Synthesis and Application of Ring-Substituted Analogues of the [4-(η-Cyclopentadienylidene)-4,7,7-trimethyl-4,5,6,7-tetrahydro-η^5-indenyl]-$ZrCl_2$ Ansa-Metallocene System

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Reaction of the 2,5-hexanedione-derived bisfulvene **1** with R–Li reagents (R = phenyl or *n*-butyl) yields the ring-closed [4-(cyclopentadienylidene)-7-R-4,7-dimethyl-4,5,6,7-tetrahydroindenyl]dilithium reagents **3**. Their reaction with MCl_4 (M = Ti, Zr, Hf) gives the corresponding ansa-group-4-metallocene dichloride complexes **4**, **6**, or **7**. In a similar way the [7-allyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl]metal dihalides (M = Ti, Zr) (**6d**, **4d**) are prepared. Two diastereomers are formed in most cases, some of which could be separated. The five representative examples *cis*- and *trans*-**4c**, *trans*-**4d**, *cis*-**6c**, and *trans*-**7c** of these complexes were characterized by X-ray diffraction. All these six-membered ring-annulated C_1-bridged ansa-metallocene dichlorides exhibit extremely small D1–Zr–D2 angles (D1 and D2 denote the centroids of the cyclopentadienyl rings) of 116.5°, i.e., they are characterized by a very open bite of the bent metallocene wedge. The homogeneous Ziegler-type catalysts derived from these ansa-zirconocenes by activation with methylalumoxane have high activities and all produce low-molecular mass atactic polypropylenes or propene oligomers.

The group-4 ansa-metallocene/methylalumoxane-derived homogeneous Ziegler-type catalyst systems are of importance for the selective production of high-molecular mass α-olefin polymers[1]. Much emphasis has been given to increase the catalyst activities and selectivities as well as the molecular mass of the polymers formed by fine-tuning the metallocene properties using specific substitution patterns[2]. Other important applications of the zirconocene/MAO-type catalyst systems can be envisaged such as their use for selective olefin coupling reactions in the organic synthesis of monomeric target molecules. In that case the overall catalyst characteristics must be changed from a high-molecular mass polyolefin-producing system ($k_{\text{termination}}/k_{\text{propagation}} \ll 1$) to a system favouring low-molecular mass α-olefin oligomer formation with a typical $k_{\text{termination}}/k_{\text{propagation}}$ rate approaching unity[3]. We have recently described the formation of the title system[4] that produces low-molecular mass polyolefins when activated with MAO[5]. The [4-(η-cyclopentadienylidene)-4,7,7-trimethyl-4,5,6,7-tetrahydro-η^5-indenyl]$Zr(CH_3)_2$/MAO catalyst gives rise to the formation of polypropylene with an averaged molecular mass of $\overline{M}_\eta \approx 1600$ at −20°C (activity a = 240 g polymer/g[Zr] · h). The polymer is close to atactic (chain-end control[6], $\sigma \approx 0.3$). This specific ansa-metallocene framework is extremely rigid, and it exhibits a very large bent metallocene bite angle: the angle between the Cp planes in the metallocene dichloride **4a** is 71.4°, in the corresponding dimethylzirconocene complex **5** it is 72.1°. The even more characteristic respective D1–Zr–D2 angles (D1 and D2 denote the Cp centroids) are 116.3° for **4a** and 115.8° for **5**[5]. To our knowledge these are the smallest D–Zr–D angles observed so far in zirconocene complexes[7]. In view of the pronounced valence orbital energy dependence of bent metallocenes[8] from the very D–M–D angle it has been suspected that the relatively high $k_{\text{termination}}/k_{\text{propagation}}$ rate observed at these systems might reflect a dominating electronic control of the catalyst action[4]. In this paper we report on a more detailed study concerning the formation and properties of these very rigid ansa-metallocene complexes and describe the synthesis and characterization of a variety of different ring-substituted derivatives of **4**.

Results and Discussion

Synthesis of the Metallocene Complexes

Our novel synthesis involves nucleophilic attack at a bisfulvene system, as previously reported[4,5]. Methyllithium was added to the fulvene **1**[9,10]. The resulting substituted cyclopentadienide then underwent an intramolecular nucleophilic attack at the adjacent remaining fulvene functionality to give the ring-closed product[11]. Subsequent deprotonation by a second equivalent of methyllithium furnished the dianionic ligand system **3**. Treatment with $ZrCl_4$ gave the six-membered ring-annulated ansa-metallocene dichloride **4a** in low but reproducible yield (ca. 20%). The chloride ligands can be exchanged for methyl groups by using methyllithium to give **5**.

The 7-substituted analogues of **4** described in this study were also prepared starting from the bisfulvene **1**. Phenyllithium (two molar equivalents) was added to **1** in ethereal

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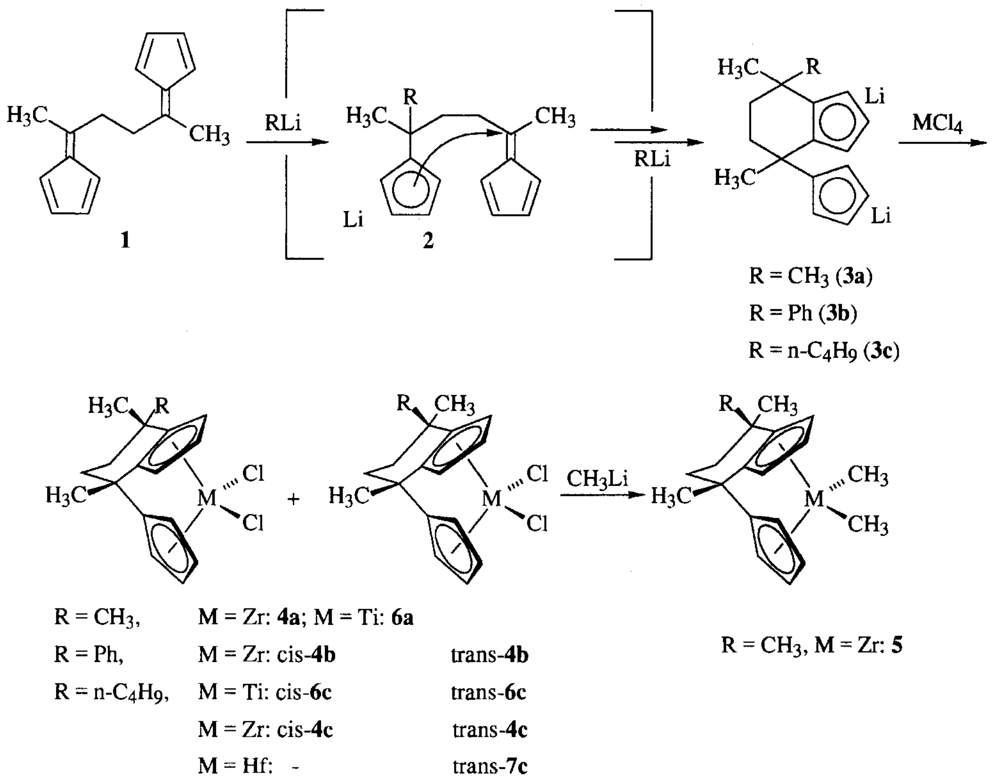
Scheme 1



