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Table 3. Polymerization of τ-Branched Olefins with $Me_2SiL_2ZrCl_2$/MAO (0.5 μmol of Zirconocene and 7.9 mmol of MAO in 15 mL of Toluene)

catalyst	L	olefin	T_p (°C)	t (h)	yield (g)	T_{mp} (°C)
I	BenzInd	3-methyl-1-butene	23	14	1.18	180–230
III	Ind	3-methyl-1-butene	23	14	0.24	180–230
I	BenzInd	(±)-3-methyl-1-pentene	60	15	2.80	180–230
III	Ind	(±)-3-methyl-1-pentene	60	15	1.76	180–230

the secondary units to 1,3-units, *via* β-H transfer and reinsertion, appears to precede the insertion of another olefin, especially at polymerization temperatures above ambient.[13,16] The virtual absence of 1,3-units for catalysts **I–IV**/MAO implies that, here, a secondary Zr–alkyl unit inserts an α-olefin faster than it rearranges to a terminal Zr–alkyl unit. The high rate of incidence of 2,1-misinsertion with **I**/MAO indicates that this catalyst system is particularly uninhibited by the steric bulk of such a secondary Zr–alkyl unit.

An increased tolerance of this catalyst system toward steric encumbrance of the olefin insertion reaction complex is also borne out by the capability of the complex **I**/MAO catalyst to induce a polymerization of olefins which are branched in the γ-position, such as 3-methyl-1-butene or 3-methyl-1-pentene (Table 3); as far as we know, such an activity has not been reported before for isospecific, metallocene-based catalysts.[20] As reported for related polymers obtained with heterogeneous catalysts,[21] the polymers obtained from these branched olefins have rather high melting points; their microstructures are being investigated at present.

The MAO-activated catalyst derived from the methyl-substituted complex **II** is intermediate in its activity between its unsubstituted analog **I** and its bis(2-methylindenyl) congener **IV** (Figure 2). Most remarkable is the unusually high molecular weight of polypropene produced by catalyst **II**/MAO (Table 2); at a propene pressure of 2 bar, it exceeds that obtained with **I**/MAO by a factor of about 4; it is marginally higher even than that obtained with **IV**/MAO under otherwise identical conditions.[6]

Increased molecular weights have been noted before for polymers produced by several *ansa*-zirconocene catalysts which contain a methyl substituent in an α-position of each C_5 ring.[6b,22,23] To study the origins of this effect, we have determined the molecular weights of polypropene produced with MAO-activated complexes **I** and **II** at varying propene pressures. An increase in molecular weights approximately proportional to the monomer concentration is to be expected if β-H transfer from the growing chain to the metal center is the dominant chain termination process.[7b,8] Alternatively, chain growth can be terminated by transfer of a β-H atom from the Zr-bound polymer chain directly to a coordinated monomer molecule.[24,25] As the rates of chain growth and chain termination would then both increase with olefin concentration, the latter would be expected to have little influence on molecular weights in this case.

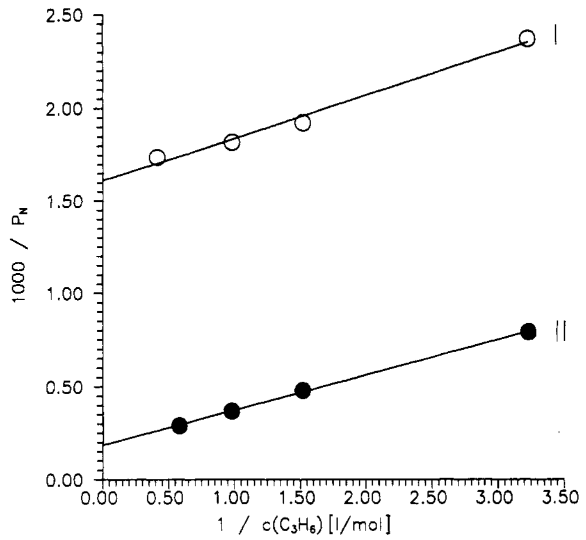

Figure 4. Reciprocal degree of polymerization, $1/P_N$, with dependence on reciprocal propene concentration, $1/[M]$, for catalysts **I**/MAO (top) and **II**/MAO (bottom). Reaction conditions are as in Table 2.

