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ansa-Zirconocenes Based on *N*-Substituted 2-Methylcyclopenta[*b*]Indoles: Synthesis and Catalyst Evaluation in Liquid Propylene Polymerization

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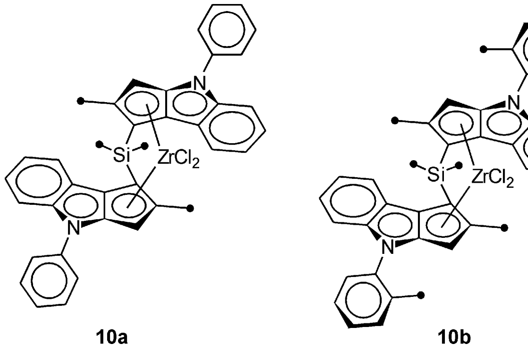
Cyclopenta[*b*]indole-based *ansa*-zirconocenes were prepared and studied as catalysts for propylene polymerization. Substituted 2-methyl-4-R-1,4-dihydrocyclopenta[*b*]indoles (R = Ph, **7a**; R = *o*-Tol, **7b**; R = Me, **7c**) were synthesized and converted into the racemic forms of the corresponding *ansa*-zirconocenes $Me_2Si(2\text{-}Me\text{-}4\text{-}R\text{-}cyclopenta[b]indolyl)_2ZrCl_2$ (R = Ph, **10a**; R = *o*-Tol, **10b**; R = Me**, 10c**). The structure of **10a** was determined by X-ray analysis. The effectiveness in polymerization catalysis of the metallocenes compared to benchmark metallocenes *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (**11**) and *rac*-$Me_2Si(2\text{-}Me\text{-}4,5\text{-}BzInd)_2ZrCl_2$ (**12**) was investigated in liquid propylene at 70 °C. Both **10a** and **10b** with MAO cocatalyst afforded highly isospecific (*mmmm* 95.9, 95.6%, respectively) and highly regisospecific polypropylene (0.17, 0.34% imbedded regioerrors), which exhibited a high melting point (T_{m2} = 154.2, 156.3 °C). The polymer properties were intermediate between those of **11** and **12**, with the molecular weight, stereospecificity, and melting point increasing in the order **12** < **10a**,**b** < **11**. Although activities 1−2 orders of magnitude lower than for **11** and **12** were found at high MAO/Zr ratios, at low cocatalyst levels activities were similar. **10a**,**b** were also successfully activated with alternative aluminoxanes based on branched alkylaluminums (e.g. $Al(CH_2CHMePh)_3$, obtained from α-methylstyrene), with measured activities up to 16.6 TON/((g of Zr) h) (**10a**/AKO). Surprisingly, no consistent effect on polymer properties of varying either the 4-aryl substituent of the cyclopenta[*b*]indole group or the cocatalyst was found.

1. Introduction

C_2-symmetric metallocenes (heterocenes) based on cyclopentadienyls ring-fused to thiophenes and pyrroles have been investigated in depth as procatalysts for isotactic polypropylene (*i*-PP) formation.[1−5] The catalysts share structural features similar to those of the best C_2-symmetric metallocene catalysts for *i*-PP, such as *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (**11**).[6] The presence of 2-methyl substituents (next to the silicon bridge) and a phenyl group on the adjacent ring (protruding at the front of the complex) result in high polymer molecular weight and high isotacticity. Zirconocenes **10a**,**b** (Figure 1), based on the 2-methyl-4-phenylcyclopenta[*b*]indolyl fragment, are closely related to systems based on the 2-methyl-1-phenylcyclopenteno[1,2-*b*]pyrrole fragment previously reported.[1,2] These complexes differ in the substitution pattern of the front-facing phenyl group, with **10b** expected on the basis of previous work with metallocenes based on thiopentalenyl ligands[3,4] to exhibit higher polymer molecular weight and stereoregularity. We report here the preparation and perfor-



10a **10b**

Figure 1.

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[†] Shell International Chemicals B. V., Shell Research and Technology Centre, Amsterdam.

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[§] Moscow State University.

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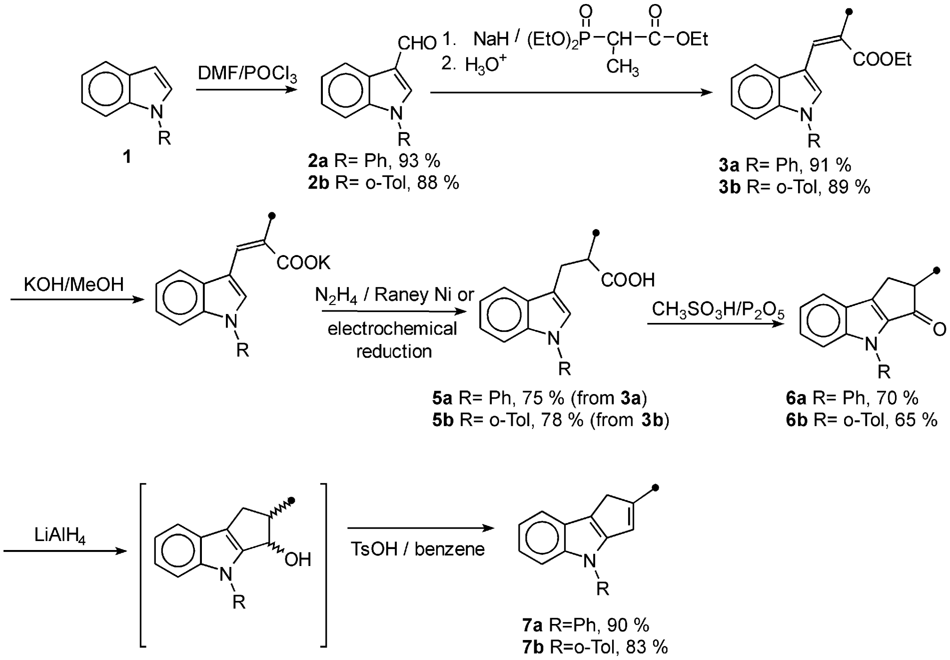


Figure 2. Preparation of dihydrocyclopenta[*b*]indoles.

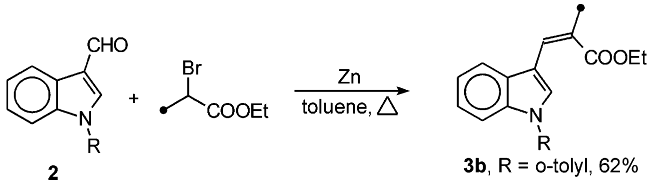
mance in isospecific propylene polymerization of this new class of heterocene catalysts. The synthesis of analogue **10c** containing a 4-methyl group is also described.

2. Synthesis of Zirconocenes

The synthesis of dihydrocyclopenta[*b*]indoles has not been reported as yet. On the other hand, tetrahydro derivatives of cyclopenta[*b*]indoles have been much studied. These compounds are readily obtained by cyclization of the corresponding cyclopentenone phenylhydrazones according to Fischer.[7,8] Attempts at using this procedure to obtain dihydrocyclopenta[*b*]indoles have failed.[9] Therefore, we decided to assemble the cyclopentadienone ring in a step-by-step manner, similar to that proposed for the synthesis of a number of aza- and thiapentalenes.[10] Figure 2 summarizes the synthetic procedure applied for the formation of 2-methyl-4-aryl-1,4-dihydrocyclopenta[*b*]indoles **7a**,**b**.

The initial compounds, *N*-substituted indoles **1**, can be obtained by alkylation or arylation of indole following known procedures.[11,12] Formylation of indoles under conditions of the Vilsmeier reaction is known to proceed with ease[13] and results in the indole-3-carboxaldehydes **2** as exclusive products in high yields (80−95%).

There are two synthetic routes to unsaturated acids **4**, namely, the Wadsworth−Emmons reaction with triethyl 2-phosphonopropionate[10] or the Reformatsky reaction[14] with ethyl 2-bromopropionate (in the latter case, the products yields are lower):



Ethyl esters **3** were saponified under the action of a methanol solution of KOH without isolation as individual compounds. The overall yield calculated with respect to free acid for the reaction with triethyl 2-phosphonopropionate was as high as 80%.

The facility of hydrogenation of **4**, to give saturated acids **5**, depends on the substituent R, and the reaction does not always proceed with ease. Because of this, different methods have been used, such as reduction of a solution of a sodium salt of the acid by hydrogen under a slightly increased pressure (3 atm) on Pd catalyst,[10] electrochemical reduction at a mercury cathode,[15] hydrogenation under the action of sodium amalgam in alkali solution,[16] and finally, reduction by hydrazine hydrate in the presence of Raney nickel.[17] The highest yields of unsaturated acids (up to 90%) were obtained using electrochemical techniques, especially for large-scale charges. In small-scale experiments, it is also convenient to use reduction by hydrazine hydrate.

Cyclization of substituted propionic acids into ketones **6** can occur under the action of polyphosphoric acid (PPA)[18] or a solution of P_2O_5 in methanesulfonic acid

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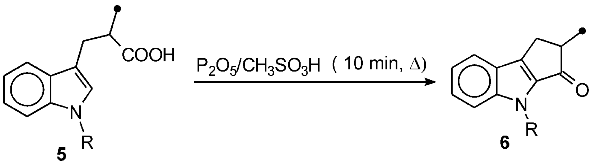
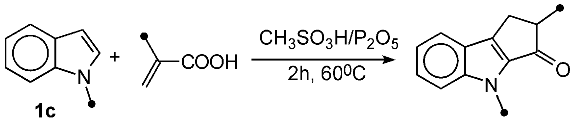
(the Eaton reagent).[19] In the latter case, the yields of ketones **6** are higher.



We investigated an alternative method for the synthesis of ketones **6c** from substituted indole **1c**, consisting of heating a mixture of indole and methacrylic acid in the presence of PPA or the Eaton reagent. This procedure appears to be of a general character and can also be used to obtain substituted indanones[20] and their heteroanalogues.[10] Some examples of the use of this reaction for the synthesis of cyclic thiophene ketones have been reported.[21]



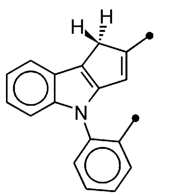
6c, 50%

Only in the case of 1-methylindole (**1c**) was the yield of the desired ketone sufficiently high. In the case of **1a**,**b**, strong resinification was observed.

Reduction of ketones into alcohols by $LiAlH_4$ in ether occurs readily. The reducing agent should not be used in large excess, since the alcohol formed in the reaction can undergo further transformation into a tetrahydrocyclopenta[*b*]indole derivative.[22]

Dehydration of alcohols occurs with ease in the presence of acid catalysts. The use of sufficiently dilute solutions is a necessary condition for obtaining of compounds **7** in high yields (80−90%).