R = CH_3 (**3a**)
R = Ph (**3b**)
R = n-C_4H_9 (**3c**)

R = CH_3, M = Zr: **4a**; M = Ti: **6a**
R = Ph, M = Zr: cis-**4b** trans-**4b**
R = n-C_4H_9, M = Ti: cis-**6c** trans-**6c**
M = Zr: cis-**4c** trans-**4c**
M = Hf: - trans-**7c**

R = CH_3, M = Zr: **5**

solution to yield the ligand system **3b**. Introduction of the phenyl substituent creates a chiral center at carbon atom C7 in addition to that at C4. Therefore, two diastereomers should be formed, characterized by a *cis* or *trans* arrangement of the single substituents with highest CIP priority (here phenyl and cyclopentadienyl, respectively) at the central six-membered ring. Attachment of the bridged biscyclopentadienyl ligand system at zirconium introduces an additional planar chirality element, so in principle three diastereomeric compounds may result, of which, however, only two are possible in a mononuclear metal complex on geometric reasons. The diastereomeric ansa-zirconocene complexes *cis*-**4b** and *trans*-**4b** are both formed. However, their relative stereochemical assignment was not possible in this case. The diastereomers were produced in a 6:1 ratio. Due to the low overall yield (15%) the intrinsic diastereoselectivity of this reaction is not known. It is conceivable that the observed diastereoselectivity is predominately governed by the different physical properties of the isomers and determined during the workup and isolation process.

Addition of *n*-butyllithium to the bisfulvene **1** produces the ligand system **3c** (as an uncharacterized mixture of diastereomers). Its reaction with titanium tetrachloride gives the ansa-titanocene dichlorides *cis*-**6c** and *trans*-**6c** in 24% yield. In the crude product the diastereoisomers are present in a 8:1 mixture. Single crystals were obtained of the major component and identified as *cis*-**6c** by an X-ray diffraction study (see below). The spectroscopic features of the *cis*- and *trans*-**6c** ansa-titanocene dichloride isomers are very similar. The composition of the mixture of the diastereomers can be determined by their different ^1H-NMR 4-CH_3 resonances with the 4-*trans*-CH_3 signal (i.e. of complex *cis*-**6c**) appearing at $\delta = 1.21$ (in $CDCl_3$ solution), whereas the 4-*cis*-CH_3 resonance of the *trans*-**6c** isomer is observed at $\delta = 1.91$.

Treatment of **3c** with $ZrCl_4$ gave the crude ansa-zirconocene dichloride complex in 30% yield. Purification was achieved by continuous extraction with pentane to give a 1:15 mixture of the *cis*-**4c** and *trans*-**4c** diastereomers in 14% yield. From the pentane mother liquor a few crystals of the minor isomers *cis*-**4c** were obtained. Recrystallization of the extracted material furnished single crystals of the major *trans*-**4c** isomer. Both isomers were characterized by X-ray diffraction (see below) and spectroscopically. Here the 7-CH_3 ^1H-NMR resonance of the *cis*-**4c** isomer occurs at the lower δ value ($\delta = 1.07$) as compared to *trans*-**4c** ($\delta = 1.25$).

The analogous reaction of **3c** with hafnium tetrachloride gave a single ansa-metallocene diastereomer. Its 7-CH_3 ^1H-NMR resonance is located at $\delta = 1.27$. The *trans*-**7c** structure of this compound was confirmed by an X-ray crystal structure analysis.

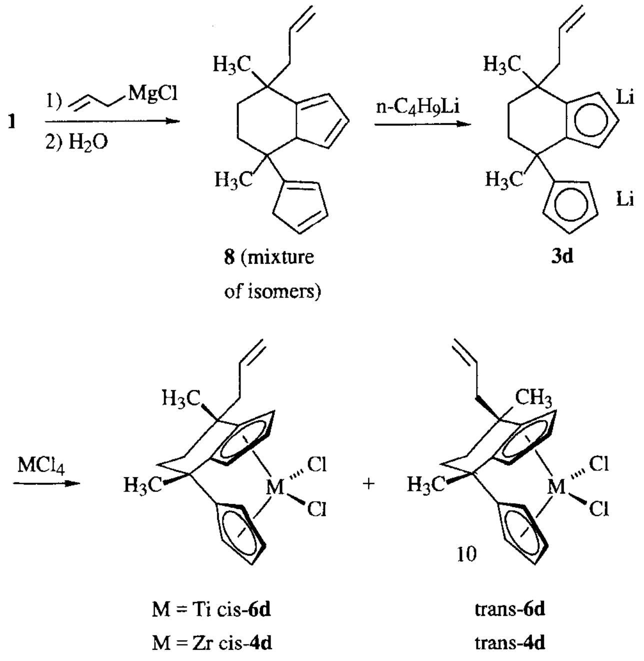
We have also attached a functional group at the C7 center of the metallocene ligand framework, following a slightly different synthetic protocol. One molar equivalent of allylmagnesium chloride was added to the bisfulvene **1**. Then the reaction mixture was quenched and the resulting mixture of the annulated biscyclopentadiene isomers **8** doubly deprotonated with *n*-butyllithium in ether to give the 7-allyl-substituted ligand system **3d** (as a non-characterized *cis*/

Table 1. ^{1}H-NMR 7-CH$_3$ and 4-CH$_3$ resonances of the ansa-metallocene dichlorides **4**–**7**[a]

R	M	compound	7-CH$_3$	10-CH$_3$	X-ray[b]
Ph	Zr	**4b**[c]	1.76[d]	1.71[d]	-
n-C$_4$H$_9$	Ti	*cis*-**6c**	1.21	1.86	+
		trans-**6c**	1.19	1.86	-
n-C$_4$H$_9$	Zr	*cis*-**4c**	1.07	1.82	+
		trans-**4c**	1.25	1.83	+
n-C$_4$H$_9$	Hf	*trans*-**7c**	1.27	1.90	+
allyl	Ti	*cis*-**6d**	1.24	1.85	-
		trans-**6d**	1.10	1.85	-
allyl	Zr	*cis*-**4d**	1.09	1.83	-
		trans-**4d**	1.27	1.83	+