For catalyst **I**/MAO, nearly constant molecular weights are indeed observed, while molecular weights increase strongly with propene pressure for catalyst **II**/MAO (Table 2). This indicates that the dominant chain termination process for catalyst system **I**/MAO is β-H transfer to an olefin, while β-H transfer to the metal dominates for catalyst **II**/MAO. A more quantitative estimate of the relative weights of these two processes is derived from a plot of the reciprocal degree of polymerization, $1/P_N$, *versus* the reciprocal monomer concentration, $1/[M]$: With the mean degree of polymerization, $P_N = M_N/42$, given as $P_N = v_P/v_T$,[26] the rate of polymer growth as $v_P = C^*k_P[M]$,[27] and the rate of chain termination as the sum of the rates of β-H transfer to the metal and to the olefin, $v_T = v_{TM} + v_{TO} = C^*(k_{TM} + k_{TO}[M])$, one obtains the equation $1/P_N = (k_{TM}/k_P)(1/[M]) + k_{TO}/k_P$.

Plots of $1/P_N$ *versus* $1/[M]$ for catalysts **I**/MAO and **II**/MAO (Figure 4) yield quite similar slopes and, hence, a similar ratio of the rate constant for β-H transfer to the metal over that for polymer growth, k_{TM}/k_P, of 2.3×10^{-4} and 1.9×10^{-4} mol·L^{-1} for the two catalysts. The y-axis intercepts of these plots, however, yield a ratio of the rate

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(27) The productivities of catalysts **I**/MAO and **II**/MAO appear to increase at higher propene pressures (Table 2). This phenomenon requires further clarification; rather than by a higher-order dependence of the rate of chain growth, v_P, on the monomer concentration [M], it might be caused by the shorter polymerization times required at higher propene pressures for comparable polymer yields, which coincide more closely with the activity maxima in Figure 2, or by local temperature excursions, which might occur with these highly active catalyst systems especially at higher propene pressures, when the reaction systems become heterogeneous by the precipitation of polymer.

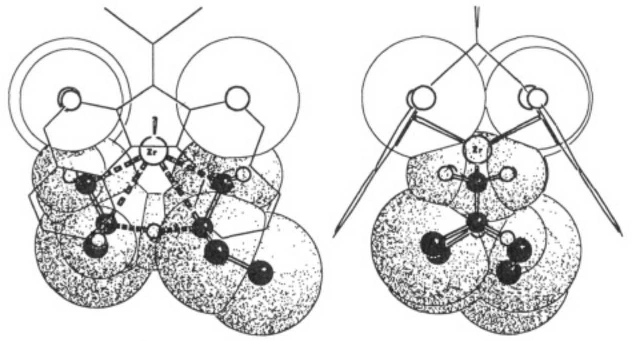

Figure 5. Transition state model for direct β-H transfer from the Zr-bound polymer chain to a coordinated propene molecule (shaded) and its steric interaction with substituents in α-positions of complex **II** (van der Waals radii: aromatic C atom, 1.6 Å; CH_3 group, 1.9 Å) (SCHAKAL modeling program, E. Keller, Universität Freiburg).

constants for β-H transfer to olefin over that for polymer growth, k_{TO}/k_P, which is almost one order of magnitude larger (1.6×10^{-3}) for catalyst **I**/MAO than that (1.8×10^{-4}) for **II**/MAO. Four to five times as many β-H transfers to the olefin than to the metal will thus occur for catalyst **I**/MAO at a propene pressure at 2 bar ([M] = 0.66 mol/L), while for catalyst **II**/MAO β-H transfer to the metal is accompanied only by a minor fraction of β-H transfers to an olefin. The increase in molecular weight between **I**/MAO and **II**/MAO thus appears to be due to a strong suppression of direct β-H transfer to the olefin by the α-methyl groups of complex **II**. In accord with this analysis, we find that polymerization in liquid propene affords polymers with even higher $M_w \approx 500\,000$ for catalyst **II**/MAO, while **I**/MAO still gives $M_w \approx 40\,000$.