It should be mentioned that no free rotation of the tolyl substituent around the plane of the indole fragment occurs in the molecule of 2-methyl-4-(2-methylphenyl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-one (**6b**). This leads to the appearance of two rotamers in a 1/1 ratio, which in turn causes doubling of the number of all signals of the cyclopentenone ring in the NMR spectrum. An analogous effect can also be observed for 2-methyl-4-(2-methylphenyl)-1,4-dihydrocyclopenta[*b*]-indole (**7**), which can have two isomers, **7bI** and **7bII**, differing in the position of the double bond.



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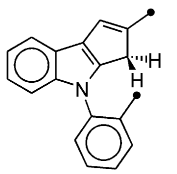
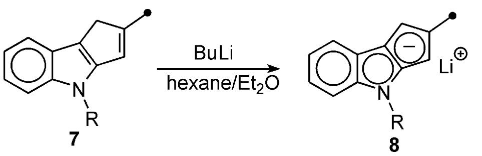


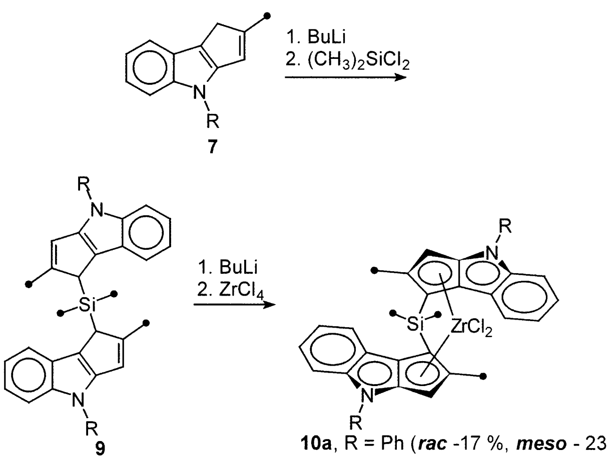
II

Reduction of ketone **6b** followed by dehydration of the alcohol formed results in kinetic product **7bI** as the only product; however, an equimolar mixture of **7bI** and **7bII** can be obtained by hydrolysis of the lithium salt (**8b**). The ^1H NMR spectrum ($CDCl_3$, 25 °C) of isomer **7bII** exhibits a characteristic signal for the AB system of diastereotopic $-CH_2-$ protons at δ 3.15 and 3.07 (J = 19 Hz). This AB pattern remains unchanged in the temperature range 20−100 °C (in toluene-d_8), consistent with the absence of free rotation of the tolyl substituent about the C−N bond under these conditions. In the ^1H NMR spectrum of compound **7bI** ($CDCl_3$, 25 °C), the signal of allylic protons is a singlet at δ 3.36, which can be due to either a free rotation of the tolyl group or the fact that the difference in the chemical shifts of diastereotopic protons is so small that it cannot be reliably measured.

By and large, methods for the synthesis of organometallic derivatives of 2-methylcyclopenta[*b*]indoles do not differ from those used to obtain, for example, indenyl or cyclopentadienyl complexes. Reactions of compounds **7** with a solution of butyllithium in ether results in crystalline lithium salts **8** (compound **8c** was isolated in pure form, yield − 71%):



Lithium salts **8a**−**c** interact with $(CH_3)_2SiCl_2$ to give high yields (conversion 100%, determined by ^1H NMR) of reaction products only when using hexane/THF or toluene/THF mixtures as solvents. In each case, the reaction results in a mixture of nearly equal amounts of racemic and meso forms of compounds **9**. Performing this reaction in ether resulted in the formation of a mixture of products; however, our attempts to identify them failed. Ligands **9** were then transformed into corresponding zirconocenes using standard methodology.



10a, R = Ph (***rac*** -17 %, ***meso*** - 23 %)
10b, R = o-tolyl (***rac*** - 6 %)
10c, R = Me (***rac*** - 23%)

The pure racemic forms of compounds **10a** (yield 17%), **10b** (6%), and **10c** (32%) as well as the meso form of compound **10a** (23%) were isolated by recrystalliza-

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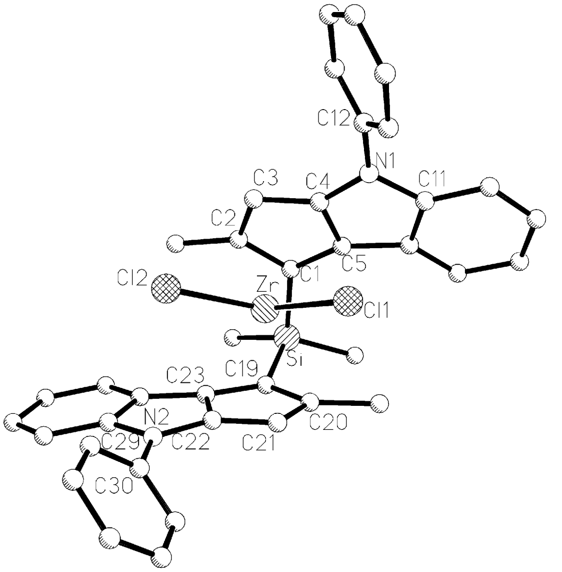

Figure 3. Molecular structure of [μ-dimethylsilanediylbis-(η^5-2-methyl-4-phenylcyclopenta[*b*]indolyl)]zirconium(IV) dichloride (**10a**).

Table 1. Essential Structural Parameters of 10a, Compared with Those of Related Zirconocenes

param	**11**[6]	**13**[3]	**14**[3]	**16**[3]	**10a**
Zr−Cl (Å)	2.419(1)	2.437(3)	2.421(5)	2.443(4)	2.4413[a]
Cl−Zr−Cl (deg)	96.8(1)	98.00(11)	99.44(3)	97.86(3)	99.90(4)
Zr−Cp[b] (Å)	2.243(4)	2.251(6)	2.256(5)	2.230(4)	2.151[a]
Zr−C(Cp) min (Å)	2.478(3)	2.484(10)	2.466(2)	2.463(3)	2.275(3)
Zr−C(Cp) max (Å)	2.640(4)	2.663(9)	2.665(2)	2.650(3)	2.635(3)
Cp-Zr−Cp (deg)	128.5(3)	128.4(6)	127.5	128.7(4)	126.51(1)
E1−E2[c]	59.2	59.8	61.3	59.9	58.1
θ[d]	131.4	139.3(9)	139.4	141.2(8)	139.1(9)
Φ[e]	44.4	30.7(55)	55.9(67)	35.5(34)	56.1

[a] Mean value. [b] Cp ring centroid. [c] Angle between least-squares planes of the Cp rings. [d] Exo angle between condensed 5/5- and 5/6-angles. [e] Torsion angle between the benzene and Cp rings least-squares planes.

tion from appropriate solvents. Single crystals of **10a** suitable for an X-ray diffraction study were obtained by storing a saturated solution in an ether−hexane mixture at 20 °C.

The structure of complex **10a** is shown in Figure 3. Key structural parameters for **10a** are compared to those for related crowded metallocene **11** and heterocenes **13**, **14**, and **16** (Figure 4) in Table 1. In the molecule **10a**, the Zr atom is coordinated by the cyclopentadienyl moieties in an η^5 fashion, the molecule having typical distortions characteristic of *ansa*-metallocene complexes with short bridges. There is no contact between the Zr and N atoms, which is also a general characteristic of heteroaromatic zirconocenes.

It is worth noting that **10a** has the lowest Zr−Cp (centroid) distance of the compounds considered and exhibits a large Φ angle between the phenyl ring and the Cp ring planes (similar to that in heterocene **14**). Other workers have suggested that the size of the dihedral angle involving this front-side phenyl group is highly sensitive to crystal-packing forces or the presence of cocrystallized solvent molecules.[3] Other structural characteristics are practically the same and are typical of these complexes.

3. Catalytic Investigation

To allow comparison to state-of-the-art metallocene catalysts, the propylene polymerization activity of the new complexes and reference zirconocenes **11** (*rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$)[6] and **12** (*rac*-$Me_2Si(2\text{-}Me\text{-}4,5\text{-}BzInd)_2ZrCl_2$)[23] has been examined under the same conditions using methylaluminoxane (MAO) as cocatalyst. Polymerizations were performed in liquid propylene (LIPP) at 70 °C in the presence of hydrogen (generally ca. 1% in the gas cap at 70 °C), which resulted in a lowering of the polymer molecular weight, facilitating polymer analysis (NMR, GPC) and affording polymers of greater industrial relevance. Catalyst precursor **11**, and to a lesser extent **10a**,**b**, gave very high molecular weight polymer in the absence of hydrogen. A cold start procedure was applied to prevent reactor fouling (deposition of polymer on the autoclave walls, stirrer, and other surfaces), which can lead to poor control of process conditions (temperature, pressure). Catalyst injection into the autoclave containing propylene at 30 °C was followed by rapid warming (6−7 min) to the polymerization temperature. At the end of the polymerization (generally about 60 min) the catalyst was deactivated by injection of methanol and the polymer isolated as a free-flowing powder. The time quoted in Tables 2 and 3 and used to calculate activity refers to the period from *initiation* of heating to catalyst quenching.

Procatalysts **10a**,**b** were also activated with alternative cocatalysts based on the hydrolysis products of alkylaluminums, in which the alkyl groups are β,γ-branched (AK, AO, Q in Figure 5). These alkylaluminoxanes (particularly AKO and AOO) have been shown to be effective cocatalysts for a range of isospecific metallocenes.[24−27] The optimum activity was obtained with a water/Al molar ratio of ca. 1/2. Alkylaluminoxanes with a β-phenyl substituent were particularly effective at high temperatures,[26] often affording catalyst activity superior to that of MAO at 70 °C in LIPP.

Comparison to Benchmark Metallocenes with Methylaluminoxane as Cocatalyst. The activities of procatalysts **10a**,**b** with MAO as cocatalyst in LIPP are compared with those for the isospecific benchmarks **11** and **12** in Table 2. All catalysts afforded highly isotactic polypropylene, and no significant reactor fouling was observed under cold start conditions with added hydrogen. The relative performance of the catalysts depended strongly on the Al/Zr molar ratio. At high MAO intakes, **12** and **11** were 1 and 2 orders of magnitude (respectively) more active than **10a**,**b**, with, for example, a remarkably high activity of 170 Ton/((g of Zr) h) found for **11** (experiment 6).[6] However, with a low aluminox-

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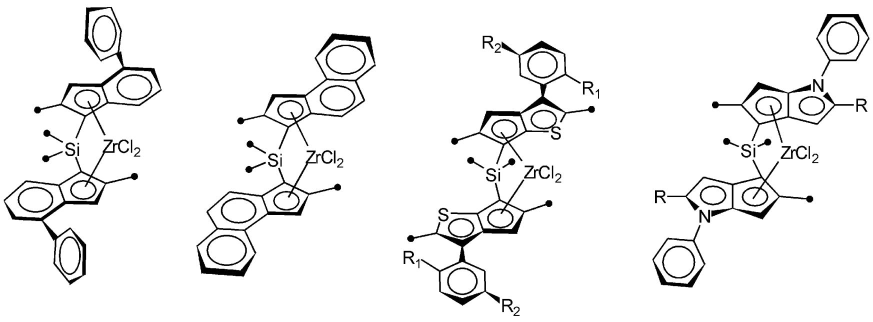


11

12

13, $R_1 = R_2 = H$
14, $R_1 = Me$, $R_2 = H$
15, $R_1 = R_2 = Me$

16, R = H
17, H = Me

Figure 4.

