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ansa-Zirconocene Complexes with Modified Benzindenyl Ligands: Syntheses, Crystal Structure, and Properties as Propene Polymerization Catalysts[1,2]

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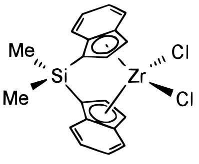
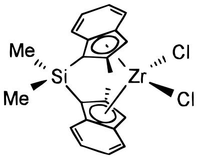
As modifications of the effective catalyst precursor [dimethylsilanediylbis(benz[*e*]indenyl)]-zirconium dichloride, the *ansa*-zirconocene complexes $Me_2Si(cyclopenta[c]phenanthryl)_2ZrCl_2$, $Me_2Si(cyclopenta[l]phenanthryl)_2ZrCl_2$, $Me_2Si(2\text{-}methylcyclopenta[l]phenanthryl)_2ZrCl_2$, and $Me_2Si(2\text{-}methyltetrahydrobenz[e]indenyl)_2ZrCl_2$ have been synthesized. When activated by methylaluminoxane (MAO), these complexes give highly active catalysts for the polymerization of propene to polymers with high isotacticities and molecular weights.

Introduction

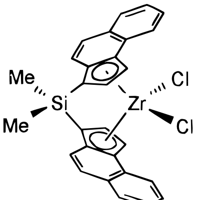
Since the first application of a chiral *ansa*-zirconocene as a catalyst for methylalumoxane (MAO) activated homogeneous propene polymerization,[3] intensive research work has been aimed at improved catalyst activities and stereospecifities and polymer properties. Recently, Spaleck and co-workers have shown that even minor structural modifications of a given ligand framework, e.g. of $Me_2Si(indenyl)_2ZrCl_2$ (**1a**), can lead to significantly enhanced catalyst activities, polymer isotacticities, and molecular weights.[4,6] Related systems are the silyl-bridged bis(benz[*e*]indenyl) zirconocene complex **2a** and its 2-methyl-substituted derivative **2b**, which react even more effectively in propene polymerizations than **1a** and its 2-methyl analog **1b**.[3,5]



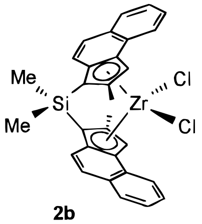
1a



1b

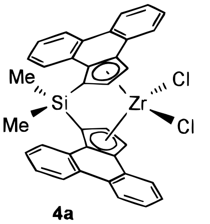


2a

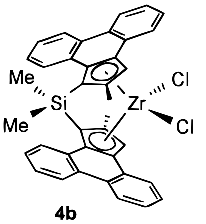


2b

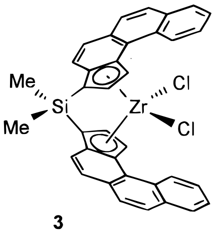
We have now prepared the four new zirconocene dichlorides **3**−**5**, derived from the bis(benz[*e*]indenyl) system **2**, either by introduction of a further annelated aromatic six-ring, leading to the cyclopenta[*c*]- and cyclopenta[*l*]phenanthryl systems **3** and **4a**,**b**, or by formal hydrogenation to give the tetrahydrobenz[*e*]indenyl compound **5**. The behavior of these complexes as polymerization catalysts in the presence of MAO and the properties of the polymers thus obtained were studied in comparison with previously described zirconocenes.[5,6]



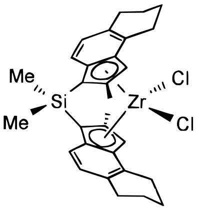
4a



4b



3



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Results

Preparation of the Benzindene Derivatives. Cyclopenta[*c*]phenanthrene (**9**) was prepared as outlined in Scheme 1, with 2-naphthylacetic acid as starting material, by a procedure analogous to the synthesis described by Lee-Ruff and co-workers[7] for cyclopenta[a]phenanthrene.[8]

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[1] *ansa*-Metallocene Derivatives. 40. Part 39: Huttenloch, M. E.; Dorer, B.; Rief, U.; Prosenc, M. H.; Schmidt, K.; Brintzinger, H. H. *J. Organomet. Chem.*, in press.

[2] Parts of this work were presented as a poster at the XVIIth International Conference on Organometallic Chemistry in Brisbane, Australia.

[3] 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.

[4] Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954.

[5] Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H. H.; Jüngling, S.; Mühlhaupt, R.; Langhauser, F. *Organometallics* **1994**, *13*, 964.

[6] 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.

[7] Lee-Ruff, E.; Hopkinson, L. H.; Dao, L. H. *Can. J. Chem.* **1981**, *59*, 1675.

[8] Oxidation of **8** (CrO_3/*t*-BuOOH), reduction ($LiAlH_4$), and dehydration ($(COOH)_2$ in toluene) gave the cyclopenta[*c*]phenanthrene **9** in a yield of 35%.

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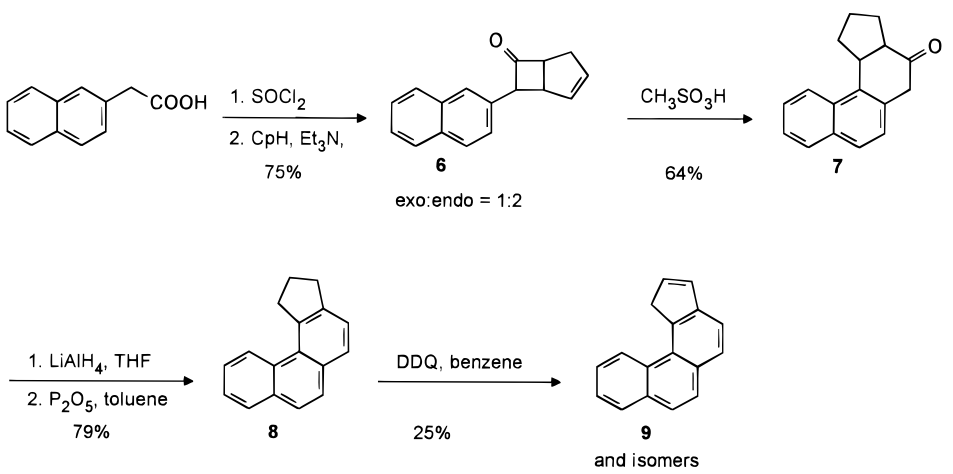
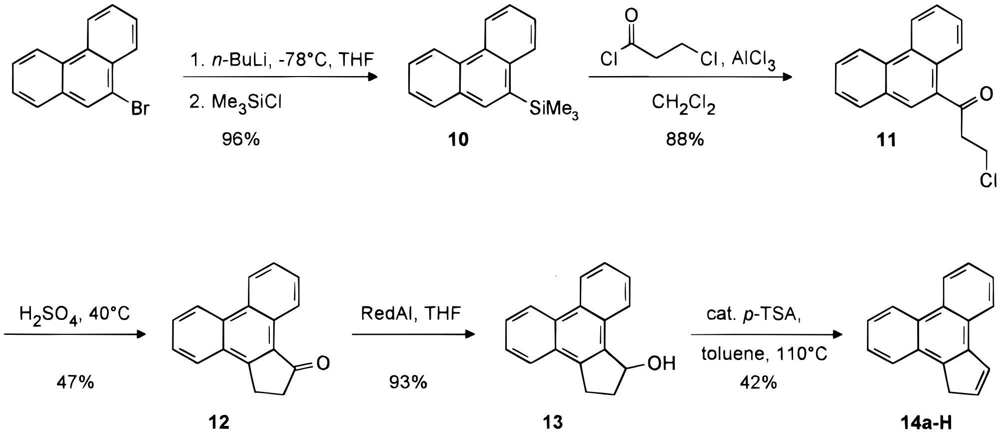
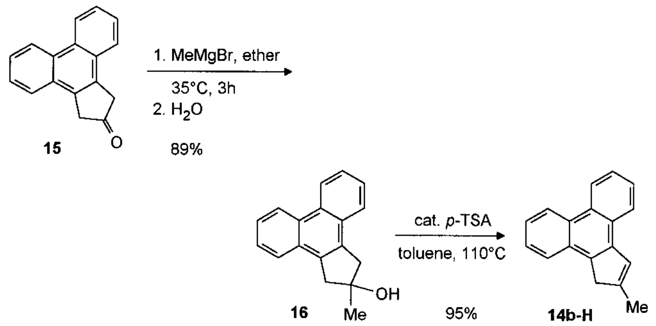
Scheme 1



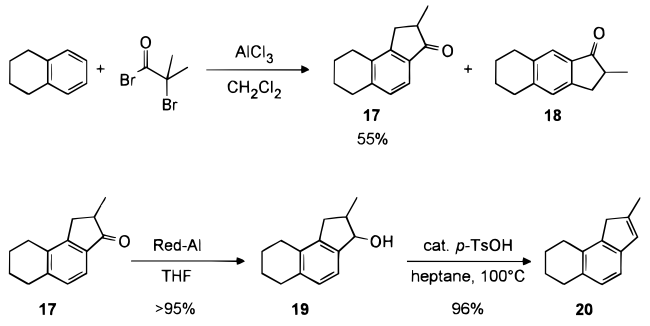
Scheme 2



Scheme 3



Scheme 4



For the preparation of cyclopenta[*l*]phenanthrene **14a-H**, we applied a strategy (Scheme 2), similar to a procedure used by Katz and co-workers,[9] which proved to be more convenient than the syntheses previously described in the literature.[10,11] The corresponding 2-methyl derivative **14b-H** was synthesized by the addition of MeMgBr to the keto group of **15**[10,11] and subsequent dehydration (Scheme 3).