Transition state models for a β-H transfer to a coordinated monomer, as that represented in Figure 5, indicate that this process requires a metallocene coordination gap with a rather wide "lateral extension" angle[28] of more than 180°. Since methyl substituents in the α-position to each bridgehead cause a severe narrowing of this lateral extension, they are likely to block this chain termination reaction channel, leaving only those chain terminations operative which occur by β-H transfer to the metal center. This hypothesis, which might prove useful for future catalyst designs, is presently being tested by further kinetic studies and other mechanistic investigations.

Experimental Part

Solvents were dried over calcium hydride or Na/benzophenone; for the preparation of ligands and zirconocenes, solvents were thoroughly degassed and all solutions handled under an Ar atmosphere. Merck or Baker flash silica gel with 60-μm mean corn diameter was used for column chromatography.

1-*H*- and 3-*H*-Benz[*e*]indene (1, 2). The preparation followed that described by Maréchal and Chaintron[29] (Scheme 1) with the following modifications: The naphthoyl acrylic acid isomers were obtained with higher yields if solid aluminum trichloride was added to maleic anhydride cooled in an ice bath; reaction with naphthalene and workup were conducted as described in ref 29. Before their thermal decarboxylation, the ketobenz[*e*]indan carbonic acids had to be thoroughly dried. For the dehydration of the benz[*e*]indanol isomers, a 0.2 M solution in toluene was treated with 4 equiv of anhydrous oxalic acid and refluxed, using a water separator to remove the evolving H_2O. The reaction mixture was then freed from oxalic acid by washing with aqueous $NaHCO_3$ and dried over Na_2SO_4. A mixture of pure **1** and **2** was obtained by chromatography over a silica gel column with petroleum ether as eluent in a yield of 37% based on the benz[*e*]indanol mixture. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.71 (t, 1.5 Hz, 2H), 6.65 (m, 1H), 7.00 (m, 1H), 7.34–7.97 (m, 6H) for 1-*H*-benz[*e*]indene: δ 3.56 (t, 1.8 Hz, 2H), 6.74 (m, 1H), 7.41–8.14 (m, 7H) for 3-*H*-benz[*e*]indene.

1-*H*- and 3-*H*-2-Methylbenz[*e*]indene (3, 4). To a suspension of 577 g (4.3 mol) of $AlCl_3$ in 250 mL of CH_2Cl_2, kept at 0 °C by an ice bath, were added first 200 mL (1.62 mol) of 2-bromoisobutyric acid bromide and then a solution of 207 g (1.62 mol) of naphthalene in 500 mL CH_2Cl_2. The mixture was stirred for 30 min at 0 °C and 90 min at room temperature and then poured on ice. The dark organic layer was separated, dried over $MgSO_4$ and filtered, mixed with 250 g of silica gel, and evaporated to dryness. By chromatography of the solid residue over a short column of 140 g of silica gel with a petroleum ether/ethyl acetate eluent mixture, one obtains a reddish, viscous mixture of the two benz[*e*]indanone isomers. Yield: 235 g (1.2 mol, 74%). ^1H NMR ($CDCl_3$, 250 MHz): δ 1.36 (d, 3H), 2.80 (m, 2H), 3.46 (dd, 1H), 7.46–8.04 (m, 5H), 9.14 (d, 1H) for 2-methylbenz[*e*]indan-1-one (main product).

To a solution of 100 g (0.51 mol) of the 2-methylbenz[*e*]indanone isomer mixture in 500 mL of tetrahydrofuran (THF) was added, under cooling with ice, 165 mL of a 3.4 M toluene solution (0.56 mol) of $NaAlH_2(OCH_2CH_2OCH_3)_2$ over a period of 90 min. After stirring for another 2 h at room temperature, the reaction mixture, which was found to be free of residual indanone by TLC, was transferred to a 2-L beaker and slowly hydrolyzed, under constant stirring, by dropwise addition of 60 mL of hydrochloric acid (10% in water). After 30 min, the precipitate was allowed to settle, the supernatant was filtered through a Büchner funnel, and the solids were extracted twice with THF. The combined THF solution was dried with $MgSO_4$ and evaporated to dryness. The oily residue, which contained the two 2-methylbenz[*e*]indanol isomers, was used without further purification.