Table 2. LIPP Activity of 10a,b Compared to Benchmark Metallocenes with Methylaluminoxane Cocatalyst (Cold Start Polymerization, 70 °C)[a]

	procatalyst		prealkylation agent		aluminoxane (reactor)							
expt	type	amt, μmol	type	amt, mmol	type	amt, mmol	Al/Zr ratio (aluminoxane)	amt of TIBA, mmol	H_2 gas cap, vol %	time, min	yield, g	activity, Ton/((g of Zr) h)
1	**10a**	1.44	MAO	0.75	MAO	4.5	3646	0.0	1.0	49	195	1.8
2	**10b**	0.48	MAO	0.75	MAO	4.5	10938	0.0	1.1	60	260	5.9
3	**10b**	1.00	MAO	0.50			500	1.0	1.0	60	320	3.5
4	**12**	0.05	MAO	0.75	MAO	4.5	105000	0.0	1.0	60	140	30.7
5	**12**	0.75	MAO	0.375			500	1.0	1.0	60	129	1.9
6	**11**	0.05	MAO	0.75	MAO	4.5	105000	0.0	1.0	34	438	169.5
7	**11**	0.75	MAO	0.375			500	1.0	0.8	60	275	4.0

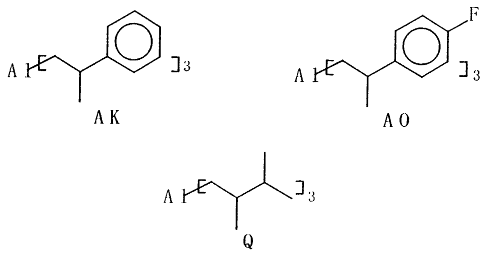
[a] Short cold start procedure, except long cold start for experiments 1 and 2. The time was measured from catalyst injection (short cold) or injection + 10 min (long cold start). Negligible reactor fouling was found.

Table 3. LIPP Activity of Heterocenes with Various Alkylaluminoxane Cocatalysts at High and Low Al/Zr Ratios (Cold Start Polymerization, 70 °C)[a]

	procatalyst		prealkylation agent		aluminoxane						
expt	type	amt, μmol	type	amt, mmol	type	amt, mmol	Al/Zr ratio (aluminoxane)	amt of TIBA, mmol	H_2 gas cap, vol %	time, min	activity, Ton/((g of Zr) h)
8	**10a**	0.40	MAO	0.75	MAO	4.5	13125	0.0	1.0	60	1.8
9	**10a**	0.48	TIOA	0.30	AKO	4.5	9375	0.0	1.0	43	16.6
10	**10a**	0.24	TIOA	0.15	AOO	2.3	9375	0.0	1.0	52	6.3
11	**10a**	0.24	TIOA	0.15	QO	2.2	9167	0.0	0.9	50	7.4
3	**10b**	0.48	MAO	0.75	MAO	4.5	10938	0.0	1.1	60	5.9
4	**10b**	1.00	MAO	0.50			500	1.0	1.0[b]	60	3.5
12	**10b**	0.48	TIOA	0.30	AKO	4.5	9375	0.0	1.3[b]	60	9.1
13	**10b**	1.00	TIOA	0.10	AKO	0.5	500	1.0	1.0	60	0.2
14	**10b**	0.48	TIOA	0.30	AOO	4.5	9375	0.0	1.8	60	5.3
15	**10b**	1.00	TIOA	0.10	AOO	0.5	500	1.0	0.7	60	3.4
16	**10b**	0.48	TIOA	0.30	QO	4.5	9375	0.0	1.5[b]	60	3.1
17	**10b**	1.00	TIOA	0.10	QO	0.5	500	1.0	0.8	60	1.4

[a] Long cold start, except short cold start for experiments 4 and 13. The time was measured from catalyst injection (short cold) or injection + 10 min (long cold start). Negligible reactor fouling was found. [b] Average H_2 concentration (varied in range 0.5% above or below).

ane/Zr molar ratio of about 500 in the premix (and utilizing 1.0 mmol of TIBA as scavenger in the autoclave),[28] the observed activities with **10b**, **11**, and **12** were similar, in the range 2−4 Ton/((g of Zr) h). Some caution should also be exercised in comparing activities at different procatalyst intake levels, as activity, in



AK

AO

Q

Figure 5. Trialkylaluminum precursors of branched alkylaluminoxanes.

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(28) Experimental studies (with other metallocenes) of the effect of scavenger intake on activity at low aluminoxane/Zr ratios indicated that the level of 1.0 mmol of TIBA applied in this work is *well above* that needed to effectively scavenge poisons, such as water, oxygen, and other reactive contaminants in the 5 L reactor containing 1.6 kg of propylene.

Table 4. LIPP Activity of 10a with Various Alkylaluminoxane Cocatalysts at High Al/Zr Ratios under Hot Start Conditions (70 °C)[a]

	procatalyst		prealkylation		aluminoxane						
expt	type	amt, μmol	type	amt, mmol	type	amt, mmol	Al/Zr ratio (aluminoxane)	H_2 gas cap, vol %	time, min	activity, Ton/((g of Zr) h)	fouling, %
18	**10a**	1.44	MAO	0.75	MAO	4.5	3646	0.01[b]	60	1.4	77
19	**10a**	1.44	MAO	0.75	MAO	4.5	3646	1.0	60	0.9	82
20	**10a**	1.44	TIOA	0.30	AKO	4.5	3125	0.02[b]	60	1.6	87
21	**10a**	1.44	TIOA	0.30	AKO	4.5	3125	0.7	60	2.4	92
22	**10a**	1.44	TIOA	0.30	AOO	4.5	3125	0.02[b]	38	2.0	80
23	**10a**	1.44	TIOA	0.30	AOO	4.5	3125	0.9	42	2.7	91
24	**10a**	1.44	TIOA	0.30	QO	4.5	3125	0.02[b]	27	2.5	96
25	**10a**	1.44	TIOA	0.30	QO	4.5	3125	0.9	17	7.1	94

[a] Time measured from catalyst injection. [b] No H_2 added: maximum H_2 concentration measured.

particular at low Al/Zr ratios, is strongly dependent on the absolute concentration of the zirconocene. For example, the activity of **11** at 70 °C (1 v % hydrogen, MAO/Zr ca. 500, 1.0 mmol TIBA) at 0.25, 0.50 and 0.75 μmol Zr intake increased in the order, 0.4, 1.0, 4.0 Ton/((g of Zr) h) (last entry, experiment 7).[29]

Branched Alkylaluminoxane Cocatalysts. The influence of the cocatalyst on polymerization with **10a**,**b** was investigated at both high and low aluminoxane/Zr ratios. Unlike MAO, effective activation of metallocene dihalides with *branched* alkylaluminoxanes requires pretreatment with an alkylaluminum species such as "tris(isooctyl)aluminum" (TIOA, actual constitution $H_{0.15}$-$Al(CH_2CHMeCH_2CMe_3)_{2.85}$), as these aluminoxanes are ineffective in prealkylation.[25] With high aluminoxane levels, the (TIOA or MAO) pretreated procatalyst was introduced into the autoclave containing liquid propylene and aluminoxane. With low aluminoxane levels, the metallocene was successively treated with TIOA (100 equiv) and aluminoxane (500−750 equiv) before being introduced into the reactor containing propylene and 1.0 mmol of TIBA.[28] In experiments with MAO at low levels (250−500 equiv), MAO was used as the sole (pre)-activation agent.

In the experiments at high aluminoxane/Zr ratio under H_2 (ca. 1 vol %) in Table 3, the aluminoxane intake was generally fixed at 4.5−5.25 mmol and the zirconium intake varied (depending on the intrinsic catalyst activity). Branched alkylaluminoxanes activated both **10a** and **10b** for isotactic polypropylene formation, with activities in the range 3.1 Ton/((g of Zr) h) (**10b**/QO, experiment 16) to 16.6 Ton/((g of Zr) h) (**10a**/AKO, experiment 9), and no reactor fouling.

The kinetic profile of the polymerizations in LIPP could be determined by continuous GC monitoring of the ratio of propane (typically 0.3 mol % in propylene feedstock) to propylene in the gas cap of the autoclave. Typically, little catalyst decay was observed over the polymerization period. For example, polymerizations using MAO, AOO, and QO cocatalysts with **10b** (long cold start procedure) exhibited constant activity for the last 50 min of a 60 min polymerization (constant temperature, after warmup period), whereas with AKO as cocatalyst, a gradual increase in activity with time could be discerned. Similarly, polymerizations with **10a** and branched alkylaluminoxanes exhibited low catalyst decay. In contrast, **10a**/MAO (experiment 1) showed significant decay over the polymerization period, partly explaining the low activity found for this system.

Results obtained with **10b** at *very low* aluminoxane/Zr levels (aluminoxane/Zr = 500) using TIBA (1.0 mmol) as autoclave scavenger are detailed in Table 3; experiment 4 with MAO cocatalyst is included for comparison. In all cases activity was lower at low Al/Zr ratios, but the effect was most dramatic for cocatalyst AKO (45-fold decrease in activity). In general, kinetic profiles for **10b** at low aluminoxane/Zr levels showed catalyst decay during the initial period of polymerization (possibly reflecting slow reaction with sub-equimolar amounts of contaminants), followed by constant activity for the final 30 min (of a 60 min polymerization). Under these conditions MAO was either equally effective as (**10b**/AOO) or superior to the branched alkylaluminoxane cocatalysts. The relative cocatalyst effectiveness differs from that at high aluminoxane/**10b** ratios, where activity increased in the order QO < MAO, AOO < AKO.

Application of a "hot start" procedure, omitting the low-temperature (pre-)polymerization step (injection into the autoclave at 70 °C), resulted in severe reactor fouling and generally lower activities, as shown by a series of experiments with **10a** at high aluminoxane/Zr levels (Table 4). Most of the polymer product was deposited on the walls, stirrer, and other surfaces. Addition of hydrogen (0.7−1.0 v %) did not lead to reduced reactor fouling, although it did afford higher activity in three of four cases. The effect of hydrogen on propylene polymerization with **10a** is illustrated in the cases of MAO and AKO by the kinetic data in Figure 6: despite the fouling, experiments performed under hydrogen exhibited no-decay kinetics over a period of 1 h. Again, changing the cocatalyst had a clear effect on activity (both without and with hydrogen), increasing in the order MAO < AKO < AOO < QO, compared to the order MAO < AOO, QO < AKO found under cold start conditions at high Al/Zr ratio.

