Hydroboration of Bis(alkenylcyclopentadienyl)zirconium Dichlorides[1)]

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The reaction of allylcyclopentadienyllithium with 0.5 molar equivalents of $MCl_4(thf)_2$ (M = Zr, Hf) furnished the $(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)_2MCl_2$ complexes **3a** (Zr) and **3b** (Hf), which cleanly added 9-borabicyclo[3.3.1]nonane (9-BBN) to form $[\eta^5\text{-}C_5H_4(CH_2)_3(9\text{-BBN})]_2MCl_2$ (**10a, b**). Treatment of **3** with butadiene-magnesium led to coupling of one Cp-bonded allyl unit with butadiene to give **5**; the remaining $CpCH_2CH{=}CH_2$ group underwent clean $H[B(C_8H_{14})]$ addition when exposed to the 9-BBN hydroboration reagent. (Alkenyl-Cp)$_2$ZrCl$_2$ complexes (**9a–d**) were prepared starting from fulvenes by deprotonation with the help of LDA and reaction with $ZrCl_4(thf)_2$. The complexes $[\eta^5\text{-}C_5H_4CH{=}C(CH_3)R]_2ZrCl_2$ **9b** (R = CH_3) and **9c** (R = Ph) added 9-BBN to give $[\eta^2\text{-}C_5H_4CH(9\text{-BBN})CH(CH_3)R]_2ZrCl_2$ **12** (R = CH_3, *rac-/meso-* ≈ 1:1) and **13** (R = Ph, *threo-/erythro-* ≈ 1:1). The mixtures of diastereoisomers were in each case separated by fractional crystallization. The stereochemical assignments of complexes *rac*-**12** and *meso*-**12** were achieved by means of the stereochemistry of polypropylene formed at the **12**/methylalumoxane-derived homogeneous Ziegler-type olefin polymerization catalysts. At −50°C the catalyst from the achiral *meso*-**12** precursor produced isotactic polypropylene only by means of "chain end control" (σ ≈ 0.7), whereas the use of *rac*-**12** led to a pronounced participation (≈ 30%) of effective "enantiomorphic site control" (α ≈ 0.95) in the CC-coupling reaction.

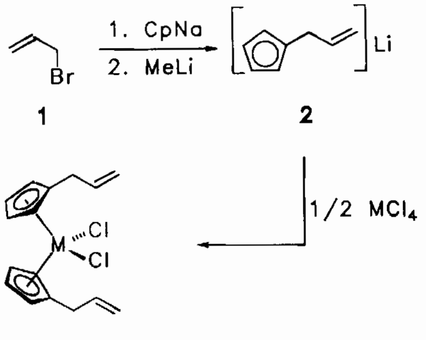
Metallocene complexes bearing substituents at the Cp rings have been of great importance for organometallic chemistry and catalysis[2)]. Such complexes of the late transition metals can often be derived from the unsubstituted parent systems by means of conventional Cp-ring functionalization. The many known electrophilic substitution reactions at the ferrocene cyclopentadienyls are typical examples[3)]. The high reactivity of the bent metallocenes of the oxophilic early transition elements is often prohibitive for a similar Cp-substitution chemistry at the organometallic stage. Therefore, Cp-substituted or -functionalized metallocene halides of e.g. the group 4d-elements have usually been prepared differently, i.e., mostly by reaction of suitably substituted R−Cp anion equivalents with the metal halides[4)].

The hydroboration reaction has been used for functionalizing Cp-alkenyl-substituted ferrocenes[5)]. We thought that the introduction of the electrophilic BR_2 functionality might be less critical and easier to be compatible with the general reactivity patterns of zirconocene and hafnocene halides than e.g. the exposure of such complexes to the rather harsh conditions typically employed in Friedel-Crafts-type chemistry. Indeed, we found that hydroboration of many (alkenyl-Cp)$_2$MCl$_2$ complexes (M = Zr, Hf) proceeded cleanly. We here describe some typical examples of forming alkyl borane Cp-substituted zirconocene dichlorides from their respective (alkenyl-Cp)$_2$ZrCl$_2$ precursors by means of the hydroboration reaction. Two of the selected examples show interesting stereochemical features, which were disclosed in propene polymerization reactions by using the respective boron-containing $(R^*Cp)_2ZrCl_2$/alumoxane catalyst systems.