Synthesis of tetrahydrobenz[*e*]indenyl (**20**) was achieved in analogy to the preparation of benz[*e*]indene (Scheme 4). Reaction of tetralin with 2-bromoisobutyric acid bromide in the presence of aluminum trichloride gave a mixture of two isomers, **17** and **18**, from which the desired **17** was isolated by crystallization[12] and reduced to **19** with Red-Al. Dehydrogenation of **19** with catalytic amounts of *p*-toluenesulfonic acid (*p*-TSA) proceeded smoothly in heptane, whereas in toluene the yield was only 30%, due to formation of side products.

Ligand Syntheses. The dimethylsilyl bridge was introduced by deprotonation of the benzindene derivatives and reaction of the resulting anions with 0.5 equiv of dichlorodimethylsilane (Scheme 5). For the cyclopenta[*l*]phenanthryl compounds **14a-H** and **14b-H**, this reaction initially led to the formation of the monosilanes

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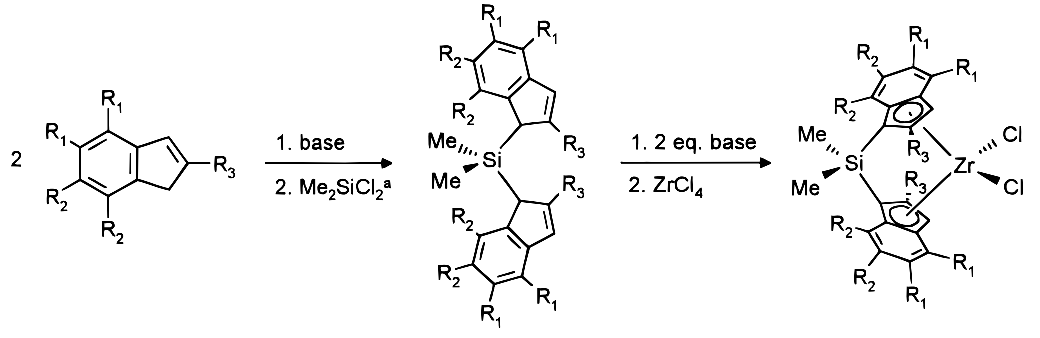
[9] Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Ward, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 3182.

[10] Cope, A. C.; Field, L.; MacDowell, D. W. H.; Wright, M. E. *J. Am. Chem. Soc.* **1956**, *78*, 2547.

[11] Eliasson, B.; Nouri-Sorkhabi, M. H.; Trogen, L.; Sethoson, I.; Edlund, U.; Sygula, A.; Rabinowitz, M. *J. Org. Chem.* **1989**, *54*, 171.

[12] A preparation method which gives the methyltetrahydrobenz[*e*]indenyl species **17** free of the isomer **18** is reported in the literature. However, this five-step procedure yielded only 28% of **17**: Martin, R. H. *J. Chem. Soc.* **1941**, 679.

Scheme 5



9	**21**: $R_1,R_1 = C_8H_6$, $R_2 = R_3 = H$	22%	**3**: 14% *rac*
14a-H	**22a**: $R_1,R_1 = C_4H_4$, $R_2,R_2 = C_4H_4$, $R_3 = H$	90%	**4a**: 38% *rac/meso* 1:1
14b-H	**22b**: $R_1,R_1 = C_4H_4$, $R_2,R_2 = C_4H_4$, $R_3 = Me$	61%	**4b**: 21% *rac/meso* 1:4.4
20	**23**: $R_1,R_1 = C_4H_8$, $R_2 = H$, $R_3 = Me$	95%	**5**: 20% *rac*

[a] For **22a** an additional 1 equiv of **14a-K** and for **22b** 1 equiv of $(TMS)_2NLi$ was added.

14a-SiMe$_2$Cl and **14b-SiMe$_2$Cl**. Apparently, the second equivalent of the cyclopenta[*l*]phenanthrene anion reacts as a base, deprotonating the monosilane.[13] Addition of a further equivalent of the potassium salt[14] **14a-K** to this reaction mixture gave the desired dimethylsilyl-bridged ligand **22a** in 90% yield, albeit under loss of 1 equiv of protonated **14a**. In the preparation of **22b** we were able to avoid this loss by deprotonating the resulting **14b-H** with lithium bis(trimethylsilyl)amide.[15] All ligands (**21**−**23**) were obtained as 1:1 mixtures of *rac* and *meso* diastereomers, as shown by the 1:2:1 ^1H NMR signal pattern of their dimethylsilyl units.

Syntheses of the Zirconocene Dichlorides. The silyl-bridged ligands **21**−**23** were deprotonated with 2 equiv of *n*-butyllithium[16] and the resulting ligand salts reacted with zirconium tetrachloride in toluene to give the corresponding zirconocene dichlorides **3**−**5** as mixtures of *rac* and *meso* diastereomers in relatively high yields (Scheme 5). The low solubility, especially of the highly annelated systems **3** and **4a,b**, made the separation of the diastereomeric complexes somewhat difficult. Furthermore, **4b** and **5** decomposed in chlorinated solvents, such as chloroform and methylene dichloride; complex **5** even decomposed in THF and ether. While we were not able to separate *rac* and *meso* isomers of the bis(cyclopenta[*l*]phenanthryl) complexes **4a** and **4b**, racemic zirconocene dichlorides **3** and **5** were isolated from toluene, free of their *meso* isomer.

From a concentrated toluene solution we obtained crystals of the racemic bis(tetrahydrobenz[*e*]indenyl) zirconocene dichloride **5**, which were suitable for an X-ray structural analysis (Figure 1). Zirconocene **5** has a crystallographic C_2 axis; bond lengths and angles are nearly identical with those observed for the corresponding bis(benz[*e*]indenyl) complex **2b**[5] (Table 1). Two conformers of the hydrogenated six-membered rings were found in the crystalline state, causing a disorder with occupation factors of 0.6 and 0.4.

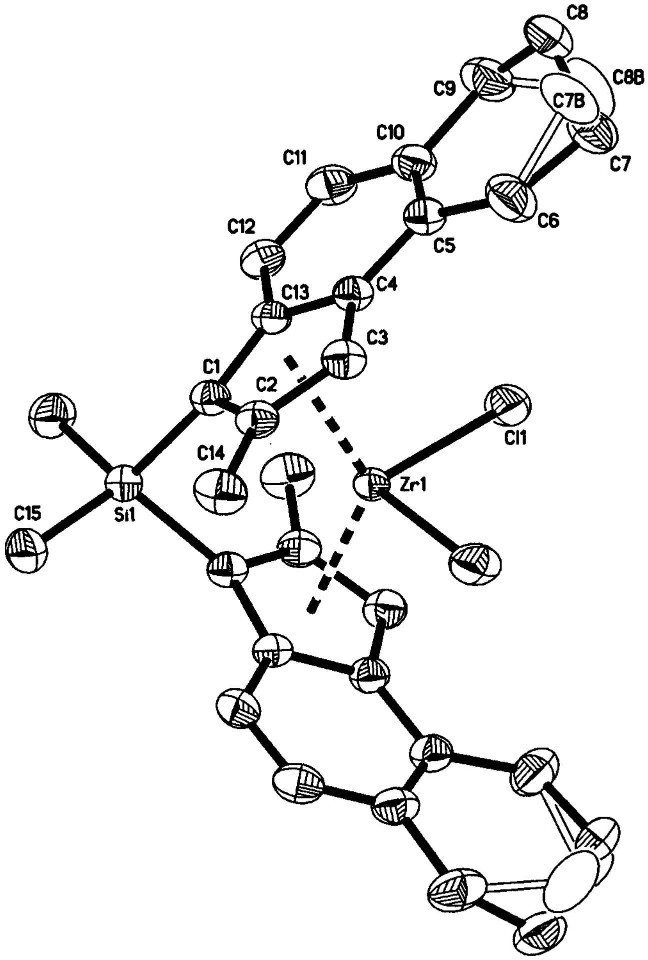


Figure 1. ORTEP drawing of Me_2Si(2-methyltetrahydrobenz[*e*]indenyl)$_2ZrCl_2$, *rac*-**5**, with 50% probability ellipsoids.