Polymerizations at 70 °C without added hydrogen were associated with hydrogen formation in the reactor, building up over 1 h to a constant level of 0.01−0.02 vol % (gas cap). Hydrogen production was presumably associated with the formation of internal vinylidene functionalities ($P-CHMeCH_2C(=CH_2)CH_2CHMe-P'$),[30,31]

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(29) The influence of Al/Zr ratio and Zr intake on activity is further illustrated by the following activity data for **11** in LIPP at 70 °C (1 vol % hydrogen, 2.1 mmol of TIBA scavenger): Al/Zr 2000, 0.25 μmol Zr, 2.5 Ton/((g of Zr) h); Al/Zr 990, 0.25 μmol Zr, 0.6 Ton/((g of Zr) h); Al/Zr 500, 0.75 μmol Zr, 2.6 Ton/((g of Zr) h); Al/Zr 250, 0.75 μmol Zr, 0.3 Ton/((g of Zr) h); Al/Zr 100, 0.75 μmol Zr, 0.0 Ton/((g of Zr) h).

(30) Horton, A. D.; Schut, P. A.; van Baar, J. F. World Patent Application WO 2001090205, 2001 (Basell).

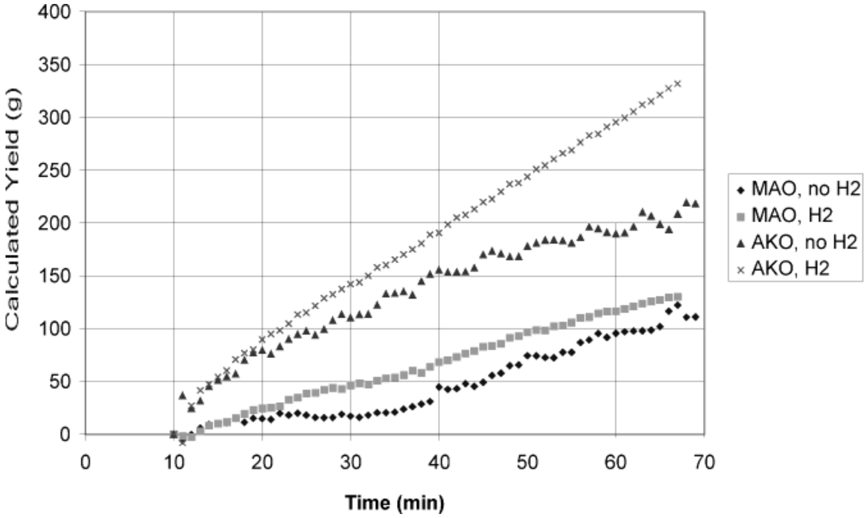

Figure 6. Influence of cocatalyst and hydrogen on **10a** catalyst under hot start conditions (no added H_2 or 0.7−1.0 vol % H_2; injection $t = 10$ min; experiments 18 and 19 (MAO) and 20 and 21 (AKO) in Table 4).

Table 5. Cocatalyst Effects on Properties of Isotactic Polypropylene Obtained with Heterocene Catalysts

expt	procatalyst type	aluminoxane type	aluminoxane Al/Zr ratio	H_2 gas cap, vol %	activity, Ton/((g of Zr) h)	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	regioerrors 2,1 and 1,3, %	*mmmm*, %	sum,[a] %	T_{m2}, °C	ΔH, J/g	XS, %
1	**10a**	MAO	3646	1.0	1.8	69.3	34.0	2.1	0.17	95.9	3.0	154.4	99.8	n.d.
9	**10a**	AKO	9375	1.0	16.6	81.0	42.1	1.9	0.23	95.8	2.6	154.6	100.4	n.d.
21	**10a**	AKO	3125	0.7	2.4	64.4	26.9	2.4	0.32	92.2	4.4	151.9	91.4	n.d.
10	**10a**	AOO	9375	1.0	6.3	49.9	12.7	3.9	0.18	94.0	3.2	154.6	102.3	n.d.
23	**10a**	AOO	3125	0.9	2.7	51.3	9.9	5.2	0.19	93.4	3.3	152.2	100.6	n.d.
11	**10a**	QO	9167	0.9	7.4	112.0	42.9	2.6	0.19	96.5	2.1	156.8	101.4	n.d.
25	**10a**	QO	3125	0.9	7.1	75.7	41.7	1.8	0.23	96.2	2.2	158.0	108.1	n.d.
2	**10b**	MAO	10938	1.1	5.9	55.5	12.6	4.4	0.34	95.6	2.3	156.3	108.7	1.4
3	**10b**	MAO	500	1.0[b]	3.5	37.8	9.3	4.1	0.24	93.0	3.9	154.6	115.6	2.8
12	**10b**	AKO	9375	1.3[b]	9.1	29.3	8.6	3.4	0.29	92.8	3.8	151.0	109.0	3.6
13	**10b**	AKO	500	1.0	0.2	25.7	8.4	3.0	0.21	95.0	2.8	156.8	127.2	4.0
14	**10b**	AOO	9375	1.8	5.3	46.1	12.2	3.8	0.26	93.8	3.1	154.0	104.8	3.6
15	**10b**	AOO	500	0.7	3.4	35.2	12.6	2.8	0.24	93.8	3.0	155.3	112.6	2.6
16	**10b**	QO	9375	1.5[b]	3.1	40.8	10.9	3.7	0.29	94.8	2.8	153.3	109.9	2.0
17	**10b**	QO	500	0.8	1.4	35.6	9.1	3.9	0.26	94.4	3.4	154.9	114.6	3.6
4	**12**	MAO	105000	1.0	30.7	21.7	11.3	1.9	0.30	91.2	6.6	145.4	103.6	1.38
5	**12**	MAO	500	1.0	1.9	27.5	14.4	1.9	0.32	92.7	5.5	147.3	96.6	0.84
6	**11**	MAO	105000	1.0	169.5	115.0	57.2	2.0	0.37	97.7	1.4	158.5	104.3	n.d.
7	**11**	MAO	500	0.8	4.0	88.6	39.4	2.2	0.31	88.9[c]	5.3	160.1	102.2	3.5

[a] "sum" refers to sum of *mmmr*, *mmrr*, and *mrrm* pentads. [b] Average H_2 concentration (varied in range 0.5% above or below). [c] Low *mmmm* value and high T_{m2} value reflect the presence of some atactic polymer (XS 3.5%); the bulk of the polymer is highly isotactic.

but this could not be confirmed by NMR due to the low solubility and high molecular weight of the polymer samples.

Effect of Catalyst and Cocatalyst on Polymer Properties. The properties of isotactic polypropylenes obtained with **10a**,**b** and benchmark systems **11** and **12** are compared in Table 5 to those prepared with benchmark metallocenes. Elucidation of the effect of catalyst and cocatalyst on polymer properties is somewhat hindered by differences in the hydrogen levels between experiments. In particular, comparison of polymer molecular weight (from GPC) and xylene solubles (XS) levels must be done with caution. Regio- and stereoregularity, determined using ^{13}C NMR spectroscopy, and melting points (DSC) were expected to be less sensitive to variation in the hydrogen levels.

Comparison to Benchmark Metallocenes with MAO Cocatalyst. In general the properties of *i*-PP obtained with **10a**,**b** were found to be intermediate between those of benchmark systems **11** and **12** (Table 5). The *i*-PP molecular weight (MW) decreased in the following order: **11** > **10a**,**b** > **12**. Polymer obtained with **10b** generally exhibited a broader MW distribution than that obtained with **10a**. The steroregularity (reflected in *mmmm* and, partially, in T_{m2}) decreased in the same order as the MW: **11** > **10a**,**b** > **12**. The relatively low *mmmm* value of 88.9% (experiment 7), for polymer prepared with **11** at a low MAO/Zr ratio, reflects the presence of some polymer of low stereoregularity (XS = 3.5%), the major (highly isotactic) compo-

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(31) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145.

nent exhibiting a high T_{m2} value of 160.1 °C. The levels of imbedded regioerrors (primarily erythro-2,1-insertions) are rather similar in all four systems, in the range 0.2−0.4%. No consistent effect of the Al/Zr ratio on polymer properties could be found.

Catalysts 10a,b: Influence of Cocatalyst on Polymer Properties. From the data in Table 5 on polymers obtained with heterocenes **10a**,**b**, no general trends concerning the effect of catalyst and cocatalyst on the properties of *i*-PP could be ascertained. *i*-PP prepared using **10b** exhibited somewhat lower molecular weight (M_w = 29 300−55 500; GPC data) than that prepared at similar H_2 levels with **10a** (M_w = 49 900−112 000). In contrast to previous results with other metallocenes (e.g. lower polymer MW with cocatalyst AOO),[27,30] no consistent cocatalyst effect on MW could be discerned.

Complexes **10a**,**b** afforded highly isotactic (*mmmm* 92.2−96.9%) and high-melting polypropylene (T_{m2} = 150.4−159.4 °C). The major stereoerrors are formed as a result of a single misinsertion of propylene, giving *mrrm* pentads (0.5−0.8%); as expected, the sum of the *mmmr*, *mmrr*, and *mrrm* pentads is approximately equivalent to 5 times the *mrrm* pentad (Table 5).[32] The polymers contained low levels of imbedded regioerrors in the range 0.16−0.23% for **10a** and 0.21−0.34% for **10b**. The regioerrors were again primarily erythro-2,1, although trace levels of 1,3-propylene insertion were found in four cases. The stereoregularity and melting points showed a reasonable correlation, as expected, given the small variation in regioregularity between samples. The increased XS levels found with **10b** may partly reflect the rather low molecular weight of these samples.

Discussion of Polymerization Results. It is clear that the polymers obtained with heterocenes **10a**,**b** exhibit properties (stereoselectivity, melting point, MW) which are intermediate between those of the analogous dimethysilyl-bridged *ansa*-metallocenes containing 2-methyl-4,5-benzindenyl and 2-methyl-4-phenyl-indenyl groups. The polymerization activity of **10a**,**b** at high aluminoxane/Zr levels is much lower than for the benchmark metallocenes but is similar at low aluminoxane/Zr levels.

In the related thiopentalene series (Tp, **13**−**15**;[3,4] see above) the substitution pattern of the phenyl group had a significant effect on polymer properties: at 70 °C (MAO, no H_2) the molecular weight (M_w = 445 000−795 000), stereoselectivity (*m* 99.2−99.5%) and melting point (T_{m2} = 156−160 °C) were all found to increase in the series Ph < 2-Me-Ph < 2,5-Me_2-Ph. The effect on polymer properties was ascribed to an increase in the torsion angle between the phenyl group and the cyclopentadienyl ring plane as phenyl ring substitution increased, resulting in higher effective bulk of the protruding phenyl group. It is not clear why the same trend in terms of polymer properties is not observed on going from **10a** to **10b**; however, such subtle changes may be masked by small changes in reaction conditions (e.g. H_2 level, start procedure). It should be noted that the phenyl−Cp ring plane torsion angle in **10a** in the solid state is already large (similar to that in **14**; see above) and further substitution of the phenyl ring may not result in further increase in this angle. The stereoselectivity of **10a** is slightly lower and the regioselectivity similar to that of **13**, which has a similar substitution pattern.