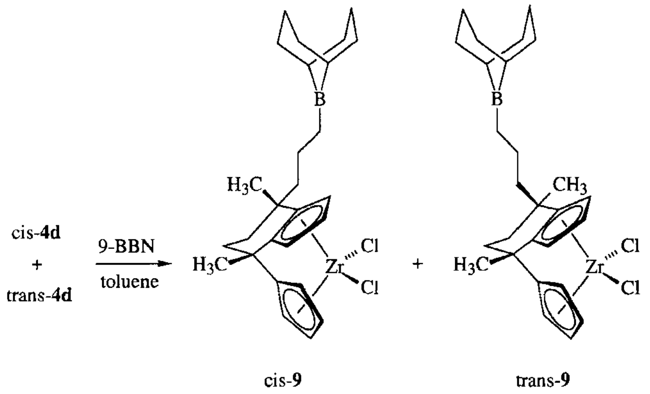
[a] ^{1}H-NMR chemical shifts rel. TMS, δ scale. – [b] +: Structural assignment confirmed by X-ray. – [c] Major component of a 6:1 mixture. – [d] Relative assignment unclear.

trans-isomeric mixture). Subsequent reaction of **3d** with titanium tetrachloride gave the *cis*-**6d**/*trans*-**6d** mixture in a 2:1 ratio which was isolated in a combined yield of 9%. The major isomer is probably *cis*-**6d** (analogously as found for the 7-*n*-butyl-substituted ansa-titanocene dichloride system **6c**). Consequently it exhibits the 7-CH$_3$ ^{1}H NMR resonance at a higher δ-value than its *trans*-**6d** isomer (see Table 1). Unfortunately, the *cis*-**6d**/*trans*-**6d** isomers could not be separated, nor were we able to obtain single crystals from any of these two 7-allyl-substituted ansa-titanocenes to confirm this tentative stereochemical assignment.



The reaction of **3d** with ZrCl$_4$ in toluene gave the corresponding 7-allyl-substituted ansa-zirconocene dichloride as a crude product in 55% yield. Purification by means of continuous extraction with pentane furnished a 1.5:1 mixture of the diastereoisomers *cis*-**4d** and *trans*-**4d** in a combined yield of 26%. The *cis*-**4d** diastereomer is characterized by a high-field ^{1}H-NMR 7-*trans*-CH$_3$ resonance at δ = 1.09, whereas *trans*-**4d** shows the 7-*cis*-CH$_3$ signal at a larger δ value (see Table 1). The minor isomer (*trans*-**4d**) was obtained crystalline by slow pentane diffusion into a dichloromethane solution of the diastereomeric mixture. So this stereochemical assignment was confirmed by an X-ray crystal structure analysis (see below).

The alkene functional group attached at C7 of the zirconium complexes was used in a hydroboration reaction. Addition of 9-BBN to a mixture of the *cis*-**4d**/*trans*-**4d** diastereoisomers[12] yielded a 1:1 mixture of the respective ring-annulated ansa-zirconocene dichlorides with a pending alkylborane substituents as a ca. 1:1 mixture of two isomers (*cis*- and *trans*-**9**).



X-Ray Crystal Structure Determinations

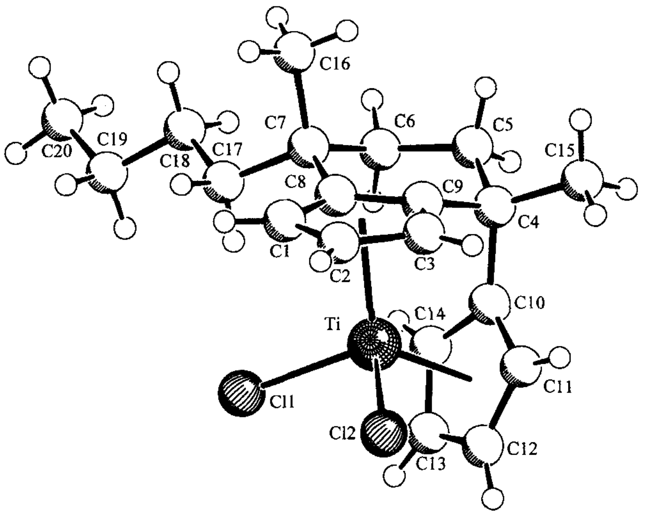
In this study five of the newly prepared complexes were characterized by X-ray diffraction. Among these are the *n*-butyl-substituted titanium complex *cis*-**6c** and the *n*-butyl-substituted hafnium compound *trans*-**7c**. The X-ray crystal structure analyses of three zirconium complexes were carried out, namely of the allyl-substituted ansa-zirconocene dichloride *trans*-**4d** and of the diastereomeric pair of the *n*-butyl-substituted zirconocene complexes *cis*- and *trans*-**4c**.

We had previously shown that the titanium atom fits very nicely into the rigid six-membered ring annulated and C$_1$-bridged ansa-ligand framework **3**[4]. Therefore, there is not too much geometric distortion observed on going from the nonbridged parent metallocene Cp$_2$TiCl$_2$ to **6a** or *cis*-**6c** (see Scheme 1). In Cp$_2$TiCl$_2$ the angle between the Cp planes is 49.1°; in **6a** it is increased by 18°, and in *cis*-**6c** it is only slightly smaller with 65.9°[13]. However, this bending back of the Cp-ring systems (i.e. opening up the bent metallocene "bite angle") is at least partially compensated by adjustment of the positional parameters of the transition metal center inside the bent metallocene wedge. This compensatory geometric effect is reflected by the observed rather small variation of the D1–Ti–D2 angle (D1 and D2 denote the centroids of the cyclopentadienyl rings) ranging from 124° (Cp_2TiCl_2) to almost identical values of 120.9° in **6a** and 121.3 in *cis*-**6c**.

Table 2. Selected bond lengths and angles of complexes **4**, **6**, and **7**

Compound (7-R/M)	cis-**6c** (n-Bu/Ti)	cis-**4c** (n-Bu/Zr)	trans-**4c** (n-Bu/Zr)	trans-**7c** (n-Bu/Hf)	trans-**4d** (allyl/Zr)
M-C1	2.459(3)	2.564(4)	2.583(2)	2.569(4)	2.574(3)
M-C2	2.391(3)	2.523(4)	2.523(2)	2.497(5)	2.518(3)
M-C3	2.296(3)	2.422(4)	2.423(2)	2.408(4)	2.417(3)
M-C8	2.419(3)	2.530(4)	2.557(2)	2.544(4)	2.542(3)
M-C9	2.325(3)	2.431(4)	2.447(2)	2.437(4)	2.438(3)
M-C10	2.328(3)	2.448(4)	2.431(2)	2.419(5)	2.432(3)
M-C11	2.345(4)	2.461(4)	2.457(2)	2.440(5)	2.458(4)
M-C12	2.436(4)	2.550(4)	2.573(2)	2.544(5)	2.551(4)
M-C13	2.428(4)	2.545(4)	2.573(2)	2.553(5)	2.553(4)
M-C14	2.332(3)	2.468(4)	2.476(2)	2.462(5)	2.463(3)
C7-C8-C9	122.5(3)	123.3(3)	122.2(2)	122.3(4)	122.7(3)
C8-C9-C4	121.2(3)	121.4(3)	122.4(2)	122.3(4)	122.2(3)
C9-C4-C5	109.2(3)	108.8(3)	109.6(2)	109.8(4)	108.9(3)
C4-C5-C6	116.8(3)	117.5(3)	117.6(2)	117.4(4)	117.3(3)
C5-C6-C7	117.0(3)	116.6(3)	115.3(2)	114.9(4)	116.3(3)
C6-C7-C8	111.0(3)	110.3(3)	108.8(2)	108.9(4)	109.0(3)
M-Cl1	2.327(1)	2.420(1)	2.430(1)	2.401(1)	2.430(1)
M-Cl2	2.347(1)	2.432(1)	2.429(1)	2.402(1)	2.439(1)