Propene Polymerization Catalysis. The modified bis(benzindenyl) zirconocene dichlorides *rac*-**3** and *rac*-**5** were studied with regard to their properties as catalysts for the polymerization of propene in reaction systems containing the respective complex, together with MAO in toluene solution at 50 °C under a constant propene

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(13) A similar result was observed by Rausch et al. for fluorenyllithium: Chen, Y. X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1995**, *497*, 1.

(14) When magnesocene **(14a)$_2$Mg** was used instead of the potassium salt **14a-K**, silylation occurred also at the 2-position of cyclopenta[*l*]phenanthrene (**14a**).

(15) This procedure cannot be applied for the synthesis of **21a**, since the deprotonated monosilane **14a-SiMe$_2$Cl** is decomposed by lithium bis(trimethylsilyl)amide.

(16) **21b** was deprotonated with potassium hydride, since reaction with *n*-butyllithum was slow.

Table 1. Selected Distances (Å) and Angles (deg) for Zirconocene 5

Zr−Cl	2.4100(7)	Zr−C(4)	2.638(2)
Zr−C(1)	2.477(2)	Si(1)−C(15)	1.858(3)
Zr−C(2)	2.493(2)	Si(1)−C(1)	1.876(3)
Zr−C(3)	2.558(3)	Zr−CR[a]	2.238
Zr−C(13)	2.566(2)		
Cl−Zr−Cl	97.35(4)	CR−Zr−CR′[a]	128.1
C(1)−Si−C(1)′	95.6(2)	PL−PL′[b]	59.2
C(15)−Si−C(15)′	105.4(2)		

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

pressure of 2 bar. For catalysts **4a** and **4b**, the inseparable mixtures of *rac* and *meso* isomers (1:1 and 1:4.4, respectively) were used as such; in this case, the resulting polymers were freed from atactic parts (ca. 25% and 56%) by exhaustive extraction with boiling pentane. Productivities of these catalysts and the properties of the resulting polypropenes are listed in Table 2, together with those of their bis(indenyl) and bis(benz[*e*]indenyl) analogs **1a**,**b** and **2a**,**b**.[5]

Each of the four catalyst systems examined were found to be highly active and very stable during the polymerization reactions. The activity of compound **5**, for example, remained nearly constant over a period of 2.5 h.[17] This low rate of deactivation might be due to the increased steric hindrance of the ligand framework, which prevents the system from formation of inactive species by the approach of an aluminum or a second zirconium center.[19] The tetrahydrobenz[*e*]indenyl complex **5** yields, with MAO, a much more active catalyst than its unhydrogenated benz[*e*]indenyl counterpart **2b**; this contrasts with substantially reduced activities for tetrahydroindenyl complexes as compared with their indenyl analogs.[4,6,18] Apparently, the presence of an indenyl (rather than a cyclopentadienyl) ligand moiety satisfies the electronic coordination requirements for high activity; further extension of the ligand framework appears to have mainly steric advantages, which are satisfied by a tetrahydro-C_6 ring better than by an aromatic one. Also remarkable is the effect of the α-methyl substituents in catalyst **4b**: while the methyl-substituted catalysts **1b**/MAO and **2b**/MAO have substantially lower activities than their unsubstituted counterparts **1a**/MAO and **2a**/MAO,[5] the reverse is found for the Cp[*l*]Phen complexes **4a** and **4b**. For the latter we observe, in fact, the highest activity of all *ansa*-zirconocene polymerization catalysts studied so far.

The expectation that a high rate of insertion might be associated with an increased molar mass of the polymer products is not borne out by the data in Table 2: polypropene produced with **4b**/MAO has almost the same molar mass M_w as that produced with either **1b**/MAO or **2b**/MAO. Similarly, the tetrahydrobenz[*e*]indenyl catalyst **5**/MAO produces polymers of lower molar mass than does **2b**/MAO, despite its higher activity. Apparently, the rates of insertion and of chain termination, v_P and v_T, which determine the mean degree of polymerization, $P_N \approx v_P/v_T$, vary in a partially compensatory manner when the structure of the zirconocene catalyst is changed.

The melting points of the polymers obtained with the α-methyl-substituted complexes **1b**, **2b**, **4b**, and **5** are all very similar (150−152 °C). The persistent melting point reduction relative to perfect isotactic polypropene appears to be caused by the occurrence of 2,1-regioerrors as well as of residual stereoerrors, as documented by the reduced melting points of the polypropenes produced with catalysts which do not carry an α-methyl substituent. This effect is particularly dramatic for the catalyst pair **4a**/MAO and **4b**/MO, where the presence of the α-methyl groups causes an increase of the relative weight of the *mmmm*-pentad signal by 17% and of the melting point by 26 °C. An improved control over the occurrence rates of both regio- and stereoerrors remains one of the challenges in the design of new metallocene-based polymerization catalysts.

Experimental Section

General Information. Moisture- and air-sensitive compounds were handled under an argon atmosphere using Schlenk or drybox techniques. Distillations were carried out as follows: THF and diethyl ether from sodium benzophenone ketyl, toluene from sodium, pentane from Na−K alloy, and CH_2Cl_2 from CaH_2. Trimethylsilyl chloride (Aldrich) was distilled from CaH_2 and dichlorodimethylsilane from quinoline. $ZrCl_4$ (Fluka) was sublimed prior to use. NMR spectra were recorded on Bruker WM-250, AC-250, and DRX-600 spectrometers.

Synthesis of [Dimethylsilanediylbis(3-cyclopenta[*c*]phenanthryl)]zirconium Dichloride (3). 7-(2-Naphthyl)bicyclo[3.2.0]hept-2-en-6-one (6). 2-Naphthylacetic acid (100 g, 0.537 mol) was stirred with 200 mL of $SOCl_2$ for 24 h at room temperature. Excess $SOCl_2$ was removed under reduced pressure and the product dried *in vacuo* at 50 °C. The resulting acetyl chloride was dissolved in 2.2 L of toluene, and 200 g of freshly cracked cyclopentadiene was added. The mixture was heated to reflux. Then, the heater was removed and 85 mL (0.611 mol) of Et_3N was added dropwise over a period of 20 min. After it was stirred for 2 h at room temperature, the reaction mixture was poured onto 2 L of ice−water and extracted with 2 L of ether. The organic layer was washed successively with water (1 L), 2 N HCl solution (1 L), saturated aqueous $NaHCO_3$ solution (1.5 L), and again with water (1 L). The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo*. The brown oily residue was taken

Table 2. Propene Polymerization with $Me_2SiL_2ZrCl_2$/MAO at 50 °C and 2 bar of Propene

cat.	L	amt of Zr (μmol)	Zr/Al[a]	t[b] (min)	productivity (kg of PP/(mol of Zr h))	amt of *mmmm* (%)	T_{mp} (°C)	M_w[c]	M_w/M_n	amt of 2,1-units (%)
3	Cp[*c*]Phen	0.50	1:15 800	180	5 800	82	126	28 100	1.62	1.2
4a[d]	Cp[*l*]Phen	1.35[e]	1:3 100	90	24 100[f]	80	126	49 400	1.59	0.5
4b[g]	2-Me-Cp[*l*]Phen	1.16[h]	1:1 300	30	55 600[f]	97	152	133 300	1.86	0.4
5	2-Me-thBenz[*e*]Ind	3.25	1:2 600	30	28 700	92	150	77 300	1.57	0.7
1a[i]	Ind	0.50	1:15 800	180	14 000	89	142	61 900	1.67	0.4
1b[i]	2-Me-Ind	0.50	1:15 800	240	9 200	90	150	135 000	1.64	0.2
2a[i]	Benz[*e*]Ind	0.50	1:15 800	120	24 600	88	140	35 100	1.60	0.8
2b[i]	2-Me-Benz[*e*]Ind	0.50	1:15 800	120	9 000	92	151	137 100	1.56	0.4