Comparison of polymer prepared with **10a** with that reported for the very closely related heterocene **17**[2,3] (see above) is also informative.[33,34] Crudely, the annelated benzene ring in **10a** was expected to have a roughly similar effect as the adjacent methyl group in **17**, increasing the angle between the aryl group and the cyclopentadienyl ring plane. The measured polymer melting point (155 °C) is within the range found for polymers prepared with **10a**. The level of regioerrors is about twice as high for **10a** as for **17** (erythro-2,1 ca. 0.2% and 0.1%, respectively), whereas the stereoselectivity is much higher (*mrrrm* ca. 0.5% and 1.4%, respectively). These two effects appear to work in opposition, leading to similar T_{m2} values. The higher stereoselectivity and lower regiospecificity of **10a** relative to **17** may reflect the more crowded nature of the ligand in **10a**, perhaps arising from interaction of the annelated benzene ring with the bridge.

The high polymerization activities found with branched alkylaluminoxanes and **10a**,**b**, particularly at high Al/Zr ratios, highlight the promising nature of this family of alternative cocatalysts. For the reference system, *rac*-$C_2H_4(Ind)_2ZrCl_2$, for which a very wide range of alkylaluminoxanes has been investigated,[24−27] those based on alkylaluminums in which the alkyl contains a β-phenyl group (e.g. $Al(CH_2CHMePh)_3$) were previously found to be the best performing cocatalysts in LIPP at 70 °C. Introduction of a 4-halo substituent in the phenyl group (in AO) was particularly favorable.[24−27] The observation that QO and AKO with **10a**,**b** were more effective cocatalysts (under some conditions) than the other aluminoxanes is rather surprising.[30] However, similar positive results with QO as cocatalyst were found with the thiopentalenes **13**−**15**.[4] This may, in some way, result from the presence of heteroatoms in the catalyst, although the exact details are unclear. The limited cocatalyst influence on polymer properties is also remarkable, in the light of previous studies with metallocenes, where cocatalyst AOO resulted in a dramatic reduction in polymer MW relative to other branched alkylaluminoxanes and MAO.[26,27,34]

4. Experimental Section

All operations with organometallic compounds were carried out using Schlenk-type glassware or in a glovebox. Ether and

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[32] A single (stereo) misinsertion of propylene affords polymer with the ...*mmmmrrmmm*... pentad structure. If this is the sole stereoerror in the polypropylene, the sum of the *mmmr*, *mmrr*, and *mrrm* pentads will be equal to 5 times the *mrrm* pentad.

[33] Unfortunately only the rac/meso (1/1) mixture of **17** was tested (MAO, 70 °C, no H_2),[4] leading to a mixture of isotactic and atactic polymer (XS 7.0%). Data in the text refer to the isotactic polymer fraction.

[34] The two systems differ in the relative activity of the rac and meso isomers. Whereas the 1:1 rac/meso mixture of **17** afforded 7% of "atactic-PP" with MAO, the 1:1 rac/meso mixture of **10a** afforded about 30% of (presumably) atactic material (70 °C, no H_2, MAO). With cocatalyst AOO and added hydrogen, the meso isomer of **10a** was more active than the rac isomer. The following activities (Ton/((g of Zr) h)) were measured for the 1/1 rac/meso mixture of **10a** at 70 °C (hot start, 0.8−1.0 vol % H_2, aluminoxane/Zr ratio in parentheses): 0.58 (MAO, 3133), 0.71 (AKO, 3136), 7.10 (AOO, 18 805), 3.47 (QO, 2808). Analysis of the *total* polymer samples afforded the following property information for MAO, AOO experiments, respectively: M_w, 38 700, 16 500; M_n, 9140, 1170; 2,1-insertions, 0.19, 0.10%; *mmmm*, 71.4, 36.2%; T_{m2}, 153.7, 144.2 °C.

THF were distilled over benzophenone sodium ketyl; hexane, toluene, and benzene were distilled over metallic Na. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer.

^{1}H and ^{13}C NMR spectra of *i*-PP were recorded using a Bruker DRX 500 spectrometer at 130 °C, under proton noise decoupling in FT mode, with 10 kHz spectral width, 60° pulse angle, and 15 s pulse repetition (2800 scans). A 5 mm probe was generally used due to the better resolution obtained. The sample concentration was 10 wt % in 1,2-dichlorobenzene solution. Pentad distributions and the proportion of 2,1- and 1,3-regioerrors were determined as described previously.[35]

Alkylaluminums TIBA (Aldrich, Akzo-Nobel, Witco) and TIOA (Witco) were obtained commercially and used without further purification. Methylaluminoxane (MAO) was purchased from Akzo or Witco as solutions in toluene. Other alkylaluminums were prepared from the reaction of TIBA or DIBAH with an excess amount of the appropriate olefin, as described previously.[24−27] The alkylaluminoxanes were prepared by the controlled hydrolysis of trialkylaluminums in toluene solvent (temperature range 4−10 °C) using a water/Al molar ratio of 0.5. Toluene (Aldrich, anhydrous grade) was stripped with nitrogen overnight and dried over 4 Å molecular sieves (H_2O level ∼5−8 ppm). Nitrogen and propylene were purified over a BTS column containing a copper catalyst (BASF R3-11) as well as a column containing a mixed bed of molecular sieves (3 Å (bottom), 4 Å (middle), and 13 Å (top)) to remove oxygen and water, respectively (O_2 level ∼0.3 ppm, H_2O level 0.5 ppm).

1-Phenylindole (**1c**) and 1-(*o*-tolyl)indole (**1b**) were synthesized by following the known procedure.[12]

General Procedure for Formylation of Indoles.[13] In a 100 mL round-bottom flask equipped with a reflux condenser and a dropping funnel, indole (0.1 mol) was dissolved in DMF (45 mL, 0.6 mol) with stirring. The mixture was cooled to 0 °C, and $POCl_3$ (9 mL, 0.1 mol) was added dropwise. On completion of the vigorous stage, the reaction mixture was heated for 2 h at 80 °C using a water bath. The resulting red solution was poured into 200 mL of a warm saturated solution of Na_2CO_3 with stirring. The aldehyle was separated, washed with water, and dried in vacuo.

1-Phenyl-1*H*-indole-3-carboxaldehyde (2a). Colorless crystals. Mp: 45−46 °C. Yield: 20.6 g (93%). ^{1}H NMR (δ, $CDCl_3$, 25 °C): 10.1 (s, 1H, CHO), 8.4 (m, 1H, CH arom), 7.9 (s, 1H, CH indole), 7.6 (m, 2H, CH arom), 7.55 (m, 4H, CH arom), 7.4 (m, 2H, CH arom). ^{13}C NMR (δ, $CDCl_3$, 25 °C): 184.7 (−CHO); 137.99, 137.3, 125.3 (>C<); 137.93, 128.8, 128.1, 124.6, 124.4, 123.2, 122.1, 110.9 (═CH−). Anal. Found: C, 81.25; H, 5.20; N, 6.12. Calcd ($C_{15}H_{11}NO$): C, 81.43; H, 5.01; N, 6.33.

1-(2-Methylphenyl)-1*H*-indole-3-carboxaldehyde (2b). Viscous oil. Yield: 20.7 g (88%). ^{1}H NMR (δ, $CDCl_3$, 25 °C): 10.1 (s, 1H, CHO), 8.4 (d, $J = 8.1$ Hz, 1H, CH arom), 7.8 (s, 1H, CH indole), 7.6−7.4 (m, 6H, arom), 7.1 (d, $J = 8.1$ Hz, 1H, CH arom), 2.1 (s, 3H, $-CH_3$). ^{13}C NMR (δ, $CDCl_3$, 25 °C): 184.7 (−CHO); 138.1, 136.4, 135.3, 124.6, 119.0 (>C<); 138.6; 131.3, 129.3, 127.6, 127.0, 124.3, 122.9, 121.9, 110.94 (═CH−); 17.2 ($-CH_3$). Anal. Found: C, 81.93; H. 6.02; N, 6.12. Calcd ($C_{16}H_{13}NO$): C, 81.68; H, 5.57; N, 5.95.

General Procedure for the Synthesis of N-Substituted 3-(1*H*-3-Indolyl)-2-methylpropionic Acids. Ethyl (*Z*)-2-Methyl-3-(1-aryl-1*H*-indol-3-yl)-2-propenoates. In a 500 mL flask equipped with a magnetic stirrer and a dropping funnel, sodium hydride (6.4 g, 0.27 mol) was suspended in THF (100 mL) under an argon atmosphere. The flask was cooled to 0 °C, and a solution of triethyl 2-phosphonopropionate (43 mL, 0.19 mol) in THF (30 mL) was added slowly to the hydride. The mixture was allowed to stay at room temperature until hydrogen evolution ceased (for ca. 40 min). Then the temperature was reduced to −15−20 °C and a solution of indole-3-carboxaldehyde (**2**; 0.18 mol) in THF (120 mL) was added dropwise. The reaction mixture was warmed to room temperature, 200 mL of saturated NH_4Cl solution was added, and the aqueous phase was extracted with ether. The combined organic extracts were dried over $MgSO_4$ and evaporated.

Ethyl (*E*,*Z*)-2-Methyl-3-(1-phenyl-1*H*-indol-3-yl)-2-propenoate (3a). Light yellow fine crystals (from aqueous ethanol). Mp: 96−97 °C. Yield: 50.2 g (91%). ^{1}H NMR (δ, $CDCl_3$, 25 °C): 8.15 (s, 1H, CH), 7.95 (m, 1H, CH arom), 7.66 (s, 1H, CH indole), 7.6 (m, 5H, CH arom), 7.45 (m, 1H, CH arom), 7.35 (m, 2H, CH arom), 4.4 (q, $J = 5.9$ Hz, 2H, $-CH_2$), 2.3 (s, 3H, $-CH_3$), 1.45 (t, $J = 5.9$ Hz, 3H, $-CH_3$). ^{13}C NMR (δ, $CDCl_3$, 25 °C): 168.7 (−C═O); 138.9, 135.6, 128.8, 123.6, 113.7 (>C<); 129.6, 129.21, 128.7, 127.1, 124.4, 123.3, 121.1, 119.1 110.5 (═CH−); 60.4 ($-CH_2-$); 15.1 ($-CH_3$); 14.3 ($-CH_3$). Anal. Found: C, 78.57; H, 6.31; N, 4.52. Calcd ($C_{20}H_{19}NO_2$): C, 78.66; H, 6.27; N, 4.59.