To a solution of the mixture of the 2-methylbenz[*e*]indanol isomers, obtained as described above, in 750 mL of toluene was added 100 g of anhydrous oxalic acid. The mixture was refluxed, using a water separator, until the formation of water subsided after about 100 min. The reaction mixture, which was found to be free of residual indanols by TLC, was washed with 1.75 L of a 10% aqueous $NaHCO_3$ solution, dried over $MgSO_4$, mixed with 80 g of silica gel, and evaporated to dryness. By chromatography of this residue over 375 g of silica gel with a petroleum ether/ethyl acetate eluent mixture (49:1), one obtains 53 g (0.3 mol, yield 58% based on indanone) of a 1-*H*- and 3-*H*-2-methylbenz[*e*]indene isomer mixture. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.25 (s, 3H), 3.60 (s, 2H), 6.61 (s, 1H), 7.30–7.88 (m, 6H) for 1-*H*-2-methylbenz[*e*]indene; δ 2.29 (s, 3H), 3.46 (s, 2H), 7.10 (s, 1H), 7.44–8.09 (m, 6H) for 3-*H*-2-methylbenz[*e*]indene. MS (EI): *m/z* 180 (M^+, 100%), 165 ($M^+ - CH_3$, 55%). Anal. Calcd for $C_{14}H_{12}$: C, 93.28; H, 6.72. Found: C, 93.11; H, 7.00.

Bis[3,3′-(3-*H*-benz[*e*]indenyl)]dimethylsilane (5). In a 200-mL Schlenk vessel, cooled to −18 °C with a salt/ice mixture, 1.7 g (42.4 mmol) of KH was suspended in 20 mL of THF. A solution of 3 g (18 mmol) of a mixture of 1-*H*- and 3-*H*-benz[*e*]indene in 35 mL of THF was added dropwise over a period of 20 min. After the dark green reaction mixture was stirred for another 1.5 h at room temperature, excess KH was allowed to settle and the supernatant solution was transferred, by way of a canula, to another Schlenk vessel. A solution of 1.2 mL (10 mmol) of $(CH_3)_2SiCl_2$ in 10 mL of THF was added dropwise under constant stirring and cooling to −10 °C. The orange reaction mixture was stirred another 2 h at room temperature and then hydrolyzed by addition of 20 mL of a saturated aqueous NH_4Cl solution. The organic phase was separated, dried with Na_2SO_4, mixed with 5 g of silica gel, and evaporated to dryness. By chromatography of the residue over 40 g of silica gel with a petroleum ether/ethyl acetate (24:1) eluent mixture and subse-

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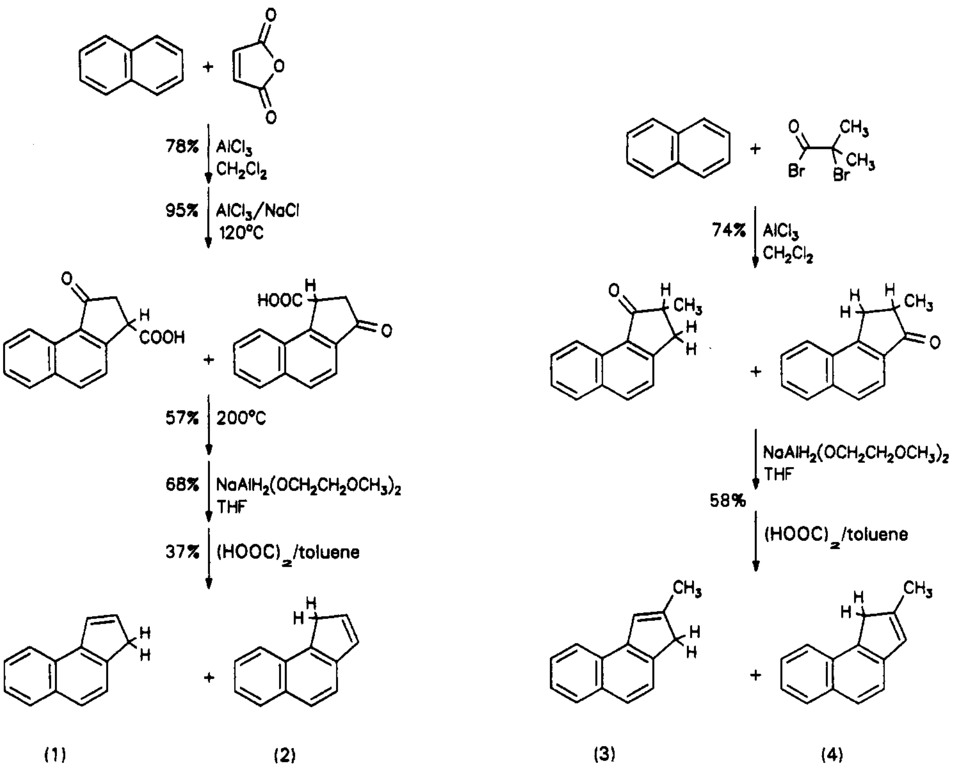
Scheme 1. Synthetic Routes to Benz[*e*]indene Tautomers 1 and 2 (Left) and 2-Methylbenz[*e*]indene Tautomers 3 and 4 (Right)