[a] Constant *c*(Al) of 0.02 mol/L. [b] Polymerization times have been chosen so as to yield ca. 10−80 g of polypropene. [c] Determined by GPC. [d] *rac*-/*meso*-**4a** (1:1). [e] 3.7 μmol of Zr, i.e. 1.35 μmol of *rac*-**4a**. [f] After extraction with pentane for 7 h. [g] *rac*-/*meso*-**4b** (1:4.4). [h] 6.25 μmol of Zr, i.e. 1.16 μmol of *rac*-**4b**. [i] Values from ref 5.

up in 400 mL of hexane. After it stood overnight at 4 °C, the supernatant solution was decanted and the remaining oil was dried *in vacuo* to yield 93.8 g (75%) of **6** as a mixture of *endo* and *exo* isomers (2:1). ^{1}H NMR (CDCl$_3$, 250 MHz): *exo*-**6**, δ 7.84−7.78 (m, 3 H), 7.69 (s, 1 H), 7.50−7.41 (m, 2 H), 7.36 (dd, J = 8.5, 1.8 Hz, 1 H), 6.04 (m, 1 H), 5.90 (m, 1 H), 4.22 (t, J = 3.4 Hz, 1H), 4.08 (m, 1 H), 3.76 (m, 1 H), 2.84 (m, 1 H), 2.61 (m, 1 H); *endo*-**6**, δ 7.79−7.74 (m, 3 H), 7.69 (s, 1 H), 7.51−7.39 (m, 2 H), 7.26 (dd, J = 8.3, 1.7 Hz, 1 H), 5.84 (m, 1 H), 5.48 (m, 1 H), 4.94 (dd, J = 8.7, 2.9 Hz, 1H), 4.05−3.93 (m, 2 H), 2.81 (m, 1 H), 2.51 (m, 1 H). MS (EI): *m/z* 234 (M$^+$, 3%), 205 (M$^+$ − CHO, 9%), 168 (M$^+$ − C$_5$H$_6$, 100%), 141 (M$^+$ − C$_6$H$_5$O, 34%).

3*H*-3a,4,5,11c-Tetrahydrocyclopenta[*c*]phenanthren-4-one (7). A solution of 37 g (157.9 mmol) of **6** in 1.6 L of diethyl ether was added dropwise to 780 mL of methanesulfonic acid at −18 °C over a period of 1 h. The purple solution was stirred for another 3 h at room temperature and then poured on 3 L of ice−water and extracted with 1 L of ether. The organic layer was washed with 1 L of saturated aqueous NaHCO$_3$ solution and with 1 L of water. The organic layer was dried over MgSO$_4$, the solvent evaporated and the product purified by adsorptive filtration over flash-silica gel, with pentane/ethyl acetate (50:1) as eluent, which was gradually made more polar to a ratio of 10:1. The product-containing fractions were collected and evaporated to dryness, to yield 23.6 g (64%) of pure **7** as a yellow solid. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.06 (d, J = 8.4 Hz, 1 H), 7.84 (d, J = 8.5 Hz, 1 H), 7.71 (d, J = 8.4 Hz, 1 H), 7.59−7.45 (m, 2 H), 7.14 (d, J = 8.4 Hz, 1 H), 5.87 (m, 1 H), 5.81 (m, 1 H), 5.09 (d, J = 8.3 Hz, 1 H), 3.80 (d, J = 17.9 Hz, 1 H), 3.63 (dd, J = 17.9, 1.5 Hz, 1 H), 3.29 (t, J = 8.3 Hz, 1 H), 3.01−2.79 (m, 2 H). MS (EI): *m/z* 234 (M$^+$, 100%), 217 (M$^+$ − OH, 23%), 205 (M$^+$ − CHO, 30%).

1*H*-2,3-Dihydrocyclopenta[*c*]phenanthrene (8). A solution of 45 g (0.192 mol) of **7** in 1 L of THF was added dropwise to an ice-cooled suspension of 4.4 g (0.116 mmol) of LiAlH$_4$ in THF. After it was stirred for 2 h at room temperature, the reaction mixture was hydrolyzed with 40 mL of a 10% aqueous HCl solution and filtered; the filtrate was treated with 20 g of solid NaHCO$_3$ and MgSO$_4$, filtered again, and evaporated to dryness. The resulting alcohol was dissolved in 700 mL of toluene and dehydrated by adding 40 g of P$_2$O$_5$ in six portions and refluxing for 30 min. After removal of insoluble material, treatment of the solution with NaHCO$_3$, and purification by adsorptive filtration over flash-silica gel using hexane as an eluent, 32.1 g (79%) of **8** was obtained as a sticky oil. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.81 (d, J = 8.3 Hz, 1 H), 7.92−7.52 (m, 7 H), 3.76 (t, J = 7.3 Hz, 2 H), 3.16 (t, J = 7.6 Hz, 2 H), 2.28 (tt, 2 H). MS (EI): *m/z* 218 (M$^+$, 100%), 204 (M$^+$ − CH$_2$, 47%), 189 (M$^+$ − C$_2$H$_3$, 45%), 178 (M$^+$ − C$_3$H$_4$, 39%). Anal. Calcd for C$_{17}$H$_{14}$: C, 93.54; H, 6.46. Found: C, 93.18; H, 6.78.

1*H*- and 3*H*-Cyclopenta[*c*]phenanthrene (9). A solution of 5.9 g (27 mmol) of **8** in 210 mL of benzene was refluxed with 9.8 g (43 mmol) of dichlorodicyanobenzoquinone (DDQ) for 6 h. Silica gel was added, and the solvent was removed *in vacuo*. The solid residue was subjected to adsorptive filtration over silica gel with hexane. From the concentrated eluate, **9** crystallizes at −30 °C as a 9:1 mixture of 1*H* and 3*H* isomers (1.46 g, 25%). ^{1}H NMR (CDCl$_3$, 250 MHz): 1*H*-**9**, δ 8.86 (d, J = 8.3 Hz, 1 H), 7.95−7.59 (m, 7 H), 7.11 (td, J = 5.5, 1.8 Hz, 1 H), 6.81 (td, J = 5.5, 1.8 Hz, 1 H), 4.13 (s, 2 H); 3*H*-**9**, δ 9.00 (d, J = 8.1 Hz, 1 H), 8.13 (td, J = 5.7, 1.9 Hz, 1 H), 7.95−7.55 (m, 7 H), 6.88 (td, J = 5.7, 1.9 Hz, 1 H), 3.58 (broad s, 2 H). MS (EI): *m/z* 216 (M$^+$, 100%), 189 (M$^+$ − C$_2$H$_3$, 10%). Anal. Calcd for C$_{17}$H$_{12}$: C, 94.41; H, 5.59. Found: C, 93.69; H, 5.62.

Bis(cyclopenta[*c*]phenanthryl)dimethylsilane (21). To a solution of 2.3 g (10.63 mmol) of **9** in 250 mL of ether was added 7 mL (11.2 mmol) of a 1.6 M solution of *n*-butyllithium in hexane at −60 °C. The solution was warmed to room temperature and stirred for 1 h, and then 0.66 mL (5.47 mmol) of dichlorodimethyl silane was added at −60 °C. After it was stirred for 2 days at room temperature, the resulting suspension was hydrolyzed with 0.4 mL of a saturated aqueous NH$_4$Cl solution and the organic layer evaporated to dryness. Flash chromatography with hexane afforded 0.56 g (22%) of a mixture of *rac*- and *meso*-**21**. ^{1}H NMR (CDCl$_3$, 250 MHz): *rac*-**21**, δ 9.08 (d, J = 8.0 Hz, 2 H), 8.21 (dd, J = 5.6, 1.2 Hz, 2 H), 7.95−7.57 (m, 14 H), 7.04 (dd, J = 5.5, 1.9 Hz, 2 H), 3.93 (t, J = 1.7 Hz, 2 H), −0.18 (s, 6 H); *meso*-**21**, δ 9.06 (d, J = 8.0 Hz, 2 H), 8.16 (dd, J = 5.6, 1.2 Hz, 2 H), 7.95−7.57 (m, 14 H), 6.82 (dd, J = 5.5, 1.9 Hz, 2 H), 3.95 (t, J = 1.7 Hz, 2 H), 0.07 (s, 3 H), −0.36 (s, 3 H). MS (EI): *m/z* 488 (M$^+$, 27%), 273 (M$^+$ − C$_{17}$H$_{11}$, 100%), 215 (C$_{17}$H$_{11}{}^+$, 45%). Anal. Calcd for C$_{36}$H$_{28}$Si: C, 88.48; H, 5.77. Found: C, 88.14; H, 6.28.