Results and Discussion

Formation of the Bis(alkenyl-Cp)MCl$_2$ Precursors

We used two groups of metallocene starting materials for the hydroboration reaction. The first contained η-cyclopentadienyl ligands to which allyl substituents were attached[6)]. They were prepared straightforwardly by first treating the cyclopentadienyl anion with allyl bromide followed by deprotonation; then two $CpCH_2CH{=}CH_2$ anion equivalents were treated with zirconium tetrachloride to give $(CpCH_2CH{=}CH_2)_2ZrCl_2$ (**3a**) in good yield. IR and NMR spectra of **3a** are in agreement with the presence of ordinary uncoordinated C=C bonds of the allyl substituents [$\tilde{\nu}$ = 1637 cm^{-1}; ^{13}C NMR: δ = 34.0 (−CH$_2$−), 135.7 (−CH=),



3a(M= Zr); 3b(M= Hf)

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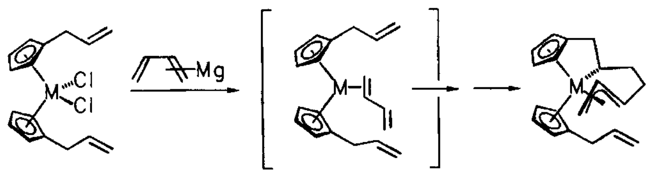
116.1 ($=CH_2$)]. $(CpCH_2CH=CH_2)_2HfCl_2$ (**3b**) was prepared analogously.

The allyl-Cp metal complexes **3a** and **3b** were used to prepare a pair of related compounds which contained only a single allylcyclopentadienyl ligand each. This was achieved by selectively coupling the C=C bond of one allyl group by the reaction with a butadiene ligand attached to the transition metal center[7].

Thus we treated $(CpCH_2CH=CH_2)_2ZrCl_2$ (**3a**) with one molar equivalent of butadiene–magnesium[8] and obtained a single reaction product (**5a**). Apparently, the initially formed (η^2-butadiene)metallocene intermediate was not stable under the reaction conditions but underwent subsequent intramolecular carbon-carbon coupling to give a (π-allyl)zironocene product. The obtained zirconium(IV) complex is chiral (C_1) exhibiting 24 hydrogen and 20 carbon atoms which are all inequivalent in the ^1H- and ^{13}C-NMR spectra, respectively. The resulting highly informative spectroscopic material (including COSY- and $^1H/^{13}C$-correlated 2D NMR and NOE difference spectra) allowed us to identify the product as **5a** and to distinguish it from the other possible diastereomeric metallacyclic (π-allyl)zirconium complex (**5a′**). The analogous reaction of $(CpCH_2CH=CH_2)_2HfCl_2$ (**3b**) with butadiene–magnesium was equally diastereoselective giving only rise to the formation of **5b** (within the limits of accuracy of the NMR analysis)[9].

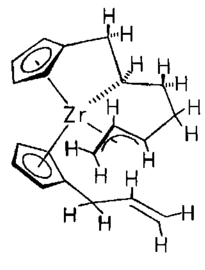


3a (M= Zr)
3b (M= Hf)

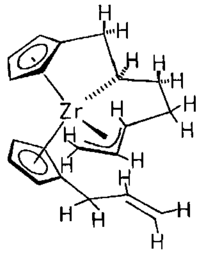
4a, b

5a (M= Zr)
5b (M= Hf)