quent evaporation, one obtains a mixture of *meso*- and *rac*-bis[3,3′-(3-*H*-benz[*e*]indenyl)]dimethylsilane as a solid residue. Yield: 1.25 g (3.2 mmol, 36% of theory). ^{1}H NMR (CDCl$_3$, 250 MHz): δ −0.47 (s, 3H), −0.05 (s, 3H), 3.91 (t, 2H), 6.68 (m, 2H), 7.43–7.74 (m, 10H), 7.91 (d, 2H), 8.18 (d, 2H) for *meso*-bis[3,3′-(3-*H*-benz[*e*]indenyl)]dimethylsilane; δ −0.28 (s, 6H), 3.89 (t, 2H), 6.86 (m, 2H), 7.36–8.21 (m, 14H), for *rac*-bis[3,3′-(3-*H*-benz[*e*]-indenyl)]dimethylsilane. MS (FAB, 3-nitrobenzyl alcohol matrix): *m/z* 388 (M$^+$, 24%). Anal. Calcd for C$_{28}$H$_{24}$Si: C, 86.55; H, 6.23. Found: C, 86.09; H, 6.18.

Bis[3,3′-(3-*H*-2-methylbenz[*e*]indenyl)]dimethylsilane (6). An entirely analogous procedure as that described above for **5**, starting from 3.3 g (83 mmol) of KH and 10 g (55 mmol) of the 2-methylbenz[*e*]indene isomer mixture (**3**, **4**), gave, from 3.7 mL (30 mmol) of (CH$_3$)$_2$SiCl$_2$, 5.7 g (13.6 mmol, 49% of theory) of *meso*- and *rac*-bis[3,3′-(3-*H*-2-methylbenz[*e*]indenyl)]dimethylsilane as a viscous, oily product mixture. ^{1}H NMR (CDCl$_3$, 250 MHz): δ −0.39 (s, 3H), −0.29 (s, 3H), 2.39 (s, 6H), 3.99 (s, 2H), 7.39–8.12 (m, 14H) for *meso*-bis[3,3′-(3*H*-2-methylbenz[*e*]indenyl)]dimethylsilane, δ −0.35 (s, 6H), 2.33 (s, 6H), 4.00 (s, 2H), 7.36–8.14 (m, 14H) for *rac*-bis[3,3′-(3-*H*-2-methylbenz[*e*]indenyl)dimethylsilane. MS (EI): *m/z* 416 (M$^+$, 17%), 237 (M$^+$ − C$_{14}$H$_{11}$, 100%), 178 (C$_{14}$H$_{10}^+$, 36%). Anal. Calcd for C$_{30}$H$_{28}$Si: C, 86.49; H, 6.77. Found: C, 86.57; H, 6.86.