Ethyl (*E*,*Z*)-2-Methyl-3-[1-(2-methylphenyl)-1*H*-indol-3-yl]-2-propenoate (3b). Dark yellow viscous oil. Yield: 51.2 g (89%). The specimen used for analytical measurements was purified by chromatography on a column with silica gel (with a benzene/ethyl acetate (4/1) mixture as eluent). ^{1}H NMR (δ, $CDCl_3$, 25 °C): 8.2 (s, 1H, CH), 7.9 (m, 1H, CH arom), 7.55 (s, 1H, CH indole), 7.46 (m, 2H, CH arom), 7.38 (m, 2H, CH arom), 7.31 (m, 2H, CH arom), 7.08 (m, 1H, CH arom), 4.35 (q**,** $J = 5.8$ Hz, 2H, $-CH_2-$), 2.25 (s, 3H, $-CH_3$), 2.1 (s, 3H, $-CH_3$), 1.4 (t, $J = 5.8$ Hz, 3H, $-CH_3$). ^{13}C NMR (δ, $CDCl_3$, 25 °C): 168.8 (−C═O); 137.3, 136.7, 135.5, 129.6, 127.9, 113.0 (>C<); 131.2, 129.7, 129.6, 128.8, 127.9, 126.9, 123.1, 120.9, 118.8, 110.6 (═CH−); 60.4($-CH_2-$); 17.4 ($-CH_3$); 15.1 ($-CH_3$); 14.3 ($-CH_3$). Anal. Found: C, 78.82; H, 6.52; N, 4.41. Calcd ($C_{21}H_{21}NO_2$): C, 78.97; H, 6.63; N, 4.39.

Hydrolysis and Reduction. The nonpurified ester (0.16 mol) obtained in the previous stage was suspended in methanol (350 mL), and a solution of KOH (23 g, 0.4 mol) in water (50 mL) was added. Refluxing the mixture for 1 h afforded a nearly transparent solution that solidified on cooling to give a compact aggregate of the potassium salt. The salt was dissolved in water (200 mL), alcohol was removed by distilled in vacuo, and the moist salt was used in the reduction.

(a) Reduction by Hydrazine (Method A). The potasium salt of the appropriate 2-methyl-3-(1-aryl-1*H*-3-indolyl)-2-propenic acid (0.16 mol) was dissolved in water (800 mL), and a suspension of Raney nickel (2.5 g) was added. The solution was heated to 90 °C with continuous stirring with a magnetic stirrer. To the hot solution was added portionwise a 85% hydrazine hydrate (2−3 mL). Complete reduction requires 60−70 mL of hydrazine hydrate and takes 7−8 h. After completion of the reaction, the catalyst was filtered off, 10% HCl was added to pH 2, and the acid that precipitated was separated. The residue was washed with water and dried in vacuo.

(b) Electrochemical Reduction. (Method B). A suspension of the potassium salt of the appropriate 2-methyl-3-(1-aryl-1*H*-3-indolyl)-2-propenic acid (0.16 mol) in 600 mL of 5% aqueous KOH was electrolyzed in a diaphragm cell with a mercury cathode and graphite anode. The cathode current density was 0.15−0.16 A/cm^2, and the temperature of the electrolyte was 40−50 °C. During electrolysis, the salt gradually dissolved. The catholyte was filtered to remove suspended particles, acidified with 10% hydrochloric acid, and isolated as described above.

2-Methyl-3-(1-phenyl-1*H*-indol-3-yl)propionic Acid (5a) (Method A). Colorless crystals (from alcohol). Mp: 155−156 °C. Yield: 36.9 g (76%). ^{1}H NMR (δ, $CDCl_3$, 25 °C): 8.3 (s, 1H, CH arom), 7.9 (m, 1H, CH arom), 7.7−7.2 (m, 8 H, arom and CH indole), 3.35 (m, 1H, CH), 2.9 (m, 2H, $-CH_2-$), 1.35 (d, $J = 8.2$ Hz, 3H, $-CH_3$). ^{13}C NMR (δ, $CDCl_3$, 25 °C): 180.2 (−COOH); 139.9, 139.2, 127.2, 117.9 (>C<); 128.1, 124.3,

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[35] Chadwick, J. C.; Morini, G.; Albizatti, E.; Balbontin, G.; Mingozzi, I.; Cristofori, A.; Sudmeijer, O.; van Kessel, G. M. M. *Macromol. Chem. Phys.* **1996**, *197*, 2501 and references therein.

122.9, 122.7, 121.8, 120.6, 118.6, 110.9, 40.1 (=CH−); 34.2 (−CH$_2$−); 14.8 (−CH$_3$). Anal. Found: C, 77.36; H, 6.08; N, 5.10. Calcd ($C_{20}H_{21}NO_2$): C, 77.4; H, 6.13; N, 5.01.

2-Methyl-3-(1-(2-methylphenyl)-1*H*-indol-3-yl)propionic Acid (5b) (Method B). Fine crystals (from alcohol). Mp: 187−188 °C. Yield: 44.2 g (86%). ^{1}H NMR (δ, DMSO-d_6, 25 °C): 7.7 (m, 1H, CH arom), 7.4 (m, 4 H, CH arom), 7.2 (s, 1H, CH indole), 7.1 (m, 2H, CH arom), 6.9 (m, 1H, CH arom), 3.1 (m, 1H, CH), 2.8 (m, 2H, −CH$_2$−), 2.0 (s, 3H, −CH$_3$), 1.2 (d, J = 6.6 Hz, 3H, −CH$_3$). ^{13}C NMR (δ, DMSO-d_6, 35 °C): 177.3 (−COOH); 137.6, 136.6, 134.9, 127.5, 113.3 (>C<); 131.2, 128.1, 127.6, 127.1, 126.9, 121.9, 119.2, 118.8, 109.9, 39.7 (=CH); 28.5 (−CH$_2$−); 17.1 (−CH$_3$); 16.8 (−CH$_3$). Anal. Found: C, 77.45; H, 6.62; N, 5.03. Calcd ($C_{21}H_{23}NO_2$): C, 77.79; H, 6.53; N, 4.77.

General Procedure for the Synthesis of 2-Methyl-4-aryl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-ones. Phosphorus pentoxide (6 g, 0.042 mol) was dissolved in methanesulfonic acid (40 mL, 0.625 mol). To the hot solution was added dry 2-methyl-3-(1-aryl-1*H*-3-indolyl)propionic acid (0.036 mol) in one portion. The mixture was stirred for 10 min, and the hot reaction mass was then poured onto 200 g of crushed ice. The ketone was extracted with methylene chloride. The organic phase was washed with water, a solution of KHCO$_3$, and again with water and then dried over MgSO$_4$, and the solvent was removed.

2-Methyl-4-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-one (6a). Fine yellow crystalline substance (after recrystallization from a hexane/ethyl acetate (1/1) mixture). Mp: 110.5−111 °C. Yield: 6.6 g (71%). ^{1}H NMR (δ, C$_6$D$_6$, 25 °C): 7.8 (d, J = 11.6 Hz, 1H, arom), 7.8−7.3 (m, 8H, CH arom), 3.44 (dd, J_1 = 6.4 Hz, J_2 = 16.1 Hz, 1H, −CH$_2$-), 3.1(m, 1H, −CH-), 2.76 (dd, J_1 = 2.4 Hz, J_2 = 16.1 Hz, 1H, −CH$_2$−), 1.45 (d, J = 7.5 Hz, 3H, −CH$_3$). ^{13}C NMR (δ, C$_6$D$_6$, 25 °C): 194.6 (>C=O); 144.9; 144.5, 137.9; 136.9; 124.4 (>C<); 129.0; 127; 121.7; 121.2; 112.6, 47.3 (=CH−); 28.0 (−CH$_2$−); 17.1 (−CH$_3$). Anal. Found: C, 82.62; H, 5.58; N, 5.41. Calcd ($C_{18}H_{15}NO$): C, 82.73; H, 5.79; N, 5.36.

2-Methyl-4-(2-methylphenyl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-one (6b). The substance was purified by chromatography on a column with silica gel (with a benzene/ethyl acetate (4/1) mixture as eluent). Yellow-brown oil. Yield: 6.4 g (65%). ^{1}H NMR (δ, CDCl$_3$, 25 °C): 7.8 (d, J = 12.1 Hz, 1H, arom), 7.5−7.1 (m, 7H, CH arom), 3.52 and 3.48 (dd, J_1 = 6.8 Hz, J_2 = 16.8 Hz, 1H, −CH$_2$−), 3.1(m, 1H, −CH−), 2.84 and 2.8 (dd, J_1 = 2.2 Hz, J_2 = 16.8 Hz, 1H, −CH$_2$−), 2.13 and 2.11 (s, 3H, Ar−CH$_3$), 1.47 and 1.45 (d, J = 4.1 Hz, 3H, −CH$_3$). ^{13}C NMR (δ, C$_6$D$_6$, 25 °C): 196.07 and 197.02 (>C=O); 144.9, 144.28 and 144.22, 144.2, 138.3, 135.9 and 135.8, 123.05 (>C<); 130.9, 128.4, 127.9, 126.9, 126.5, 121.3, 120.6, 112.2, 47.1 and 47.0 (=CH−); 28.4 (−CH$_2$−); 17.3 (−CH$_3$); 17.15 and 17.07 (−CH$_3$). Anal. Found: C, 82.73; H, 6.49; N, 5.14. Calcd ($C_{19}H_{17}NO$): C, 82.88; H, 6.22; N, 5.09.

2,4-Dimethyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-one (6c). In a flask equipped with a reflux condenser and a dropping funnel, P$_2$O$_5$ (7.2 g, 0.05 mol) was dissolved with stirring in CH$_3$SO$_3$H (60 mL, 0.9 mol) heated to 120 °C. Then, a mixture of 1-methylindole (30 mL, 0.23 mol), methacrylic acid (23 mL, 0.26 mol), and methylene chloride (30 mL) was added dropwise to the hot solution. The reaction mixture was stirred for 2.5 h at 70 °C, cooled, and poured into 200 mL of water. The crude product was extracted with ether, and the organic phase was washed with a solution of KHCO$_3$ and dried over MgSO$_4$. After removal of the solvent the residue was purified by chromatography on a column with silica gel (with a benzene/ethyl acetate (4/1) mixture as eluent) to obtain 25.7 g of dark yellow oil. Yield: 51%. ^{1}H NMR (δ, CDCl$_3$, 25 °C): 7.7 (d, J = 12.1 Hz, 1H, CH arom) 7.4−7.2 (m, 3H, arom), 3.9 (s, 3H, −CH$_3$, indole), 3.4 (dd, J_1 = 8.1 Hz, J_2 = 17.5 Hz, 1H, −CH$_2$−), 3.1 (m, 1H, CH), 2.7 (dd, J_1 = 4.2 Hz, J_2 = 17.5 Hz, 1H, −CH$_2$−) 1.4 (d, J = 8.1 Hz, 3H, −CH$_3$). Anal. Found: C, 78.85; H, 7.25; N, 6.91. Calcd ($C_{13}H_{13}NO$): C, 78.36; H, 6.58; N, 7.03.