Scheme 1. Diastereomeric structures **5a** and **5a′**

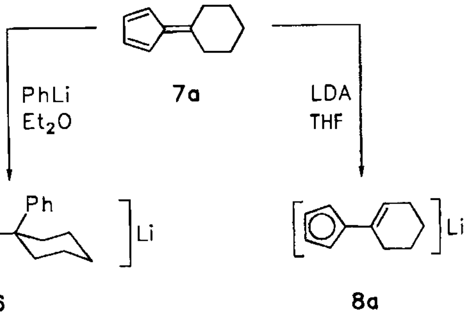


5 a



5 a′

The second group of starting materials for the hydroboration reaction (see below) contained various bis(alkenyl-Cp)zirconium halides $(CpCR^1=CR^2R^3)_2ZrCl_2$. It is well-known that pentafulvenes behave in some way as analogs of organic carbonyl compounds[10] and can be α-deprotonated at the substituents attached to C-6[11]. A typical example is the fulvene **7a**. It was prepared from cyclopentadiene and cyclohexanon in methanol as solvent with the aid of pyrrolidine as a base[12]. α-Deprotonation[11] to give the (cyclohexenyl-Cp)lithium system **8a** was achieved by treating **7a** with lithium diisopropylamide (LDA) in tetrahydrofuran solution (83% isolated), whereas the reaction of **7a** with phenyllithium in ether resulted only in aryl addition to give **6** (43% isolated).



6

8a

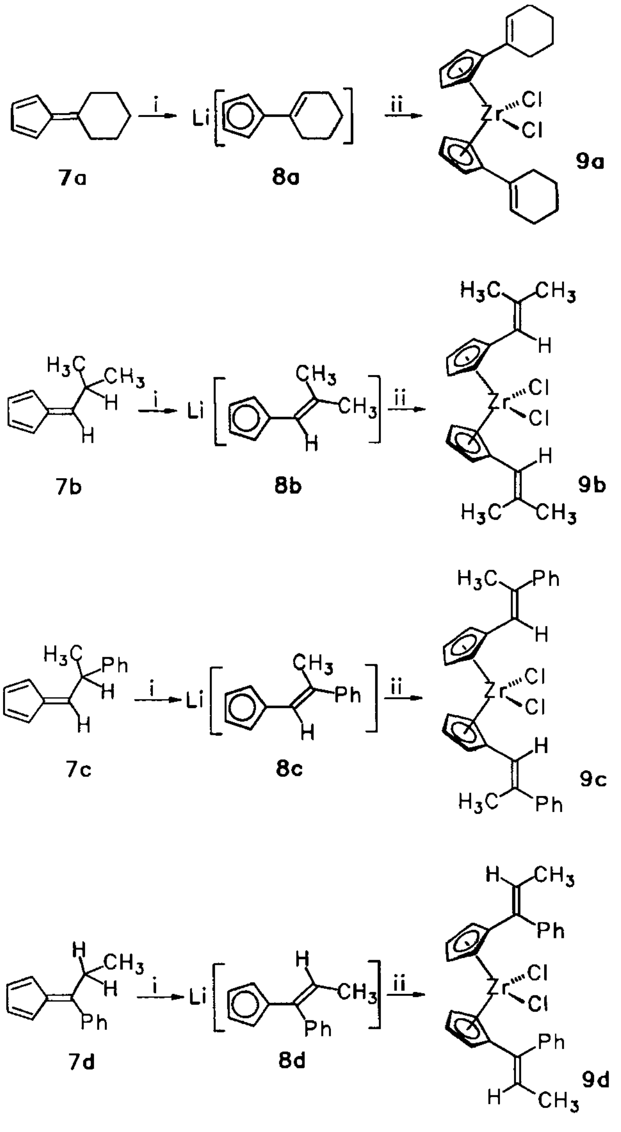
Sufficiently mild reaction conditions were required to achieve a clean preparation of the $(alkenyl\text{-}Cp)_2ZrCl_2$ complexes from the corresponding alkenylcyclopentadienyllithium reagents. The use of the bis(tetrahydrofuran)zirconium tetrachloride allowed this substitution reaction to proceed at temperatures between 0 and 25°C. We thus obtained pure $[(1\text{-cyclohexen-1-yl})Cp]_2ZrCl_2$ (**9a**) from **8a** and $ZrCl_4(thf)_2$ in 74% yield.