[Dimethylsilanediylbis(3-cyclopenta[*c*]phenanthryl)]-zirconium Dichloride (3). To a solution of 0.26 g (0.53 mmol) of **21** in 20 mL of THF and 80 mL of ether was added 0.85 mL (1.36 mmol) of a 1.6 M solution of methyllithium in ether at 0 °C. After the mixture was stirred at room temperature for 45 min, the solvent was removed *in vacuo* and the oily orange residue was treated with 123 mg of ZrCl$_4$ (0.53 mmol) and 100 mL of toluene. The resulting suspension was stirred at 80 °C for 3 h and then for 3 days at room temperature. The supernatant toluene was decanted. The solid residue was suspended in 120 mL of toluene, heated to 80 °C, and filtered. From the concentrated filtrate, containing a mixture of *rac*- and *meso*-**3**, an orange solid precipitated, which was isolated and dried *in vacuo* to give 50 mg (14%) of *rac*-**3**, slightly contaminated with inorganic salts. Extraction with boiling toluene caused decomposition of **3**. Further purification of **3** was thus not feasible. Nevertheless, the material thus obtained gave a clean ^{1}H NMR spectrum without traces of any *meso* isomer or of organic impurities. Due to its low solubility in commonly used solvents, a ^{13}C NMR spectrum could not be obtained. ^{1}H NMR (CDCl$_3$, 250 MHz): *rac*-**3**, δ 8.88−8.83 (m, 2 H), 8.00 (d, J = 3.3 Hz, 2 H), 7.93−7.49 (m, 14 H), 6.41 (d, J = 3.5 Hz, 2 H), 1.27 (s, 6 H); *meso*-**3**, δ 8.92−8.87 (m, 2 H), 8.11 (d, J = 3.1 Hz, 2 H), 7.93−7.42 (m, 14 H), 6.46 (d, J = 3.4 Hz, 2 H), 1.50 (s, 3 H), 1.10 (s, 3 H). MS (EI): *m/z* 648 (M$^+$, 100%), 633 (M$^+$ − Me, 11%), 611 (M$^+$ − Cl, 53%), 595 (M$^+$ − Me − Cl, 10%), 553 (M$^+$ − Me$_2$SiCl, 9%).

Synthesis of [Dimethylsilanediylbis(1-(cyclopenta[*l*]-phenanthryl))]zirconium Dichloride (4a). 9-(Trimethylsilyl)phenanthrene (10). A solution of (10.0 g, 38.9 mmol) of 9-bromophenanthrene in 100 mL of THF was cooled to −78 °C, and 25.5 mL (40.8 mmol) of a 1.6 M solution of *n*-butyllithium in hexane was added. The green suspension was stirred for 20 min, and then 7.9 mL (62.2 mmol) of trimethylsilyl chloride was added dropwise. The mixture was stirred at −78 °C until the precipitate had disappeared; it was then slowly warmed to room temperature and stirred for another 2 h. The solution was concentrated *in vacuo* to a volume of about 30 mL and treated with 100 mL of water. After extraction with 300 mL of ether and washing of the combined ether fractions with 100 mL of brine, drying over MgSO$_4$, and evaporation of the solvent, a pale yellow solid was obtained. Recrystallization from ethanol yielded 9.39 g of **10** (96%). ^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.68−8.79 (m, 2 H), 8.24−8.20 (m, 1 H), 8.01 (s, 1 H), 7.91 (m, 1 H), 7.71−7.61 (m, 4 H), 0.57 (s, 9 H). MS (EI): *m/z* 250 (M$^+$, 37%), 235 (M$^+$ − CH$_3$, 100%).

9-(3-Chloropropionyl)phenanthrene (11). A solution of 4 mL (33.7 mmol) of freshly condensed 3-chloropropionyl chloride in 10 mL of CH$_2$Cl$_2$ was added dropwise to 4.95 g (37.1

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(17) For this study, the reaction was conducted with only 0.5 μmol of zirconocene dichloride **5**.

(18) (a) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (b) Rieger, B.; Chien, J. W. C. *Polym. Bull.* **1989**, *21*, 159. (c) Kaminsky, W.; Engehausen, R.; Zoumis, K.; Spaleck, W.; Rohrmann, J. *Makromol. Chem.* **1992**, *193*, 1643. (d) Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* **1991**, *10*, 2061.

(19) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1134.

mmol) of aluminum trichloride in 20 mL of CH_2Cl_2. The orange solution was cooled to −78 °C, and a solution of 8 g (32.0 mmol) of **10** in 40 mL of CH_2Cl_2 was added over a period of 30 min. The suspension was stirred for another 10 min at −78 °C and then warmed to room temperature. The orange-brown reaction mixture was poured on 300 mL of ice and 50 mL of concentrated HCl and extracted with 400 mL of CH_2Cl_2. The combined organic layers were washed with 400 mL of water and dried with $MgSO_4$. After evaporation of the solvent, the product was purified by flash chromatography using an eluent mixture of pentane and ethyl acetate (25:1), to yield 7.92 g of **11** (88%) as a colorless solid. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.68 (d, J = 8.3 Hz, 1 H), 8.64 (d, J = 8.3 Hz, 1 H), 8.10 (s, 1 H), 7.92−7.61 (m, 6 H), 4.01 (t, J = 6.6 Hz, 2 H), 3.58 (t, J = 6.6 Hz, 2 H). MS (EI): m/z 268 (M^+, 18%), 232 ($M^+ - HCl$, 14%), 205 ($M^+ - (CH_2CH_2Cl)$, 100%), 177 ($M^+ - (COCH_2CH_2Cl)$, 62%).

2,3-Dihydro-1-oxocyclopenta[*l*]phenanthrene (12). Compound **11** (3.66 g, 13.6 mmol) was treated with 13.6 mL of concentrated H_2SO_4 and stirred for ca. 1.5 h at 40 °C. When evolution of gas had stopped, the reaction mixture was poured onto an ice−water mixture (300 mL), whereupon a pink solid precipitated. The solid was filtered and washed with water. After it was suspended in methanol and filtered, **12** remained as a colorless sticky solid (1.49 g, 47%). ^1H NMR ($CDCl_3$, 600 MHz): δ 9.26 (d, J = 7.5 Hz, 1 H), 8.65 (d, J = 8.2 Hz, 1 H), 8.59 (d, J = 7.1 Hz, 1 H), 8.03 (d, J = 7.6 Hz, 1 H), 7.78 (t, J = 7.2 Hz, 1 H), 7.71−7.66 (m, 3 H), 3.33 (m, 2 H), 2.84 (m, 2 H). MS (EI): m/z 232 (M^+, 84%), 203 ($M^+ - CHO$, 100%), 176 ($M^+ - (COCH_2CH_2)$, 25%).

2,3-Dihydro-1-hydroxycyclopenta[*l*]phenanthrene (13). Reduction of **12** (0.5 g, 2.2 mmol) was achieved by treatment either with 0.9 mL (1.85 mmol) of a 2.06 M solution of Red-Al ($NaAlH_2(OCH_2CH_2OCH_3)_2$) in 30 mL of THF for 45 min at room temperature or with 1.5 equiv of $NaBH_4$ in ethanol and stirring overnight. Hydrolysis with 20 mL of a saturated aqueous NH_4Cl solution, extraction with 100 mL of ether, drying with $MgSO_4$, and evaporation of the solvent yielded **13** as a colorless solid (0.47 g, 91%). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.70 (d, J = 7.4 Hz, 2 H), 8.22 (d, J = 6.4 Hz, 1 H), 7.91 (d, J = 7.7 Hz, 1 H), 7.68−7.62 (m, 4 H), 5.87 (d, J = 6.5 Hz, 1 H), 3.53−3.48 (m, 1 H), 3.26−3.21 (m, 1 H), 2.72−2.70 (m, 1 H), 2.30-2.27 (m, 1 H), 1.80 (broad s, OH). MS (EI): m/z 234 (M^+, 100%), 217 ($M^+ - OH$, 55%), 191 ($M^+ - (COHCH_2)$, 38%).