Figure 1. Projection of the molecular structure of the titanocene complex *cis*-**6c**



The much larger zirconium atom does not fit nearly as well into the bent metallocene wedge of this ligand system. Therefore, quite large distortions are observed for the zirconium (and hafnium) complexes. Ordinary unbridged zirconocene complexes typically exhibit D1–Zr–D2 angles of around 130°[8], many ansa-zirconocenes show only slightly decreased D1–Zr–D2 angles (with a few notable exceptions)[7]. The D1–Zr–D2 angles of the [7-alkyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl]zirconocene dichloride complexes looked at here and in a related study[5] are the smallest observed so far in a zirconium bent metallocene series. In complex **4a** the D1–Zr–D2 angle is 116.3°. In the zirconium complexes prepared in this study uniformly angles of ca. 116.5° are found (and 117.0° for the hafnium complex *trans*-**7c**).

The bonding parameters of all these complexes are very similar, even among the pair of *cis*-**4c**/*trans*-**4c** diastereoisomers (see Table 3). There is hardly a notable variation of the metallocene bite angle in this series. The parent hafnium dichloride complex **7a** in ref.[5] exhibits an angle of 69.8° between the Cp planes. Introduction of an *n*-butyl substituent at C7 has caused only a marginal increase of the metallocene bite angle.

Table 3. Comparison of characteristic structural parameters of related [7-alkyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl] group-4 metal dichloride complexes

Compound (7-R/M)	**6a**[a] (CH_3/Ti)	cis-**6c** (n-Bu/Ti)	**4a**[a] (CH_3/Zr)	cis-**4c** (n-Bu/Zr)	trans-**4c** (n-Bu/Zr)	trans-**4d** (allyl/Zr)	**7a**[a] (CH_3/Hf)	trans-**7c** (n-Bu/Hf)
(D1-M-D2)[b]	120.9	121.3	116.3	116.5	116.6	116.5	117.1	117.0
(C9-C4-C10)	97.1(2)	97.3(3)	99.9(2)	99.6(3)	100.2(1)	99.9(3)	100.5(5)	100.5(3)
(Cp^A-Cp^B)[c]	67.3	65.9	71.4	70.6	71.8	71.2	69.8	70.8
(Cl1-M-Cl2)	95.3(1)	97.79(4)	98.3(1)	100.01(5)	100.00(3)	98.44(4)	96.79(7)	98.78(6)
(C2-C1-C8-C7)	-167.0	-165.0(3)	166.6	164.4(4)	-166.2(2)	166.6(3)	167.0(7)	-166.3(4)
(C3-C9-C8-C7)	169.3	166.8(3)	-168.4	-166.1(4)	167.6(2)	-168.3(3)	-168.5(6)	167.3(4)
(C2-C3-C9-C4)	-161.4	-160.5(3)	162.1	162.3(4)	-159.9(2)	161.2(3)	160.7(7)	-159.0(4)
(C1-C8-C9-C4)	162.1	161.8(3)	-162.5	-162.8(3)	160.1(2)	-161.4(3)	-161.4(6)	159.8(4)
(C13-C14-C10-C4)	162.3	-159.8(3)	161.4	160.4(4)	-161.7(2)	161.5(3)	-160.8(7)	-161.0(5)
(C12-C11-C10-C4)	-160.0	161.0(3)	-160.7	-162.0(4)	163.0(2)	-162.6(3)	158.8(7)	162.1(4)

[a] From ref.[4,5]. – [b] D1 and D2 denote the centroids of the cyclopentadienyl ring systems. – [c] Angle between the cyclopentadienyl planes.

In the parent zirconium dichloride complex **4a** the angle between the cyclopentadienyl planes is 71.4° whereas in *cis*-**4c** it is 70.6°. In the diastereomeric complex *trans*-**4c** this angle is 71.8° which seems to be a typical value of the 7-substituted *trans* series (an angle of 71.2° between the cyclopentadienyl planes is observed in *trans*-**4d**).

So it appears that the introduction of alkyl substituents which are more bulky then CH_3 at C7 has only a marginal

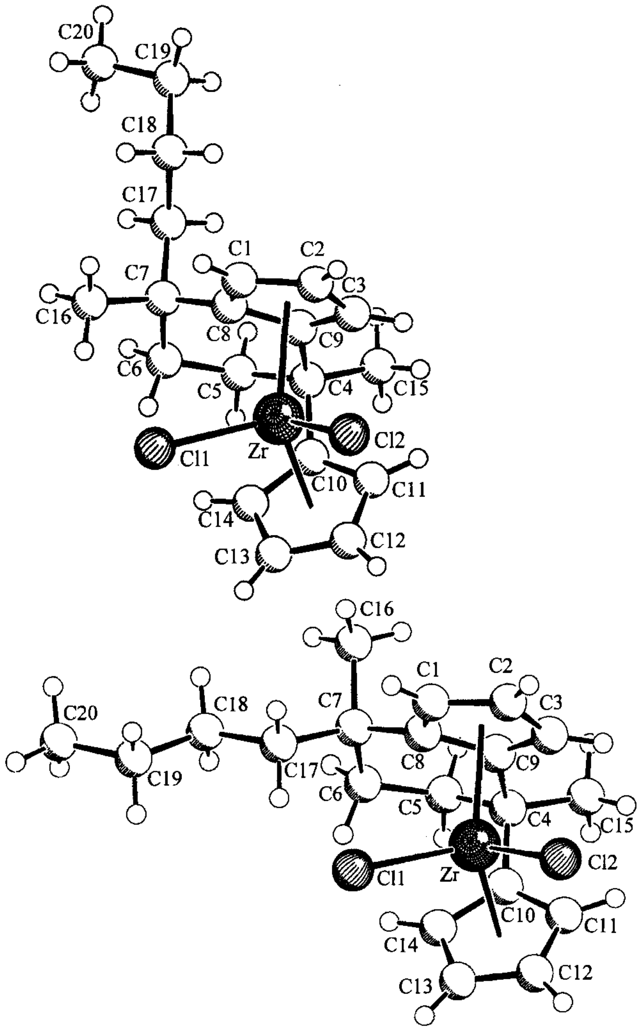


Figure 2. Views of the molecular structures of the diastereomeric ansa-zirconocene dichloride complexes *cis*-**4c** (above) and *trans*-**4c** (below)