Analogous zirconium complexes with Cp ligands bearing disubstituted acyclic alkenyl substituents could be obtained by this route in high yields as well. The fulvene **7b**, prepared by base-induced coupling of cyclopentadiene with isobutyric aldehyde, was deprotonated with LDA to give **8b**. Subsequent reaction with $ZrCl_4(thf)_2$ produced $[CpCH=C(CH_3)_2]ZrCl_2$ (**9b**).

Deprotonation of the fulvene $(C_5H_4)=CHCH(CH_3)Ph$ (**7c**) produced only one of the corresponding $[CpCH=C(CH_3)Ph]Li$ isomers (65% isolated). Exact stereochemical assignment (*E* or *Z* isomer) turned out to be difficult at the stage of the lithium compound and was therefore carried out only with the subsequently formed zirconocene complex. The latter was obtained as a slightly yellow solid (ca. 80% isolated) by treatment of the lithium compound **8c** with bis(tetrahydrofuran)zirconium tetrachloride. The obtained $[CpCH=C(CH_3)Ph]_2ZrCl_2$ (**9c**) was isomerically pure. A detailed ^1H-NMR/NOE investigation revealed that the phenyl and hydrogen substituents were 1,2-*cis*-positioned at the C=C bond [e.g. irradiation of the ^1H-NMR signal of the *ortho*-phenyl hydrogens (δ = 7.44) resulted in a positive NOE effect at the olefinic hydrogen signal (δ = 6.59; 9%) and vice versa (20%); the alkenyl methyl group (δ = 2.29) is oriented *cis* to the Cp ring [α-hydrogen signal at δ = 6.51 is NOE-enhanced (12%) upon irradiation at δ = 2.29 and vice versa (12%)].

A similarly *E*-selective alkenyl-Cp ligand formation was observed upon deprotonation of 6-ethyl-6-phenylfulvene (**7d**). Subsequent addition of **8d** to the zirconium reagent produced only one of the two $[CpCPh=CH(CH_3)]_2ZrCl_2$ isomers, namely complex **9d** with an *E*-configurated Cp-bonded alkenyl substituent. This assignment was again based on a detailed investigation of its NMR spectra, es-

Scheme 2. Synthesis of bis(alkenyl-Cp)zirconium dichlorides

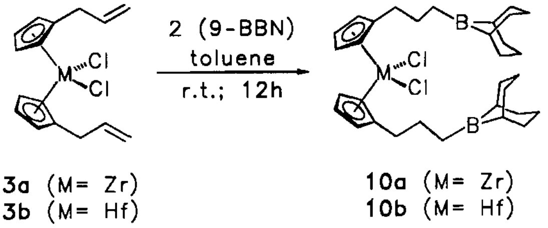


i: LDA. – ii: $ZrCl_4(thf)_2$.

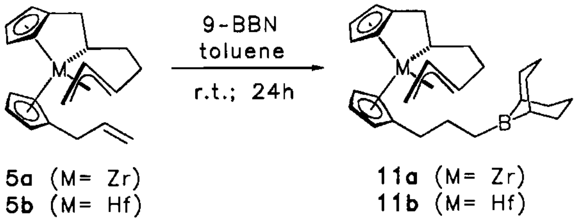
pecially the ^{1}H-NMR/NOE difference spectra obtained at 300 K in [D_6]benzene (with a 44-s saturation time). A strong NOE enhancement (19%) of the $=CH-CH_3$ signal at $\delta = 6.21$ was observed upon irradiation of the CH_3 doublet centered at $\delta = 1.56$. At the same time, the intensity of the *o*-phenyl-H resonance at $\delta = 7.18$ was enhanced by 6%. Irradiation at $\delta = 6.00$ (Cp-α hydrogens) resulted in a 23% NOE enhancement of the signal at $\delta = 6.21$ ($=CH-$) and vice versa (13%).