1*H*-Cyclopenta[*l*]phenanthrene (14a-H). A suspension of 0.6 g (2.56 mmol) of **13** and 100 mg of *p*-toluenesulfonic acid in 150 mL of toluene was heated for ca. 15 min, until a homogeneous solution was obtained. Then the heating bath was removed immediately, since longer reaction times lead to the formation of a dimer. Hydrolysis with 40 mL of a saturated aqueous $NaHCO_3$ solution, extraction with 300 mL of ether, drying with $MgSO_4$, and evaporation of the solvent yielded **14a-H** as a colorless solid (230 mg, 42%), which was purified by flash chromatography using an eluent mixture of pentane and ethyl acetate (50:1). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.73 (m, 1 H), 8.70 (d, J = 8.0 Hz, 1 H), 8.19 (m, 1 H), 8.02 (d, J = 7.0 Hz, 1 H), 8.64−7.65 (m, 2 H), 7.61−7.55 (m, 2 H), 7.49 (d, J = 5.4 Hz, 1 H), 6.77 (d, J = 5.4 Hz, 1 H), 3.84 (s, 2 H). MS (EI): m/z 216 (M^+, 100%). These NMR data are in agreement with those previously obtained by others.[10,11]

Bis(cyclopenta[*l*]phenanthryl)dimethylsilane (22a). A solution of 5.88 g of 1*H*-cyclopenta[*l*]phenanthrene **14a-H** (27.22 mmol) in 90 mL of THF was added at 0 °C to a suspension of 3 equiv of KH (3.27 g, 81.66 mmol) in THF. After it was stirred for 2 days, the deep red solution was freed by filtration from unreacted KH. Then 1.13 mL of dichlorodimethylsilane (0.33 equiv, 9.3 mmol) was added at room temperature. The reaction mixture was stirred overnight and the solvent removed under reduced pressure. The disubstituted silane **22a** was extracted with toluene (3 × 150 mL). The toluene solution was evaporated to dryness and the residue washed with pentane (3 × 150 mL) to remove unreacted **14a-H**, yielding a 1:1 mixture of *meso*- and *rac*-**22a** as a beige solid (4.09 g, 90%). ^1H NMR ($CDCl_3$, 600 MHz): *rac*-**22a**, δ 8.75−8.66 (m, 4 H), 8.26−7.47 (m, 14 H), 7.10 (d, J = 4.1 Hz, 2 H), 4.30 (s, 2 H), −0.36 (s, 6 H); *meso*-**22a**, δ 8.75−8.66 (m, 4 H), 8.26−7.47 (m, 14 H), 6.60 (d, J = 4.1 Hz, 2 H), 4.42 (s, 2 H), −0.46 (s, 3 H), −0.13 (s, 3 H). MS (EI): m/z 489 (M^+, 5%), 273 (M^+ − **14a**, 65%), 216 (**14a-H**, 100%).

[Dimethylsilanediylbis(1-(cyclopenta[*l*]phenanthryl))]-zirconium Dichloride (4a). A solution of 3.36 g (6.87 mmol) of **22a** in 200 mL of toluene was treated with 8.6 mL (13.74 mmol) of a 1.6 M solution of *n*-butyllithium in hexane at 0 °C. After it was stirred for 2 days, the toluene solution was decanted from the insoluble, yellow lithium salt, which was washed with pentane. This yellow residue was added to 1.6 g (6.87 mmol) of zirconium tetrachloride; 150 mL of toluene was added and this mixture stirred for 3 days at room temperature. The resulting suspension was evaporated to dryness and the residue Soxhlett-extracted with toluene for 12 h, to yield the zirconium complex **4a** in a *rac*:*meso* ratio of 3:2. The extract was dried *in vacuo* and subsequently washed with three 50 mL portions of pentane and ether. The insoluble residue consisted of the nearly pure *rac*-**4a**, contaminated with unbridged zirconocene ($(Cp[l]Phen)_2ZrCl_2$). The pentane fractions were discarded. From the ether fraction the *meso* isomer crystallized at −70 °C as fine yellow needles (70 mg, 3%). On evaporation of the mother liquor, an analytically pure mixture of *rac*- and *meso*-**4a** in a ratio of 1:1 was obtained (38%). The total yield of **4a** was 1.9 g (42%). ^1H NMR (C_6D_6, 600 MHz): *rac*-**5**, δ 8.34−8.23 (m, 4 H), 8.03−7.74 (m, 4 H), 7.48−7.04 (m, 8 H), 7.13 (d, J = 3.3 Hz, 2 H), 6.02 (d, J = 3.3 Hz, 2 H), 0.97 (s, 6 H). MS (EI): m/z 648 (M^+, 10%), 377 (M^+ − **14** − Me_2Si, 12%), 216 (**14-H**, 100%). ^1H NMR (C_6D_6, 600 MHz): *meso*-**5**, δ 8.34−8.23 (m, 4 H), 8.03−7.74 (m, 4 H), 7.48−7.04 (m, 8 H), 7.50 (d, J = 3.5 Hz, 2 H), 6.10 (d, J = 3.5 Hz, 2 H), 1.25 (s, 3 H), 0.65 (s, 3 H). Anal. Calcd for $C_{36}H_{26}SiZrCl_2 \cdot C_7H_8$: C, 69.70; H, 4.62. Found: C, 69.45; H, 4.78.

Synthesis of [Dimethylsilanediylbis(1-(2-methylcyclopenta[*l*]phenanthryl)]zirconium Dichloride (4b). 3-Hydro-2-hydroxy-2-methyl-1*H*-cyclopenta[*l*]phenanthrene (16). To 5 g (21.19 mmol) of 2,3-dihydro-2-oxo-1*H*-cyclopenta[*l*]phenanthrene (**15**),[10,11] suspended in 20 mL of ether, was added 8.83 mL (26.49 mmol) of a 3 M solution of MeMgBr in ether and the mixture refluxed for 3 h. The mixture was hydrolyzed with 10 mL of an aqueous 2 N solution of HCl and extracted three times with ether (200 mL). The combined organic fractions were washed successively with saturated aqueous solutions of $NaHSO_3$ (50 mL), $NaHCO_3$ (50 mL), and water (50 mL). After drying with $MgSO_4$ and evaporation of the solvent, **16** remained as a colorless solid (4.68 g, 89%). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.70−8.68 (m, 2 H), 7.79−7.77 (m, 2 H), 7.63−7.59 (m, 4 H), 3.44 (2 d, J = 15.8 Hz, 4 H), 1.98 (broad s, OH), 1.66 (s, 3 H). MS (EI): m/z 248 (M^+, 33%), 205 ($M^+ - CH_3CO$, 100%).

1*H*-2-Methylcyclopenta[*l*]phenanthrene (14b-H). Compound **16** (4.56 g, 18.39 mmol) was refluxed with 0.25 g of *p*-toluenesulfonic acid in 300 mL of toluene for 1 h. The mixture was washed with 100 mL of a saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated to dryness. Further purification by adsorptive filtration over flash-silica gel with pentane/ethyl acetate (50:1) as an eluent yielded 4.02 g (95%) of pure **14b-H**. ^1H NMR ($CDCl_3$, 250 MHz): δ 8.75−8.68 (m, 2 H), 8.13−8.10 (m, 1 H), 7.96−7.93 (m, 1 H), 7.65−7.53 (m, 4 H), 7.07 (s, 1 H), 3.74 (s, 2 H), 2.31 (s, 3 H). MS (EI): m/z 230 (M^+, 100%), 215 ($M^+ - CH_3$, 38%). Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.63; H, 6.17.