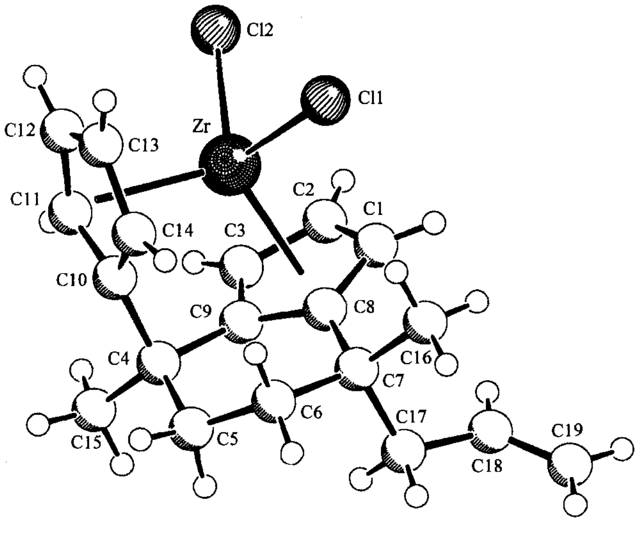


Figure 3. Molecular structure of *trans*-**4d**

conformational influence on the anulated cyclohexane-type half chair. Also, the substituents at C7 have almost no influence on the D1−M−D2 angle in these complexes.

Table 4. Details of the X-ray crystal structure analyses. Programs used: SHELXS-86, SHELXL-93, SCHAKAL-92. – Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers, CSD-401370 (**6c**), -401372 (*cis*-**4c**), -401369 (*trans*-**4c**), -401371 (**7c**), -401368 (**4d**), the names of the authors, and the journal citation

Compound (7-R/M)	cis-**6c** (n-Bu/Ti)	cis-**4c** (n-Bu/Zr)	trans-**4c** (n-Bu/Zr)	trans-**7c** (n-Bu/Hf)	trans-**4d** (allyl/Zr)
a(Å)	8.1489(6)	8.176(1)	10.1352(7)	10.1133(5)	9.774(2)
b(Å)	10.1531(8)	10.418(1)	10.1454(7)	10.1321(9)	10.089(2)
c(Å)	11.9383(9)	11.921(2)	10.4153(8)	10.3933(8)	17.983(4)
(°)	100.957(6)	100.12(1)	64.073(6)	89.252(7)	
(°)	106.460(6)	106.26(1)	89.204(6)	64.056(5)	92.27(3)
(°)	92.868(6)	94.21(1)	77.661(6)	77.764(5)	
volume(Å^3)	924.3(1)	951.5(2)	937.1(1)	932.1(1)	1771.9(6)
spacegroup	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P2$_1$/n (No.14)
R (I≥2 σ(I))	0.043	0.038	0.024	0.030	0.029
wR^2 (I≥2 σ(I))	0.086	0.082	0.061	0.081	0.077
reflections	3750	3849	3804	3779	2400
parameters	211	211	211	211	201

Propene Polymerization Reactions

It was known that only the [4,7,7-trialkyl-4-(η-cyclopentadienylidene)-4,5,6,7-tetrahydro-η^5-indenyl]zirconium-derived catalysts produce low-molecular mass propene polymers with a high catalyst activity[4,5]. Therefore, we have generated active homogeneous ansa-metallocene/methylalumoxane catalysts from the ansa-zirconocene dichlorides **4b** (7-R = phenyl, 6:1 mixture of the diastereomers), *trans*-**4c** (7-R = *n*-butyl), **4d** (7-R = allyl, 1:1 diastereomeric mixture), and **9** (7-R = [CH$_2$]$_3$-9BBN, 1:1 mixture of the diastereomers). For the purpose of comparison we have also carried out a propene polymerization reaction at the parent catalyst system obtained by activating 4,7,7-trimethyl-containing ansa-zirconocene dimethyl complex **5** with MAO[14] (Al:Zr ≈ 550; catalyst activity a ≈ 240 g polypropylene/g [Zr] · h). The polymerization reaction was carried out at −20°C for 3 h. Then the mixture was quenched (CH$_3$OH/HCl) and the polymer isolated. The polymer is atactic (with a small syndiotactic component). Its molecular mass was determined by ^{1}H-NMR spectroscopical end group analysis. The thus obtained polypropylene PP1 has a molecular mass of $\bar{M}$ ≈ 1600.

The 7-phenyl-substituted ansa-zirconocene **4b**/MAO catalyst system produces[9] low-molecular mass propene oligomers with a similar activity (a ≈ 180 at −30°C). Again, the product is atactic. Its average molecular mass is about 950. The *trans*-**4c**/MAO catalyst system was employed at two temperatures, −20 and 0°C. On the average a product with half the molecular mass was obtained from the 4,7,7-trimethyl-substituted parent system. At 0°C the catalyst activity here was >1000 (see Table 5).

This overall tendency to form lower molecular mass propene oligomers at the 7-alkyl-substituted catalyst systems is also observed for the two remaining examples employed in this study. Both the catalysts derived from the 4-allyl- and the 4-boroalkyl-substituted systems **4d**/MAO and **9**/MAO produce propene oligomers with an average molecular mass slightly below 1000. In both cases the stereochemistry of the products is close to atactic.

Table 5. Propene oligomerisation at the ansa-zirconocene-derived homogeneous Ziegler-type catalyst systems

metallocene cis/trans-ratio	**5** -	**4b** 6:1[a]	**4c** <1:15	**4c** <1:15	**4d** 1:1	**9** 1:1
[μmol]metallocene[b]	66.5	42.3	56.0	46.7	50.9	39.3
Al/Zr ratio	550	860	650	780	720	930
T(°C)	-20	-30	-20	0	-16	-20
activity[c]	240	180	150	1100	250	230
M_η[d]	1600	950	870	830	920	960

[a] Rel. assignment unclear. – [b] Reactions were carried out in 200 ml of toluene in a glass autoclave. – [c] In g polypropylene/g[Zr] · h. – [d] Determined by ^{1}H-NMR spectroscopical end group analysis.