General Procedure for the Synthesis of 2-Methyl-4-aryl-1,2,3,4-tetrahydrocyclopenta[*b*]indoles. Lithium aluminum hydride (4.8 g, 0.13 mol) was suspended in 400 mL of ether under an argon atmosphere. The suspension was cooled to 0 °C, and a solution of 2-methyl-4-aryl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-one (0.18 mol) in ether (150 mL) was added slowly. The reaction mixture was stirred for an additional 2 h at room temperature and then decomposed using a solution of ammonium chloride. Aluminum hydroxide was filtered off, the organic phase was separated, washed with water, and dried over Na$_2$SO$_4$. After removal of the solvent the alcohols obtained could be used without further purification.

A corresponding alcohol (15 g) was dissolved in benzene (300 mL), TsOH (0.05 g) was added, and the mixture was refluxed with a Dean−Stark trap until the evolution of water ceased. The reaction mixture was cooled, and the organic layer was washed with a solution of NaHCO$_3$, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by chromatography on a column with silica gel (with a hexane/benzene (3/2) mixture as eluent).

2-Methyl-4-phenyl-1,4-dihydrocyclopenta[*b*]indole (7a). Yellow crystals. Mp: 121.5−122 °C. Yield (overall): 39.7 g (89%). ^{1}H NMR (δ, C$_6$D$_6$, 25 °C): 7.8 (d, J = 12.1 Hz, 1H, CH arom), 7.6 (d, J = 11.9 Hz, 1H, CH arom), 7.4 (m, 3H, CH arom), 7.2 (m, 3H, CH arom), 7.1 (m, 1H, CH arom), 6.3 (s, 1H, =CH), 3.1 (s, 2H, −CH$_2$−), 1.9 (s, 3H, −CH$_3$). ^{13}C NMR (δ, C$_6$D$_6$, 25 °C): 149.1, 148.9, 140.1, 139.3, 119.2, 118.3 (>C<); 129.6, 126.0, 124.9, 120.9, 120.5, 118.1, 111.5 (=CH−), 36.5 (−CH$_2$−), 17.3 (−CH$_3$). Anal. Found: C, 87.91; H, 6.26; N, 5.83. Calcd ($C_{18}H_{15}N$): C, 88.13; H, 6.16; N, 5.71.

2-Methyl-4-(2-methylphenyl)-1,4-dihydrocyclopenta[*b*]indole (7b). Viscous yellow oil. Yield (overall): 38.7 g (83%). ^{1}H NMR (δ, CDCl$_3$, 25 °C): 7.6 (d, J = 12.1 Hz, 1H, CH arom), 7.4 (m, 5H, CH arom), 7.2 (m, 1H, CH arom), 7.0 (m, 1H, CH arom), 6.2 (sext, J = 1.5 Hz, 1H, =CH-), 3.3 (s, 2H, −CH$_2$−), 2.3 (d, J = 1.6 Hz, 3H, −CH$_3$), 2.1 (s, 3H, −CH$_3$). ^{13}C NMR (δ, CDCl$_3$, 25 °C): 149.7, 149.4, 140.4, 137.2, 135.9, 124.5, 117.3 (>C<); 131.1, 128.1, 127.7, 126.6, 119.8, 119.4, 117.6, 117.3, 110.9 (=CH−); 36.6 (−CH$_2$−); 17.6 (−CH$_3$); 17.4 (−CH$_3$). Anal. Found: C, 87.73; H, 7.02; N, 5.25. Calcd ($C_{19}H_{17}N$): C, 87.99; H, 6.61; N, 5.40.

2,4-Dimethyl-1,4-dihydrocyclopenta[*b*]indole (7c). Colorless oil (after chromatographic purification with a hexane−methylene chloride (1:1) mixture as eluent), which undergoes transition into a glassy state on cooling. Yield (overall): 23.7 g (72%).^{1}H NMR (δ, C$_6$D$_6$, 25 °C): 7.8 (d, J = 10.1 Hz, 1H, CH arom), 7.2 (m, 3H, CH arom), 6.1 (s, 1H, CH), 3.1 (s, 3H, N−CH$_3$), 3.0 (s, 2H, −CH$_2$−), 2.0 (m, 3H, −CH$_3$). ^{13}C NMR (δ,C$_6$D$_6$, 25 °C): 149.8, 148.7, 140.9, 125.3, 110.0 (>C<); 119.8, 119.5, 117.9, 117.1, 109.9 (=CH−); 53.2 (−CH$_2$−); 30.2 (N−CH$_3$); 17.4 (−CH$_3$). Anal. Found: C, 85.30; H, 7.33; N, 7.37. Calcd ($C_{13}H_{13}N$): C, 85.21; H, 7.15; N, 7.64.

[*μ*-Dimethylsilanediylbis(*η*^{5}-2-methyl-4-phenylcyclopenta[*b*]indolyl)]zirconium(IV) Dichloride (10a). 2-Methyl-4-phenyl-1,4-dihydrocyclopenta[*b*]indole (**7a**; 3.6 g, 14 mmol) was dissolved in a mixture of toluene (40 mL) and THF (5 mL), and a solution of butyllithium in hexane (8.8 mL, 14 mmol, 1.6 M) was added on cooling. Then, (CH$_3$)$_2$SiCl$_2$ (0.9 mL, 7 mmol) was added to the solution of the lithium salt and the reaction mixture was stirred at room temperature.

The reaction was monitored by ^{1}H NMR spectroscopy. After 24 h the ^{1}H NMR spectrum (C$_6$D$_6$, 25 °C) of the reaction mixture showed the complete conversion of starting compound **7a**. Signals typical of a mixture of the rac and meso forms of bridged compound **9a** were observed at δ 6.48 and 6.45 (t, J = 1.4 Hz, 1H, =CH−), 4.50 (s, 1H, =CH−Si rac form), 4.04 (s, 1H, =CH−Si meso form), − 0.03 and −0.19 (s, 3H, Si−CH$_3$ meso form), and −0.26 (s, 3H, Si−CH$_3$ rac form). After completion of the reaction, the solution was decanted from the LiCl precipitate and concentrated, and the oily residue was dissolved in toluene (40 mL). After this solution was cooled to −40 °C, a solution of BuLi in hexane (10 mL, 1.6 M) was added and the mixture was stirred for 2 h at room temperature and cooled again; $ZrCl_4$ (1.6 g, 7 mmol) was added, and the mixture was stirred for an additional 5 h at 20 °C. Then the solvent was removed. Recrystallization from ether resulted in a mixture of rac and meso forms of compound **10a** as an orange crystalline substance (3.5 g, 76%). Fractional crystallization from an ether/hexane mixture gave the pure racemic form as yellow crystals (0.76 g, 17%) and the pure meso form as orange crystals (1.04 g, 23%). ^1H NMR (δ, CD_2Cl_2, 25 °C): rac form, 7.9 (d, $J = 6.1$ Hz, 2H, $=$CH$-$ arom), 7.7 (m, 4H, $=$CH$-$ arom), 7.5 (m, 10 H, $=$CH$-$ arom), 7.2 (m, 2H, $=$CH$-$ arom), 6.35 (s, 2H, $=$CH$-$), 2.1 (s, 6H, $-CH_3$), 1.45 (s, 6H, Si$-CH_3$); meso form, 8.1 (d, $J = 7$ Hz, 2H, $=$CH$-$ arom), 7.6 (m, 4H, $=$CH$-$ arom), 7.5 (m, 10 H, $=$CH$-$ arom), 7.0 (m, 2H, $=$CH$-$ arom), 6.25 (s, 2H, $=$CH$-$), 2.5 (s, 6H, $-CH_3$), 1.65 (s, 3H, Si$-CH_3$), 1.3 (s, 3H, Si$-CH_3$). Anal. Found for ***rac*-10a**: C, 64.41; H, 4.63; N, 4.11. Calcd ($C_{38}H_{32}Cl_2N_2SiZr$): C, 64.57; H, 4.56; N, 3.96.

[μ-Dimethylsilanediylbis(η^5-2-methyl-4-(2-methylphenyl)cyclopenta[*b*]indolyl)]zirconium(IV) Dichloride (10b). 2-Methyl-4-(2-methylphenyl)-1,4-dihydrocyclopenta[*b*]indole (**7b**; 2.6 g, 10 mmol) was dissolved in a mixture of toluene (50 mL) and THF (5 mL), and a solution of butyllithium in hexane (6.5 mL, 10.4 mmol, 1.6 M) was added on cooling. Then $(CH_3)_2SiCl_2$ (0.65 mL, 5.3 mmol) was added to the solution of the lithium salt and the mixture maintained at room temperature for 24 h. The solution was decanted and concentrated, the semisolid residue was dissolved in 40 mL of toluene, and the solution was cooled to −40 °C. A solution of BuLi in hexane (6.5 mL, 1.6 M) was added, the mixture was stirred for 2 h at room temperature and cooled again to −40 °C, $ZrCl_4$ (1.6 g, 7 mmol) was added, the mixture was stirred for an additional 24 h, and then the solvent was removed. Recrystallization from ether gave a mixture of rac and meso forms of compound **10b** as a dark orange crystalline substance (1.32 g, 33%). Repeated recrystallization from hexane−ether mixture allowed isolation of the pure rac form (0.21 g, 6%). ^1H NMR (δ, CD_2Cl_2, 25 °C): rac form, 7.95 (m, 4H, $=$CH$-$ arom), 7.3 (m, 6 H, $=$CH$-$ arom), 7.25 (m, 6H, $=$CH$-$ arom), 5.95 (s, 2H, $=$CH$-$), 2.1 (s, 6H, CH_3-), 1.9 (s, 6H, CH_3-), 1.45 (s, 6H, CH_3-Si); meso form, 8.1 (d, $J = 5.9$ Hz, 2H, $=$CH$-$ arom), 7.85 (d, $J = 6$ Hz, 2H, $=$CH$-$ arom), 7.35 (m, 6 H, $=$CH$-$ arom), 7.0 (m, 4H, $=$CH$-$ arom), 6.7 (d, $J = 7$ Hz, 2H, $=$CH$-$ arom), 6.0 (s, 2H, $=$CH$-$), 2.5 (s, 6H, CH_3-), 1.8 (s, 6H, $-CH_3-$), 1.65 (s, 3H, Si$-CH_3$), 1.4 (s, 3H, Si$-CH_3$). Anal. Found for ***rac*-10b**: C, 64.93; H, 5.06; N, 3.52. Calcd ($C_{40}H_{36}Cl_2N_2SiZr$): C, 65.37; H, 4.94; N, 3.81.