Bis(2-methylcyclopenta[*l*]phenanthryl)dimethylsilane (22b). A solution of 14.75 g (64.14 mmol) of **14b-H** in 150 mL of THF was treated with 33.0 mL (33 mmol) of a 1 M solution of di-*n*-butylmagnesium in hexane and refluxed for 4−5 h. The resulting dark red solution was cooled to room temperature and stirred overnight with 3.89 mL (32.06 mmol) of dichlorodimethylsilane. Then a solution of 5.36 g (32.06 mmol) of lithium bis(trimethylsilyl)amide in 15 mL of THF was added. After the mixture was stirred overnight, the disubstituted silane **22b** was obtained as a precipitate. The THF solution was decanted and the solid residue washed with pentane (3 × 50 mL). The product was purified by flash chromatography (10:1 pentane/ethyl acetat, 1% Et_3N), to yield 10.25 g (61%) of *rac*- and *meso*-**22b**. ^1H NMR ($CDCl_3$, 600 MHz): *rac*-**22b**, δ 8.72−8.65 (m, 4 H), 8.16−8.13 (m, 2 H), 7.62−7.28 (m, 10 H), 7.25 (s, 2 H), 4.36 (s, 2 H), 2.55 (s, 6 H), −0.38 (s, 6 H); *meso*-**22b**, δ 8.72−8.65 (m, 4 H), 8.16−8.13 (m, 2 H), 7.62−7.28 (m, 10 H), 7.19 (s, 2 H), 4.54 (s, 2 H), 2.32 (s, 6 H), −0.79 (s, 3 H), −0.12 (s, 3 H). MS (EI): *m/z* 516 (M^+, 10%), 287 (M^+ − **14b**, 100%), 271 (M^+ − **14b-H** − Me, 7%), 229 (**14b**, 10%). Anal. Calcd for $C_{38}H_{32}Si$: C, 88.37; H, 6.24. Found: C, 87.38; H, 6.58.

[Dimethylsilanediylbis(5-(2-methylcyclopenta[*l*]-phenanthryl))]zirconium Dichloride (4b). A mixture of 2.8 g (5.4 mmol) of **22b** and 1.31 g of KH (32.6 mmol) in 50 mL of THF was stirred overnight and filtered. The filtrate was evaporated under reduced pressure. The resulting yellow powder (2.0 g, 3.38 mmol) was mixed with 787 mg (3.38 mmol) of zirconium tetrachloride; then, 100 mL of toluene was added. After it was stirred for 2 days at room temperature, the toluene solution was decanted and evaporated to dryness, yielding *meso*-**4b**, which was washed with 20 mL of CCl_4. The solid residue was extracted with hot toluene for 8 h and washed with CCl_4 to yield a mixture of the *rac* and *meso* complexes **4b** in a ratio of 1:4.4 (480 mg, 21%). The racemic zirconocene complex *rac*-**4b** could not be separated from the *meso* isomer, but no organic impurities were apparent in the ^1H NMR spectrum. ^1H NMR (C_6D_6, 250 MHz): *rac*-**6**, δ 8.44−8.25 (m, 2 H), 7.85−7.72 (m, 4 H), 7.37−7.28 (m, 2 H), 7.12−7.03 (m, 8 H), 7.20 (s, 2 H), 1.87 (s, 6 H), 1.19 (s, 6 H); *meso*-**6**, δ 8.43−8.42 (m, 2 H), 7.84−7.73 (m, 6 H), 7.29−7.03 (m, 8 H), 7.22 (s, 2 H), 2.42 (s, 6 H), 1.48 (s, 3 H), 0.93 (s, 3 H). MS (EI): *m/z* 676 (M^+, 4%), 625 (M^+ − Me − Cl, 1%), 516 (M^+ − $ZrCl_2$, 2%), 457 (M^+ − Me_2Si − $ZrCl_2$, 2%), 230 (**22b-H**, 100%), 215 (**22b** − Me, 40%). Anal. Calcd for $C_{38}H_{30}SiZrCl_2$: C, 67.43; H, 4.47. Found: C, 66.38; H, 4.33.

Synthesis of [Dimethylsilanediylbis(3,3′-(2-methyltetrahydrobenz[*e*]indenyl))]zirconium Dichloride (5). 2-Methyltetrahydrobenz[*e*]indanone (17). To a suspension of 57.7 g (0.433 mol) of aluminum trichloride in 20 mL of dry CH_2Cl_2 was added 20 mL (0.16 mol) of 2-bromoisobutyric acid bromide at 0 °C. After the mixture was stirred for 40 min at 0 °C, a solution of 22 mL (0.16 mol) of tetralin in 70 mL of CH_2Cl_2 was slowly added. The resulting orange suspension was stirred at room temperature for 1 h and then hydrolyzed by pouring it carefully on ice. A colorless solid precipitated, which gave a yellow oil upon warming to room temperature. The mixture was diluted with 200 mL of CH_2Cl_2, and the layers were separated. The water layer was saturated with NaCl and extracted twice with 100 mL of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to dryness. The resulting mixture of a colorless solid and a yellow oil was taken up in 60 mL of pentane. The insoluble isomer **17** was collected by filtration and washed with pentane until colorless, to yield 16.05 g of pure **17**. A second crop of 1.9 g of crystalline **17** separated at 4 °C from the concentrated filtrate to give a total yield of 55%. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.50 (d, J = 7.8 Hz, 1 H), 7.09 (d, J = 7.8 Hz, 1 H), 3.22 (dd, 1 H), 2.85 (m, 2 H), 2.70 (m, 3 H), 2.50 (dd, 1 H), 1.85 (m, 4 H), 1.30 (d, J = 7.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 144 MHz): δ 209.50, 153.2, 144.50, 134.50, 133.82, 128.94, 120.67, 41.92, 33.43, 30.12, 25.44, 22.65, 22.55, 16.57. Structural assignment of **17** was established by HMBC studies. MS (EI): *m/z* 200 (M^+, 77%), 185 (M^+ − CH_3, 100%,), 172 (M^+ − CO, 13%). Anal. Calcd for $C_{14}H_{16}O$ (200.3): C, 83.96; H, 8.02. Found: C, 83.80; H, 7.97.

A yellow oil, containing mainly isomer **18**, was obtained from the filtrate by removing the solvent *in vacuo*. ^1H NMR (250 MHz, $CDCl_3$): δ 7.46 (s, 1 H), 7.14 (s, 1 H), 3.29 (dd, 1 H), 2.81 (m, 4 H), 2.65 (m, 2 H), 1.85 (m, 4 H), 1.28 (d, J = 7.3 Hz, 3 H). MS (EI): *m/z* 200 (M^+, 89%), 185 (M^+ − CH_3, 100%), 172 (M^+ − CO, 22%).

2-Methyltetrahydrobenz[*e*]indanol (19). Compound **17** (14.85 g, 74.15 mmol) was dissolved in 100 mL of dry THF; this solution was cooled to 0 °C and treated dropwise with 40 mL (81.63 mmol) of a 2.06 M solution of sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al) in toluene. The resulting solution was stirred overnight at room temperature and then hydrolyzed by slow addition of 10% aqueous HCl to pH 6−7. The layers were separated, and the turbid water layer was extracted twice with 80 mL of ether. The combined organic layers were dried over $MgSO_4$ and filtered and the solvent removed *in vacuo* to give 15.74 g of the diastereomeric alcohols **19** as a colorless solid, which was used without further purification. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.16 (m, 1 H), 7.0 (m, 1 H), 4.71 and 4.96 (2 broad t, 1 H), 2.4−3.1 (m, 6 H), 2.26 (m, 1 H), 1.8 (m, 4 H), 1.32 and 1.62 (2 broad d, 1 H), 1.18 and 1.25 (2 d, 3 H). MS (EI): *m/z* 202 (M^+, 100%), 185 (M^+ − OH, 24%), 173 (M^+ − COH, 32%).

2-Methyltetrahydrobenz[*e*]indene (20). The diastereomeric alcohols **19** (12.5 g, 62.2 mmol) were suspended in 150 mL of heptane, treated with a solution of 1.18 g (6.2 mmol) of *p*-toluenesulfonic acid in 10 mL of water, and refluxed for 3.5 h. A yellow solution was obtained to which, after cooling to room temperature, 50 mL of a saturated aqueous NH_4Cl solution was added. The layers were separated, and the water layer was extracted with 50 mL of heptane. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated to dryness. The resulting yellow oil was dissolved in pentane and filtered over silica gel using pentane as eluent. The solvent was removed *in vacuo* to yield 10.9 g of pure **20** as a colorless solid (96% yield). ^1H NMR (250 MHz, $CDCl_3$): δ 7.0 (2 d, 2 H), 6.47 (broad s, 1 H), 3.14 (s, 2 H), 2.84 (t, 2 H), 2.74 (t, 2 H), 2.18 (s, 3 H), 1.86 (m, 4 H). MS (EI): *m/z* 184 (M^+, 100%), 169 (M^+ − CH_3, 21%), 156 (M^+ − C_2H_4, 30%). Anal. Calcd for $C_{14}H_{16}$ (184.3): C, 91.25; H, 8.75. Found: C, 90.95; H, 8.61.