Conclusions

The [4,7,7-trialkyl-4-(η-cyclopentadienylidene)-4,5,6,7-tetrahydro-η^5-indenyl]zirconium(IV)-derived homogeneous Ziegler-catalyst systems all produce very low molecular mass propene oligomers at high catalyst activities. Our study has shown that only a little substituent fine tuning of such catalyst systems is achieved by replacement of a 7-methyl group by bulkier substituents. On the average this has led to a slight overall decrease of the product molecular mass. In the ansa-zirconocene series investigated, the obtained $\bar{M}$ values were almost cut in half compared to the 4,7,7-trimethyl-substituted parent system. However, this effect is too small to be paralleled by a systematic structural change at the ansa-metallocene backbone. Consequently, for all three 7-substituted ansa-zirconocene dichloride examples the D1–Zr–D2 angles are almost identical and independent of the substitution pattern. The general characteristics of these catalysts may be of importance for a future development of the bent metallocene/methylalumoxane catalyst systems for applications in organic synthesis. It can be envisaged that e.g. the formation of cyclic target molecules by selective intramolecular coupling of unfunctionalized non-conjugated diolefin precursors could be achieved this way[15]. Such studies are actively being carried out in our laboratory.

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Experimental

All reactions were carried out under Ar using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under Ar prior to use. For general experimental details including a list of spectrometers used see ref.[16]. Propene polymerisation reactions were carried out in toluene solution[16] analogously as previously described in detail using a glass autoclave.

[4-(Cyclopentadienylidene)-4,7-dimethyl-7-phenyl-4,5,6,7-tetrahydroindenyl]dilithium (**3b**): 83.4 ml of an ethereal phenyllithium solution (0.89 M, 74.3 mmol) was added dropwise at 0°C to a solution of 7.1 g (33.7 mmol) of the bisfulvene **1** in 100 ml of ether. After 5 min a precipitate formed. The mixture was allowed to warm to ambient temp. and stirred for additional 12 h. The dilithio reagent **3b** was collected by filtration, washed with pentane, and dried in vacuo. The resulting product **3b** · Et_2O (10.4 g, 82%) was used without further characterization.

Dichloro[4-(η-cyclopentadienylidene)-4,7-dimethyl-7-phenyl-4,5,6,7-tetrahydro-η^5-indenyl]zirconium (**4b**): To a suspension of **3b** (4.37 g, 11.7 mmol) in 200 ml of toluene at −78°C was added 2.72 g (11.7 mmol) of zirconium tetrachloride in several portions. The mixture was allowed to warm to ambient temp. and then stirred for 20 h. It was filtered and the clear filtrate concentrated in vacuo. The oily residue was treated with pentane (20 ml) to solidify. Removal of the pentane gave 2.64 g (50%) of crude **4b** as a yellow-orange-colored solid. The diastereomer ratio was ≈8:1 as judged by ^{1}H-NMR spectroscopy. The crude product was continuously extracted with 100 ml of pentane for 2 d to give 780 mg (15%) of the ansa-zirconocene dichloride **4b** as a fine yellow powder. The diastereomeric ratio is ca. 6:1; the amount of the minor diastereomer was determined from the relative ^{1}H-NMR intensity of a separed aryl-H resonance of δ = 5.85. – $C_{22}H_{22}Cl_2Zr$ (448.5): calcd. C 58.91, H 4.94; found C 56.10, H 4.95. Major isomer: ^{1}H NMR ($CDCl_3$): δ = 7.24–6.89 (m, 5H, Ph), 6.75 (threefold intensity), 6.52 (double intensity), 6.21, 5.95 (m, 7H, Cp-CH), 2.28, 1.88 (m, 4H, 5,6-H), 1.76, 1.71 (s, each 3H, 4-CH_3, 7-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 150.2 (*ipso*-C, Ph), 135.4, 121.2, 115.5 (C10, C8, C9), 128.1, 125.7 (both double intensity, phenyl-CH), 126.5, 126.0, 124.5, 117.1, 117.0, 111.5, 107.5, 106.4 (phenyl-CH, Cp-CH), 40.5, 37.8 (C4, C7), 37.2, 31.7 (C5, C6), 27.9, 26.8 (4-CH_3, 7-CH_3). – IR (KBr): $\tilde{\nu}$ = 3103 cm^{-1}, 2973, 2959, 2935, 1494, 1455, 1438, 1375, 1090, 1074, 1031, 820, 806, 769, 765.

[7-Butyl-4-(cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydroindenyl]dilithium (**3c**): A solution of 15.0 g (71.3 mmol) of the bisfulvene **1** in 100 ml of ether was cooled to −30°C. To this was added dropwise with stirring 94 ml (150 mmol) of a 1.60 M *n*-butyllithium solution in hexane. After ca. 3 min a yellow precipitate appeared. The mixture was allowed to warm to room temp. and stirred for 24 h. The precipitated product was collected by filtration, washed with pentane, and dried in vacuo to give 23.0 g (91%) of **3c** · Et_2O which was used without further characterization.

[7-Butyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl]dichlorotitanium (**6c**): To a suspension of 5.95 g (16.8 mmol) of the reagent **3c** in 120 ml of toluene was added 3.18 g (16.8 mmol) of $TiCl_4$ at −78°C. The mixture immediately turned dark red. After stirring for 36 h at ambient temp. a precipitate was removed by filtration. Solvent was removed from the clear dark red filtrate in vacuo to give the crude 8:1 mixture of *cis*- and *trans*-**6c** in 24% yield (1.54 g). The red-brown solid was continuously extracted with pentane (100 ml) for 2 d to give pure *cis*-**6c** as a precipitate (720 mg, 11%) m.p. 134°C (DSC). From the pentane solution a 1:1 mixture of *cis*- and *trans*-**6c** was recovered (150 mg, 2.3%). Single crystals of *cis*-**6c** for the X-ray crystal structure analysis were obtained by letting pentane slowly diffuse into a solution of the pure *cis*-**6c** in dichloromethane. – *cis*-**6c**: $C_{20}H_{26}Cl_2Ti$ (385.2): calcd. C 62.36, H 6.80; found C 62.70, H 6.98. – ^{1}H NMR

($CDCl_3$): δ = 7.01, 6.94, 6.78 (double intensity), 5.87, 5.81, 5.62 (m, 7H, Cp-CH), 2.34, 1.82 (m, 4H, 5,6-H), 1.86 (s, 3H, 4-CH_3), 1.35−0.89 (m, 6H, butyl-CH_2), 1.21 (s, 3H, 7-CH_3), 0.81 (m, 3H, butyl-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 134.3, 123.4, 116.1 (C10, C8, C9), 124.7, 121.6, 116.4, 115.8, 108.0, 105.3, 103.7 (Cp-CH), 37.8, 35.5 (C4, C7), 47.0, 34.3, 32.2, 27.0, 23.1 (C5, C6, butyl-CH_2), 26.7, 25.1 (4-CH_3, 7-CH_3), 14.0 (butyl-CH_3). − IR (KBr): $\tilde{\nu}$ = 3093 cm^{-1}, 2962, 2853, 1474, 1453, 1375, 1071, 1053, 817, 803, 776, 739.