Hydroboration Reactions

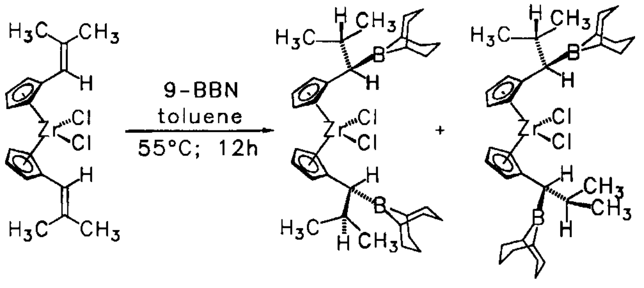
Within the scope of this study $H-BR_2$ addition reactions were carried out exclusively by using the 9-borabicyclo-[3.3.1]nonane (9-BBN) hydroboration reagent[13]. With two molar equivalents of this reagent the bis(allyl-Cp)zirconium dichloride complex **3a** reacted in the course of 12 h in toluene solution at ambient temperature to give a single addition product (**10a**), which was isolated (white needles) in ca. 95% yield. The characteristic NMR spectra showed that both allylic $C=C$ bonds had been consumed and the 9-BBN addition was completely regioselective[14] giving only $[CpCH_2CH_2CH_2B(C_8H_{14})]_2ZrCl_2$ (**10a**) [^{1}H NMR, [D_6]benzene: $\delta = 5.87, 6.01$ (m, 4H each, Cp); 2.75 (t, 4H, $CpCH_2$); 1.36 (t, 4H, CH_2B); ^{13}C NMR, [D_6]benzene: $\delta = 111.8, 117.1, 134.7$ (Cp); 23.6, 33.5, 31.4 (9-BBN); 33.6, 26.3, 28.3 ($CpCH_2CH_2CH_2B$)]. The 9-BBN addition to the double bonds of the hafnium complex **3b** proceeded equally facile, regioselective and complete.



(π-Allyl)metallocene units appeared not to interfere with the hydroboration reaction, nor did they adversely influence the high regioselectivity as observed for the examples described above. The diastereomerically pure complexes **5a** and **5b** reacted cleanly with the 9-BBN hydroboration reagent. Only one of the respective possible diastereoisomeric products (**11**) was observed in each case. According to the NMR spectra the relative configurations at the chiral metal center were the same for the starting materials and hydroboration products (details are given in the experimental section). The $H-B(C_8H_{14})$ addition reaction of the sterically more hindered substrates **5** was somewhat slower as compared to **3**. A period of 24 h was required to achieve a complete reaction at ambient temperature.



The bis(alkenyl-Cp)zirconium dichlorides **9** turned out to be much less reactive towards 9-BBN. Too high temperatures were required to initiate the 9-BBN/**9a** and 9-BBN/**9d** addition reactions. In both cases product formation was not clean, and the resulting mixture of organometallics was not separated or identified. In contrast, the 9-BBN hydroboration of the substrates **9b** and **9c** proceeded well at moderate temperatures. Clean product formation in high overall yield was observed. The 9-BBN addition to the trisubstituted $C=C$ bonds of $[CpCH=C(CH_3)_2]_2ZrCl_2$ (**9b**) was carried out at 55°C in toluene solution. The reaction was complete after ca. 12 h. Within the limits of the NMR analysis the addition was completely regioselective. The hydride had added to the higher substituted $=C(CH_3)_2$ carbon of the $C=C$ bond. Attachment of $B(C_8H_{14})$ in the α-position to the