Bis[3,3′-(3*H*-2-methyltetrahydrobenz[*e*]indenyl)]-dimethylsilane (23). To a solution of 4 g (21.71 mmol) of **20** in 30 mL of THF, cooled to 0 °C, was added 15 mL (24 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. When the resulting yellow solution was warmed to room temperature and stirred for 1.5 h, it became brown. The solvent was removed *in vacuo*. The solid residue was stirred in 50 mL of pentane for 30 min, collected by filtration, and washed with 20 mL of pentane. It was then suspended in 200 mL of ether and stirred with 1.4 g (10.86 mmol) of Me_2SiCl_2 overnight. When the suspension was treated with 80 mL of THF and stirred for another 4 h, most of the solid dissolved. The solvent was removed *in vacuo* to give a colorless solid, which was taken up in 100 mL of ether and filtered. The insoluble residue was treated with saturated aqueous NH_4Cl solution and extracted with ether. The organic layers were combined, dried over $MgSO_4$, and filtered. Removal of the solvent gave 860 mg of pure racemic **23**. From the filtrate 4.1 g of a *rac*/*meso* mixture of **23** (containing also traces of **20**) was obtained by evaporation to dryness and used without further purification. ^1H NMR ($CDCl_3$, 250 MHz): *rac*-**23**, δ 7.27 (d, 2 H), 6.82 (d, 2 H), 6.66 (broad s, 2 H), 3.69 (s, 2 H), 2.83 (m, 8H), 2.20 (s, 6 H), 1.84 (m, 8 H), B0.34 (s, 6 H); *meso*-**23**, δ 7.12 (d, 2 H), 6.81 (d, 2 H), 6.66 (broad s, 2 H), 3,68 (s, 2 H), 2.83 (m, 8 H), 2.26 (s, 6 H), 1.84 (m, 8 H), 0.07 (s, 3 H), −0.31 (s, 3 H). MS (EI): *m/z* 424 (12%, M^+), 241 (100%, M^+ − $C_{14}H_{13}$), 181 (22%, $C_{14}H_{13}^+$). Anal. Calcd for $C_{20}H_{36}Si$ (424.7): C, 84.84; H, 8.54. Found: C, 85.77; H, 8.66.

[Dimethylsilanediylbis(3,3′-(2-methyltetrahydrobenz-[*e*]indenyl))]zirconium Dichloride (5). To a solution of 4.1 g (9.65 mmol) of **23** in 80 mL of THF at 0 °C was added 12 mL (19.3 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The reaction mixture was stirred for 30 min in the cold and

Table 3. Crystallographic and Experimental Data[a] for $C_{30}H_{34}Cl_2SiZr$ (5)

formula	$C_{30}H_{34}Cl_2SiZr$	T, K	233
fw	584.78	scan mode	adaptive ω
cryst color, form	yellow orthogonal prisms	θ range, deg	2.23−27.50
cryst syst	monoclinic	scan speed, deg/min	3−30
space group	$C2/c$	no. of rflns collected	4072
a, Å	20.278(2)	no. of indep rflns	3065 (R(int) = 0.0263)
b, Å	13.303(2)	no. of obsd rflns	2495 ($I > 2\sigma(I)$)
c, Å	12.538(2)	soln[b]	direct methods
β, deg	127.934(9)	no. of params[c]	179
V, Å^3	2667.7(7)	abs cor	none
d_{calcd}, g/cm^3	1.456	$R(F)$[d]	0.0357
Z	4	$R_w(F^2)$[e]	0.0813
cryst size, mm	0.3 × 0.3 × 0.2	largest diff peak (e Å^{-3})	0.335
abs coeff (μ), cm^{-1}	6.75	goodness of fit (F^2)	0.998

[a] Conditions: Siemens P4 four-circle diffractometer, Mo Kα radiation (0.710 73 nm), graphite monochromator. [b] SHELXL-93. [c] All non-hydrogen atoms were refined anisotropically. Hydrogens were refined on the calculated positions with fixed isotropic U values using riding model techniques. The C−C bond distances of the disordered fragment (C(6)−C(9)) were restrained to be equal. [d] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [e] $R_w(F^2) = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)_2)^{1/2}$; weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0434P)^2 + 1.0734P$, with $P = (F_o^2 + 2F_c^2)/3$.

then overnight at room temperature. The red solution thus obtained was evaporated to dryness. The resulting solid was washed with 100 mL of pentane, dried *in vacuo*, and mixed with 2.25 g (9.65 mmol) of $ZrCl_4$. Addition of 150 mL of toluene gave an orange suspension, which was stirred for 24 h. The crude product, which contained *rac*- and *meso*-**5** in a 1:1 ratio, was filtered and washed with 60 mL of toluene. The filtrate was concentrated *in vacuo* until crystallization began and then stored at −70 °C for 4 days. The resulting yellow crystalline solid was collected by filtration to give 1.2 g of a 6:1 mixture of *rac*- and *meso*-**5**. A second crop of 790 mg of *rac*-enriched **5** (11:1) was obtained from the concentrated mother liquors. Further crystallization gave 770 mg of *meso*-**5** as an orange solid. The *rac*-enriched fractions were combined and recrystallized from a concentrated toluene solution at −30 °C, to yield 1.11 g of pure *rac*-**5** (20%). *rac*-**5**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.36 (d, J = 8.8 Hz, 2 H), 6.74 (d, J = 8.8 Hz, 2 H), 6.66 (s, 2 H), 2.7 (m, 8 H), 2.19 (s, 6 H), 1.7 (m, 8 H), 1.26 (s, 6 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 135.43, 134.20, 133.29, 132.96, 128.67, 125.49, 121.84, 119.42, 83.43, 29.45, 26.51, 23.00, 22.38, 18.52, 2.45; MS (EI) *m/z* 584 (12%, M$^+$), 546 (8% M$^+$ − HCl − 2H), 185 (100%, $C_{14}H_{16}^+$). Anal. Calcd for $C_{30}H_{34}SiZrCl_2$ (584.8): C, 61.61; H, 5.86. Found: C, 61.24; H, 5.91. *meso*-**5**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.30 (d, J = 8.8 Hz, 2 H), 6.53 (s, 2 H), 6.47 (d, J = 8.8 Hz, 2 H), 2.7 (m, 8 H), 2.41 (s, 6 H), 1.7 (m, 8 H), 1.40 (s, 3 H), 1.21 (s, 3 H).

Polymerizations and Polymer Analysis. Into a Büchi 1-L autoclave (previously cleaned by stirring with a 0.5% solution of Al^iBu_3 in toluene and subsequently dried *in vacuo* at 50 °C) were added, in the following order, 350 mL of toluene, 4.50 g of methylaluminoxane (MAO; 5.21 mass % Al, molar mass ca. 800, Witco AG) in 10 mL of toluene, and 10 mL of a toluene solution of the zirconocene complex (Table 2). After the reaction mixture was stirred for 30 min at 50 °C under an argon atmosphere of 1 bar, the autoclave was pressurized with a propene pressure of 2 bar (i.e. to a total pressure of 3 bar). During the polymerization reaction, the total pressure of 3 bar was kept constant by further addition of propene. 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. Molecular weight distributions were determined by GPC and melting points by DSC (Kunststoff-Labor, BASF AG). Polymer ^{13}C NMR spectra were measured in $C_2D_2Cl_4$ (δ 74.1 ppm) at 120 °C on a 250 MHz spectrometer operated at 62.9 MHz and analyzed by methods described in the literature.[19,20]

Crystal Structure Determinations. Crystals of **5** were obtained from a solution of a 2:1 mixture of *rac*- and *meso*-**5** in hot toluene by cooling slowly to room temperature. Space group determinations, diffraction data collection, solution, and refinement of the structures were conducted as summarized in Table 3. Additional crystallographic data are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen 2, upon quotation of depository number CSD-406557, the authors, and the journal reference for this article.

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Supporting Information Available: Tables giving crystal data and refinement details, atomic positional and thermal parameters, and bond distances and angles for **5** (8 pages). Ordering information is given on any current masthead page.

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