[7-Butyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl]dichlorozirconium (**4c**): To a suspension of 7.80 g (22.0 mmol) of the dilithio reagent **3c** in 200 ml of toluene was added 5.10 g (22.0 mmol) of zirconium tetrachloride in several portions at −78°C. The mixture was allowed to warm to room temp. and stirred for 48 h. A precipitate was removed by filtration and the solvent removed in vacuo from the filtrate. The resulting oil solidified by stirring it vigorously with pentane to give the crude complex **4c** in 30% yield (2.72 g). Purification was achieved by continuous extraction with 100 ml of pentane during 2 d. A yellow precipitate and a yellow pentane solution was obtained. The pentane was kept at −30°C to yield a few crystals (ca. 20 mg) of pure *cis*-**4c** suited for the X-ray crystal structure analysis. The yellow precipitate (1.35 g, 14%) consisted of a 15:1 mixture of *trans*- and *cis*-**4c** (m.p. 135°C, DSC). Single crystals of *trans*-**4c** were obtained by pentane diffusion into a dichloromethane solution of the yellow precipitate. − Major product *trans*-**4c**: $C_{20}H_{26}Cl_2Zr$ (428.6): calcd. C 56.05, H 6.12; found C 55.69, H 6.16. − ^1H NMR ($CDCl_3$): δ = 6.70 (double intensity), 6.49, 6.39, 6.06, 5.85, 5.75 (m, 7H, Cp-CH), 2.48−2.16 (m, 3H, 5-H, 6-H_{ax}), 1.88 (m, 1H, 6-H_{eq}), 1.83 (s, 3H, 4-CH_3), 1.35−0.85 (m, 6H, butyl-CH_2), 1.25 (s, 3H, 7-CH_3), 0.79 (m, 3H, butyl-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 137.5, 121.4, 113.8 (C10, C8, C9), 126.0, 123.2, 117.6, 116.7, 110.5, 107.2, 106.1 (Cp-CH), 37.6, 35.3 (C4, C7), 46.5, 34.1, 31.9, 26.8, 23.1 (C5, C6, butyl-CH_2), 26.6, 24.9 (4-CH_3, 7-CH_3), 13.9 (butyl-CH_3). − IR (KBr): $\tilde{\nu}$ = 3112 cm^{-1}, 3090, 2960, 2930, 1469, 1457, 1376, 1109, 1051, 867, 819, 806, 796, 748. − Minor product *cis*-**4c**: ^1H NMR ($CDCl_3$): δ = 6.68 (double intensity), 6.52, 6.46, 6.03, 5.82, 5.72 (m, 7H, Cp-CH), 2.43, 2.29, 1.91, 1.75 [m, 4H, ^2J = 12.0 Hz, ^3J = 6.0 (ax,eq), 4.0 (eq,eq), 14.7 (ax,ax), 7.0 (eq,ax), 5,6-H], 1.82 (s, 3H, 4-CH_3), 1.75 (m, 2H, butyl-CH_2), 1.35−1.26 (m, 4H, butyl-CH_2), 1.07 (s, 3H, 7-CH_3), 0.92 (m, 3H, butyl-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 137.0, 125.6, 123.3, 121.1, 118.4, 116.5, 113.9, 109.8, 107.4, 106.1, 39.9, 37.6, 35.4, 33.4, 32.1, 30.9, 26.4, 25.7, 23.4, 13.2.

[7-Butyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl]dichlorohafnium (**7c**): Hafnium tetrachloride (1.81 g, 5.65 mmol) was added to a suspension of 2.00 g (5.64 mmol) of **3c** in 80 ml of toluene at −78°C. The orange-colored reaction mixture was warmed to room temp. and stirred for 2 d. The mixture was filtered and the solvent removed in vacuo. The oily residue solidified by treatment with 30 ml of pentane to give 700 mg (24%) of the crude product **7c** (which contains only a single isomer as judged by ^1H NMR). Continuous extraction with pentane (100 ml) and recrystallization from dichloromethane/pentane gave the crystalline *trans*-**7c**, 70 mg (2.4%), m.p. 151°C (DSC). − $C_{20}H_{26}Cl_2Hf$ (515.8): calcd. C 46.57, H 5.08; found C 46.70, H 5.03. − ^1H NMR ($CDCl_3$): δ = 6.61 (double intensity), 6.41, 6.32, 5.98, 5.80, 5.65 (m, 7H, Cp-CH), 2.38, 2.23, 1.98, 1.85 [m, 4H, ^2J = 14.0 Hz, ^3J = 5.7 (ax,eq), 3.2 (eq,eq), 14.4 (ax,ax), 6.8 (eq,ax), 5,6-H], 1.90 (s, 3H, 4-CH_3), 1.27 (s, 3H, 7-CH_3), 1.35−1.07 (m, 6H, butyl-CH_2), 0.80 (m, 3H, butyl-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 134.3, 123.4, 116.1 (C10, C8, C9), 124.7, 121.6, 116.4, 115.8, 108.0, 105.3, 103.7 (Cp-CH), 37.8, 35.5 (C4, C7), 47.0, 34.3, 32.2, 27.0, 23.1 (C5, C6, butyl-CH_2), 26.7, 25.1 (4-CH_3, 7-CH_3), 14.0 (butyl-CH_3). − IR (KBr): $\tilde{\nu}$ = 3093 cm^{-1}, 2961, 2931, 2863, 1470, 1458, 1383, 1111, 1052, 867, 832, 822, 807, 797, 751.

[7-Allyl-4-(cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydroindenyl]dilithium (**3d**): To a solution of 16.8 g (79.8 mmol) of the bisfulvene **1** in a mixture of 100 ml of ether and 50 ml of tetrahydrofurane was added with vigorous stirring 293 ml of a 0.60 M ethereal allylmagnesium chloride solution (175 mmol) at 0°C with 1 h. The mixture was stirred overnight at room temp. Then the yellow-orange-colored suspension was cooled to 0°C and carefully mixed with aqueous ammonium chloride solution. The organic phase was separated, washed with brine (3 × 50 ml), and dried with magnesium sulfate. The solvent was then removed in vacuo to give 17.5 g of **8** (as a mixture of isomers, 87% yield). − IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1}, 2960, 2927, 2875, 1638, 1453, 1374, 995, 953, 911, 898, 755, 680. − HRMS: $C_{19}H_{24}^{+}$ calcd. 252.1878, found 252.1875. − *n*-Butyllithium (57.6 ml of a 1.60 M solution in hexane, 92.0 mmol) was added dropwise to a solution of 10.5 g of **8** in 100 ml of ether at 0°C. The mixture was stirred for 18 h at room temp. The precipitated product **3d** was recovered by filtration, washed several times with pentane, and dried in vacuo to give the reagent **3d** · Et_2O that was employed without further characterization.