[Dimethylsilanediylbis(3,3′-benz[*e*]indenyl)]zirconium Dichloride (I). To a well-stirred suspension of 0.65 g (16.2 mmol) of KH in 20 mL of THF was added, at −60 °C, a solution of 1.5 g (3.9 mmol) of the bis[3,3′-(3-*H*-benz[*e*]indenyl)]dimethylsilane diastereomer mixture (**5**) in 40 mL of THF. The mixture was slowly warmed to room temperature and stirred for another 1 h. Excess KH was then allowed to settle and the supernatant solution transferred, by way of a canula, to a solution 0.9 g (3.9 mmol) of ZrCl$_4$ in 20 mL of THF. After stirring at room temperature for 2 days, the precipitate formed was collected by filtration and washed first with 15 mL of toluene and then with 30 mL of CH$_2$Cl$_2$ to remove most of the meso isomer of **I** and other side products. Subsequent extraction of the precipitate with hot CH$_2$Cl$_2$ in a Kumagawa-type extractor yielded 420 mg (0.77 mmol, 20% of theory) of pure *rac*-**I** as orange crystals. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 1.17 (s, 6H), 6.20 (d, 2H), 7.37–8.01 (m, 14H). MS (EI): *m/z* 548 (M$^+$, 100%), 533 (M$^+$ − CH$_3$, 28%). Anal. Calcd for C$_{28}$H$_{22}$SiZrCl$_2$: C, 61.29; H, 4.04. Found: C, 61.15; H, 4.16.

The meso isomer was not isolated in pure form; its ^{1}H NMR spectrum was obtained from a second crop of **I** containing the racemic and meso isomers in a ratio of ca. 2:1: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.01 (s, 3H), 1.36 (s, 3H), 6.28 (d, 2H), 7.35–8.01 (m, 14H).

[Dimethylsilanediylbis(3,3′-(2-methylbenz[*e*]indenyl))]-zirconium Dichloride (II). In a procedure analogous to that described above for **I**, 2.8 g (70 mmol) of KH in 50 mL of THF was reacted with 7.0 g (16.7 mmol) of the bis[3,3′-(3-*H*-2-methylbenz[*e*]indenyl)]dimethylsilane diastereomer mixture (**6**), dissolved in 120 mL of THF. The resulting ligand dianion solution was transferred into a solution of 3.9 g (16.7 mmol) of ZrCl$_4$ in 80 mL of THF. The reaction mixture was stirred for 3 days at room temperature and then evaporated to dryness. The residue was stirred with 140 mL of toluene for 1 day. The undissolved, microcrystalline solid was collected by filtration through an Ar-protected frit and washed, in that order, with 15 mL of toluene, 20 mL of THF, and 10 mL of CH$_2$Cl$_2$. Drying in vacuo gave 3.4 g of a yellow, microcrystalline substance which was extracted with hot toluene to yield 950 mg (1.65 mmol, 10% of theory) of pure *rac*-[dimethylsilanediylbis(3,3′-(2-methylbenz[*e*]indenyl))]-zirconium dichloride (**II**). ^{1}H NMR (CDCl$_3$, 250 MHz): δ 1.34 (s, 6H), 2.35 (s, 6H), 7.14–7.96 (m, 14H). MS (EI): *m/z* 576 (M$^+$, 100%), 561 (M$^+$ − CH$_3$, 12%), 237 (C$_{14}$H$_{11}$Si(CH$_3$)$_2^+$, 23%), 178 (C$_{14}$H$_{10}^+$, 39%).

The meso isomer of **II**, 240 mg (0.4 mmol) of which crystallized from the mother liquors upon cooling to −20 °C, gave the following data: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.25 (s, 3H), 1.44 (s, 3H), 2.53 (s, 6H), 7.06–7.91 (m, 14H).

Crystal Structure Determination. Space group *C*2/*c*, with a = 12.555(3) Å, b 12.971(3) Å, c = 15.541(4) Å, β = 92.33(2)°, Z = 4, V = 2528.9(11) Å^3, and d_{calc} = 1.515 g/cm^3 was determined for a crystal of **II** ($\approx$0.3 × 0.3 × 0.3 mm) at 296 K on a Syntex-P3 four-circle diffractometer (Mo Kα radiation; graphite monochromator; Wyckoff scan with $\Delta\omega$ 0.70°, $2.3 \le \omega \le 29.3$°/min, $4.0 \le 2\theta \le 54.0$°). Of 6010 reflections collected, 2766 independent reflections with $F > 6\sigma(F)$ were used, without absorption correction, for solving and refining the structure. The structure