Lithium Salt of 2,4-Dimethyl-1,4-dihydrocyclopenta[*b*]indole (8c). 2,4-Dimethyl-1,4-dihydrocyclopenta[*b*]indole (**7c**; 7.1 g, 0.04 mol) was dissolved in 200 mL of dehydrated ether, and a solution of butyllithium in hexane (50 mL, 1.6 M) was added on cooling. The reaction mixture darkened and a thin light-coffee precipitate began forming after some time. The precipitate was decanted with ether (5 × 150 mL) and dried in vacuo to give the desired product as a beige powder (5.5 g, 71%). ^1H NMR (δ, THF-d_8, 25 °C): 7.2 (d, $J = 11.9$ Hz, 1H, Ar H), 6.9 (d, $J = 11.9$ Hz, 1H, Ar H), 6.7 (m, 2H, Ar H), 5.5 and 5.1 (both s, 1H each, Cp H), 3.4 (s, 3H, N$-CH_3$), 2.3 (s, 3H, $-CH_3$). ^{13}C NMR (δ, THF-d_8, 25 °C): 144.1, 139.2, 125.8, 117.3, 106.9 ($>$C$<$); 118.1, 116.7, 116.5, 109.3, 87.8, 78.2 ($=$CH$-$); 31.3 (N$-CH_3$); 17.3 ($-CH_3$).

[μ-Dimethylsilanediylbis(η^5-2,4-dimethylcyclopenta[*b*]indolyl)]zirconium(IV) Dichloride (10c). Lithium salt **8c** (3.75 g, 20 mmol) was dissolved in a mixture of toluene (50 mL) and THF (5 mL), and $(CH_3)_2SiCl_2$ (1.2 mL, 10 mmol) was added on cooling to −40 °C. The solution was decanted and concentrated, and the viscous residue was dissolved in 30 mL of ether. The ethereal solution was cooled again, and a solution of butyllithium in hexane (9.5 mL, 2.11 M) was added. After 30 min, $ZrCl_4$ (2.2 g, 10 mmol) was added. The mixture was stirred for 5 h at room temperature, and the solution was decanted and concentrated. The product was isolated as a yellow-brown crystalline substance (the pure rac form). Yield: 1.72 g (32%). ^1H NMR (δ, CD_2Cl_2, 25 °C): 7.6 (d, $J = 8.8$ Hz, 2 H, $=$CH$-$ arom), 7.2 (m, 6H, $=$CH$-$ arom), 6.05 (s, 2H, $=$CH$-$), 3.7 (s, 6H, N$-CH_3$), 2.1 (s, 6H, $-$ CH_3), 1.4 (s, 6H, Si$-CH_3$). Anal. Found: C, 57.48; H, 5.01; N, 4.55. Calcd ($C_{28}H_{28}Cl_2N_2SiZr$): C, 57.71; H, 4.84; N, 4.81.

Table 6. Crystal Data and Structure Refinement for 10a

empirical formula	$C_{38}H_{32}Cl_2N_2SiZr$
fw	706.87
temp	93(2) K
wavelength	0.710 69 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a	9.295(2) Å
b	12.914(3) Å
c	15.619(3) Å
α	111.88(3)°
β	81.03(3)°
γ	117.77(3)°
V	539.0(6) Å^3
Z	1
density (calcd)	1.525 g/cm^3
abs coeff	602 mm^{-1}
$F(000)$	724
cryst size	0.4 × 0.3 × 0.2 mm
θ range for data collection	1.41−29.60°
index ranges	$-11 \le h \le 11$, $-16 \le k \le 15$, $0 \le l \le 12$
no. of rflns collected	5252
no. of indep rflns	5242 (R(int) = 0.0128)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	5242/0/526
goodness of fit on F^2	0.879
final R indices ($I > 2\sigma(I)$)	R1 = 0.0364, wR2 = 0.0961
R indices (all data)	R1 = 0.0438, wR2 = 0.0991
extinction coeff	0.0069(9)
largest diff peak and hole	0.487 and −0.487 e/Å^{-3}

Crystal Structure Determination of 10a. Heavy-atom positions were determined by a Patterson map using the AREN-88 program,[36] and the remaining hydrogen atoms were located from successive difference Fourier map calculations. Refinements were carried out with the SHELXL-93 program[37] by using full-matrix least-squares techniques minimizing the function $\sum w(||F_o| - |F_c||)$.[2] Crystal data and structure determination details are given in Table 6.

LIPP Test Procedures. Polymerizations were carried out in a 5 L batch reactor provided with a turbine stirrer. A steam/water system was used for temperature control. Exotherms were monitored by determining the temperature difference between the reactor contents and the incoming cooling water (thermocouple). A specially designed injection system, which can withstand the high pressures in the reactor, was applied to introduce the catalyst components into the reactor.

Procedures for aluminoxane preparation, metallocene prealkylation, polymerization in LIPP, and workup of the polymer products are outlined below. Gas-cap composition during propylene polymerization was analyzed by means of a GC apparatus from Interscience (propane/propylene ratio for yield versus time measurements) and an Orbisphere hydrogen analyzer.

The autoclave was heated to 150−160 °C overnight, while being purged with nitrogen, cooled, and then pickled at 70 °C

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(36) Adrianov, V. I. *Kristallografiya* **1987**, *32*, 228.

(37) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1993.

using a mixture of TIBA (0.25 g), toluene (20 mL), and propylene (500 g). The pickle mixture was removed, the temperature reduced to 20 °C, and the reactor then charged with 1650 g of liquid propylene, while the temperature was increased from 20 to 30 °C. Then 4−5 vol % hydrogen was added to the gas cap, aiming at 1−1.5 vol % hydrogen in the gas cap at 70 °C.

Typical Long Cold Start Procedure at High Al/Zr Ratio. (a) AKO Cocatalyst (Experiment 9). A 1.73 g amount of tris(2-phenylpropyl)aluminum, $Al(CH_2CHMePh)_3$ (4.5 mmol), was dissolved in 20 mL of toluene in a bottle with a septum cap. The solution was cooled to 0−4 °C using an ice bath, and 41 μL of water (2.28 mmol) was added in two shots using a 100 μL syringe, while the temperature was maintained below 15 °C. The resulting solution was injected into the reactor using 20 mL of toluene. Meanwhile, 6.6 mg of **10a** (9 μmol) was dissolved in 14.5 g of toluene, and 0.743 g of the obtained solution containing 0.48 μmol of Zr was reacted with 0.11 g of TIOA (0.3 mmol), resulting in a color change from yellow to light yellow. Ten minutes after the introduction of the hydrolyzed alkylaluminum mixture containing 4.5 mmol of aluminoxane into the reactor, the alkylated zirconocene (aged for 5 min) was injected into the reactor at 30 °C using 20 mL of toluene. After 10 min the temperature was raised over 6−7 min to 70 °C and polymerization was continued (43 min from *initiation of warming*), using 840−1100 rpm stirring, keeping the hydrogen concentration at 1 vol % in the gas cap. The polymerization was stopped by injection of 5−10 mL of methanol. The heating was then discontinued, the propylene was rapidly vented, and the powdered polypropylene was collected. The polypropylene fractions were dried (70−80 °C, 200 mbar, nitrogen purge) and combined to give the total yield of polypropylene.

(b) MAO Cocatalyst (Experiment 1). A 2.44 g amount of a toluene solution of MAO (4.98 w % Al, 4.5 mmol) was injected into the reactor using 20 mL of toluene. Meanwhile, 6.6 mg of **10a** (9 μmol) was dissolved in 14.5 g of toluene, and 2.228 g of the obtained solution containing 1.44 μmol of Zr was reacted with 0.405 g of MAO solution (0.75 mmol), resulting in a color change from yellow to red. Ten minutes after the introduction of the MAO solution, the alkylated zirconocene (aged for 5 min) was injected into the reactor (20 mL of toluene) at 30 °C. The remaining procedure is identical with that described above. The polymerization time (as measured from *initiation of warming*) was 49 min.

Polymerization at Low Al/Zr Ratio (Experiment 13). A solution of 0.20 g of TIBA (1 mmol) in toluene was introduced into the reactor with ca. 25 mL of toluene. Separately, a solution of $Al(CH_2CHMePh)_3$ (AK) in 20 mL of toluene was hydrolyzed using $^1/_2$ equiv of water. Meanwhile, 1.935 g of a toluene solution of **10b** (1.0 μmol) was reacted with 0.038 g of TIOA (0.10 mmol). After 5 min, 2.5 g of a solution of the alkylaluminoxane containing 0.5 mmol of aluminoxane was added to the alkylated zirconocene solution. Twenty minutes after the introduction of the TIBA into the reactor, the activated heterocene (aged for 5 min) was injected into the reactor (at 30 °C) using 20 mL of toluene. The remaining procedure is identical with that described above. The polymerization time (as measured from *initiation of warming*) was 60 min.

When MAO was used as cocatalyst at low Al/Zr levels, the above procedure was followed, but the metallocene dichloride was simply mixed with MAO (500 equivalents) and, after 5 min, injected into the autoclave.

Short Cold Start and Hot Start Procedures. In short cold start experiments, the above procedures were followed, but the temperature of the autoclave (under 4−5 vol % H_2) was raised immediately from 30 °C (to 70 °C) after injection of the catalyst solution. In the hot start procedure the catalyst was injected into the autoclave at 70 °C (for experiments with hydrogen, under 1.0 vol % H_2). Fouled material, if present, was removed using hot xylene and precipitated with methanol.

Polymer Analysis Procedures. GPC Analysis. High-temperature GPC analyses were carried out by Rapra Technology Ltd. A single solution of each sample was prepared by adding 15 mL of solvent to a weighed quantity of sample and refluxing gently for 20 min. The solutions were then filtered through a fiber pad at 140 °C, and part of each filtered solution was transferred into special glass sample vials. The vials were then placed in a heated sample compartment, and after an initial delay of 20 min to allow the samples to equilibrate thermally, injection of part of the contents of each vial was carried out automatically in series. The following chromatographic conditions were used: column, PLgel 2 x mixed bed-B, 30 cm, 10 μm; solvent, 1,2-dichlorobenzene with antioxidant; flow rate, 1.0 mL/min; temperature, 140 °C; detector, refractive index; calibration, polystyrene.

DSC Characterization. DSC analysis of the copolymers was performed on a Perkin-Elmer DSC-4. The following temperature program was used: (1) temperature 1 25 °C, time 1 1.0 min, rate 1 10.0 °C/min; (2) temperature 2 160 °C, time 2 0.1 min, rate 2 20.0 °C/min; (3) temperature 3 25 °C, time 3 1.0 min, rate 3 10.0 °C/min; (4) temperature 4 160 °C, time 4 0.1 min, rate 4 20.0 °C/min. (5) temperature 5 25 °C.

Xylene Solubles. The fraction of xylene solubles at 25 °C was determined using ca. 2 g of polymer sample and 100 mL of xylene or ca. 2.5 g in 250 mL of xylene.

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Supporting Information Available: For **10a**, tables of bond lengths and angles, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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