[7-Allyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl]dichlorotitanium (**6d**): The dilithio reagent **3d** (2.45 g, 7.24 mmol) was dissolved in 80 ml of tetrahydrofuran. At −78°C 2.42 g (7.24 mmol) of $TiCl_4$ · 2 THF was added. The reaction mixture turned dark red instantaneously. It was allowed to warm to ambient temp. and stirred for 2 d, the solvent was removed in vacuo and the brown residue extracted continuously with pentane to give 223 mg (9%) of a 2:1 mixture of *cis*- and *trans*-**6d**. − $C_{19}H_{22}Cl_2Ti$ (369.2): calcd. C 61.81, H 6.01; found C 61.39, H 6.23. − ^1H NMR ($CDCl_3$): δ = 7.03, 6.93, 6.83, 6.74, 5.84, 5.81, 5.62 (m, Cp-CH), 5.63−5.40 and 5.15−4.80 (m, $CH=CH_2$), 2.38−2.17, 2.10−2.06, 1.86−1.77 (m, 5,6-H, allyl-CH_2), 1.85 (s, 4-CH_3, both isomers), 1.24 (s, CH_3 of *cis*-**6d**), 1.10 (s, 7-CH_3 of *trans*-**6d**). − ^{13}C NMR ($CDCl_3$): δ = 142.0, 140.7 (C10 of *cis*- and *trans*-**6d**), 134.1, 134.0, 133.8, 133.7, 133.6, 133.4, 131.6, 131.2, 127.0, 126.7, 126.5, 126.3, 122.2, 112.3, 111.4 (double intensity) (Cp-CH and vinyl-CH), 118.2 (double intensity), 107.5, 107.1 (C8, C9), 118.7, 118.6 (=CH_2), 51.3, 44.2 (allyl-CH_2), 36.2, 34.6 (double intensity), 34.1 (C4, C7), 37.0, 33.2, 33.1, 31.3 (C5, C6), 31.6, 25.5 (double intensity), 24.9 (4-CH_3, 7-CH_3).

[7-Allyl-4-(η-cyclopentadienylidene)-4,7-dimethyl-4,5,6,7-tetrahydro-η^5-indenyl]dichlorozirconium (**4d**): Zirconium tetrachloride (5.21 g, 22.3 mmol) was added in several portions at −78°C to a suspension of the dilithio reagent **3d** (7.56 g, 22.3 mmol) in 200 ml of toluene. The mixture was stirred at −78°C for 30 min and then warmed to room temp. where it was stirred for 12 h. The orange-colored suspension was filtered, the residue washed with toluene (2 × 30 ml), and the filtrates were combined. The toluene solvent was removed in vacuo. The resulting oil was treated with 50 ml of pentane to give 5.04 g (55%) of **4d**. Purification was carried out by continuous extraction with pentane (100 ml) for 2 d to give 2.34 g (26%) of a 1.5:1 mixture of *trans*- and *cis*-**4d**, m.p. 99°C (DSC). − $C_{19}H_{22}Cl_2Zr$ (412.5): calcd. C 55.32, H 5.38; found C 55.39, H 5.49. − ^1H NMR ($CDCl_3$): δ = 6.70 (double intensity), 6.51, 6.39, 6.06, 5.87, 5.74 (m, Cp-CH of both isomers), 5.62−5.41, 5.20−4.83 (m, $CH=CH_2$), 2.55−2.17, 2.09−2.05, 1.97−1.69 (m, 5,6-H, allyl-CH_2), 1.83 (s, 4-CH_3 of both isomers), 1.27 (s, 7-CH_3 of *trans*-**4d**), 1.09 (s, 7-CH_3 of *cis*-**4d**). − ^{13}C NMR ($CDCl_3$): δ = 137.5, 136.3 (C10 of the two isomers), 121.5, 118.0, 114.2, 113.9 (C8, C9), 134.2, 134.1, 133.8, 125.9, 125.7, 123.5, 123.2, 118.2, 118.0, 116.8, 116.2, 110.3, 110.0, 107.4, 107.3, 106.1 (Cp-CH and vinyl-CH), 118.5,

118.2 ($=CH_2$), 50.8, 44.6 (allyl-CH_2), 37.6, 36.0, 35.4 (C4, C7, one resonance not located), 33.6, 33.5, 31.9, 31.8 (C5, C6), 31.2, 26.5, 26.4, 25.1 (4-CH_3, 7-CH_3). – IR (KBr): $\tilde{\nu}$ = 3105 cm^{-1}, 3085, 3070, 2966, 2925, 2891, 1637, 1469, 1459, 1452, 1383, 1084, 1050, 925, 818, 809, 799, 750. – Very slow diffusion of pentane into a solution of the *cis*-**4d**/*trans*-**4d** mixture produced single crystals of *trans*-**4d** that were used for the X-ray crystal structure analysis.

Hydroboration of **4d**: A sample of 210 mg (0.51 mmol) of the mixture of the *cis*- and *trans*-**4d** diastereomers was dissolved in 50 ml of toluene. At room temp. 62 mg (0.51 mmol) of 9-BBN was added. The mixture was stirred for 36 h at ambient temp. Then the solvent was removed in vacuo and the orange-yellow oil taken up with 30 ml of ether. The clear solution was concentrated in vacuo to a volume of 10 ml and kept for several hours at −30°C to give 208 mg (78%) of a ca. 1:1 mixture of the **9** diastereoisomers, m.p. 78°C (DSC). – $C_{27}H_{37}BCl_2Zr$ (534.5): calcd. C 60.67, H 6.98; found C 60.01, H 7.14. – ^1H NMR ($CDCl_3$): δ = 6.70 (double intensity), 6.49, 6.41, 6.00, 5.84, 5.74 (m, Cp-CH of both isomers), 2.50–2.11, 1.82–1.10 (m, 5,6-H, 4-CH_3, 7-CH_3 and $[CH_2]_3$-BBN). – ^{13}C NMR ($CDCl_3$): δ = 138.3, 137.4 (C10 of both isomers), 126.0, 125.4, 123.3, 123.1, 118.5, 117.6, 116.8 (double intensity), 110.5, 109.5, 107.5, 107.2, 106.1, 106.0 (Cp-CH), 121.8, 121.3, 113.9, 113.8 (C8, C9), 50.1, 43.6 (7-CH_2), 37.7, 37.6, 36.0, 35.7 (C4, C7), 34.4, 33.4, 32.1 (double intensity) (C5, C6), 33.1, 31.0, 23.2 (9-BBN), 26.6, 26.3, 25.0 (double intensity) (4-CH_3, 7-CH_3), 19.6, 18.3 ($CH_2CH_2CH_2$–), ≈29 (br., CH_2B). – IR (KBr): $\tilde{\nu}$ = 3105 cm^{-1}, 3088, 3072, 2961, 2958, 2925, 2918, 2902, 2879, 1469, 1453, 1446, 1379, 1366, 1084, 1049, 875, 798.

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