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Complex II

	x	y	z	U(eq)
Zr(1)	0	2995(1)	2500	28(1)
Si(1)	0	5557(1)	2500	36(1)
Cl(1)	1220(1)	1785(1)	1876(1)	55(1)
C(1)	603(3)	4576(3)	3265(3)	32(1)
C(2)	53(3)	4008(4)	3919(3)	34(2)
C(3)	-897(4)	4227(4)	4373(3)	41(2)
C(4)	-1218(4)	3554(5)	4978(3)	46(2)
C(5)	-647(4)	2624(4)	5196(3)	43(2)
C(6)	-992(5)	1934(5)	5833(3)	58(2)
C(7)	-407(5)	1083(5)	6058(4)	63(2)
C(8)	537(5)	874(5)	5668(4)	60(2)
C(9)	901(5)	1520(4)	5033(3)	48(2)
C(10)	321(4)	2391(4)	4792(3)	38(2)
C(11)	648(3)	3102(4)	4140(3)	34(1)
C(12)	1562(3)	3096(4)	3633(3)	34(1)
C(13)	1544(3)	3994(3)	3123(3)	32(1)
C(14)	2458(3)	4250(4)	2549(3)	40(2)
C(15)	1015(4)	6415(4)	2034(4)	50(2)

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

was solved by Patterson methods (SHELXTL PLUS) and refined, using the weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$, with thermal parameters anisotropic for Zr, Si, Cl, and C atoms and isotropic for H atoms, the latter in calculated positions (riding model). The refinement converged at $R = 0.0417$ and $R_w = 0.0415$, with goodness-of-fit 1.25 and residual electron density ≤ 0.42 e $Å^{-3}$. The structural parameters for complex **II** thus obtained are listed in Table 4, with selected bond distances and angles in Table 1.

Polymerizations and Polymer Analysis. Into a Büchi 1-L autoclave (cleaned by stirring with a 0.5% toluene solution of triisobutylaluminum and subsequent drying at 50 °C in vacuo) were added, in the following order, 350 mL of toluene (purified by refluxing first over sodium, then as a solution of 0.25% triisobutylaluminum and 0.0045% $TiCl_4$, and finally by distillation), a solution of 0.45 g of methylaluminoxane (Schering, $M \approx 900$) in 35 mL of toluene and a solution of 0.5 μmol of the zirconocene complex in 20 mL of toluene (Al:Zr ≈ 15 800). After the reaction mixture was stirred for 30 min at 50 °C, propene was added to the desired total pressure, which was kept constant over the entire reaction period. Finally, the autoclave was vented and the reaction mixture drained into 1 L of methanol acidified with 10 mL of concentrated aqueous HCl. The precipitated polymer was collected by filtration, washed with methanol, and dried at 50 °C to a constant weight.

Measurements of catalyst activities as a function of time were conducted as previously described,[7,30] except that 8.7 mL of a 10% solution of MAO in toluene (Schering, $M \approx 1000$) was added to 700 mL of purified toluene, of which 600 mL was introduced into the autoclave and saturated at 40 °C with propene at a pressure of 2 bar, while another 30 mL was used to dissolve 2.4 μmol of the zirconocene complex. After 20 min, 15 mL of this solution was injected into the autoclave via a pressure buret to start the polymerization; the concentration of zirconocene in the reaction mixture is thus 2 μmol/L, that of MAO 20 mmol/L, with Al:Zr = 10 000. The rate of polymerization was monitored by the pressure drop in the propene storage vessel.

Polymerizations of 3-methyl-1-butene and of 3-methyl-1-pentene were conducted in a 60-mL Schlenk vessel containing 0.5 μmol of the zirconocene complex dissolved in a solution of 0.45 g of MAO (Schering, $M \approx 900$) in 15 mL of toluene (Al:Zr ≈ 15 800). To this solution was added 6–7 g of olefin by syringe and the mixture stirred at the temperature indicated in Table 3. At the end of the reaction period the reaction mixture was poured into 30 mL of methanol acidified with 5 mL concentrated aqueous HCl. After stirring for 24 h at room temperature, the precipitated polymer was collected by filtration, washed with methanol, and dried at 70 °C for 1 h.

Stereo- and regioregularities of the polymers obtained were determined by ^{13}C NMR spectroscopy in $C_2D_2Cl_4$ solution at 120 °C and evaluated as described in the literature.[31] Melting points were determined by DSC, molecular weights and polydispersities by GPC; the latter analyses were performed in the polymer research division of BASF AG.

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Supplementary Material Available: Tables of crystal data, atomic parameters, bond distances and angles, and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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