9b rac-12 (1 : 1) meso-12

Cp ring created a new chirality center at each substituted cyclopentadienyl moiety. Therefore, the formation of two diastereoisomers was expected differing in their overall symmetry properties: a *rac* and a *meso* form. The products *rac*-**12** and *meso*-**12** were indeed obtained as a mixture in a 1:1 molar ratio. Fortunately, the diastereomers could rather easily be separated by fractional crystallization. It was possible to obtain both isomers almost pure and characterize them separately spectroscopically. This did not lead to an absolute assignment of the chiral vs. the achiral diastereomer of **12**. However, this structural discrimination could be deduced by means of a subsequent chemical reaction, transforming the inherent stereochemical information of each of the diastereomeric organometallic complexes to easily analyzable organic products (see below).

Three successive crystallizations of the reaction product **12** from toluene at 5°C yielded a sample which was >99:1 enriched with the achiral complex *meso*-**12**. The remaining mother liquor was thereby enriched with *rac*-**12** (ca. 85:15). Further fractional crystallization of this solution at −15°C eventually gave a fraction containing >99:1 of the chiral reaction product *rac*-**12**.

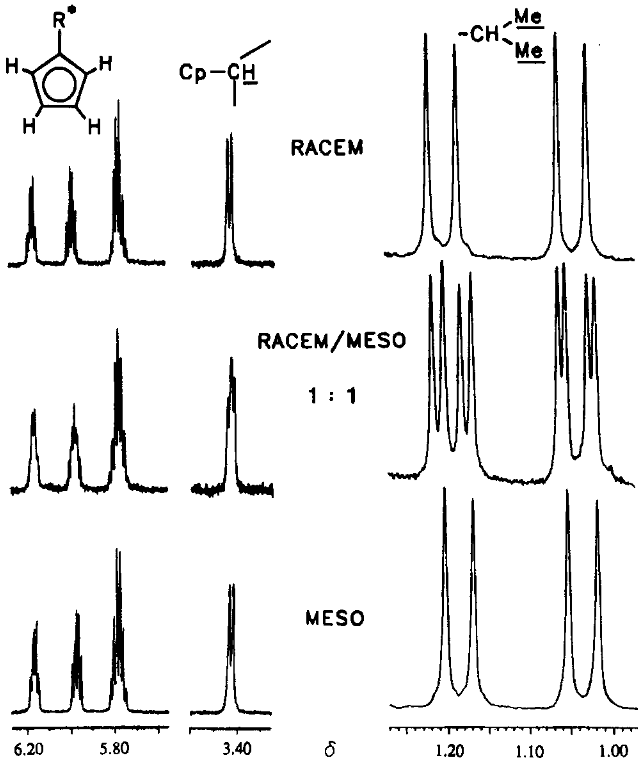
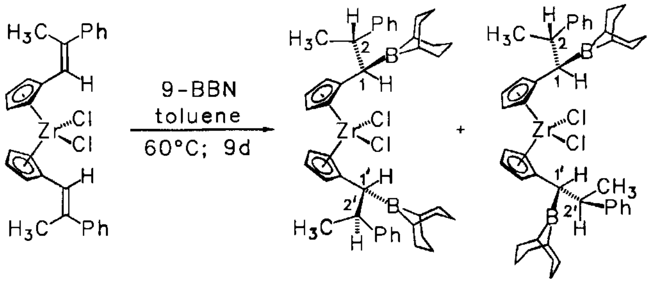


Figure 1. Comparison of three characteristic sections of the ^{1}H-NMR spectra (in [D$_6$]benzene) of [CpCH(BC$_8$H$_{14}$)-CH(CH$_3$)$_2$]$_2$ZrCl$_2$: *rac*-**12** (above) and *meso*-**12** (below). The spectrum of the respective original reaction mixture is shown in the center line

The ^{1}H-NMR spectra of the two diastereoisomers of **12** showed differences of the CH(C*H*$_3$)$_2$ as well as the Cp−C*H*[B] chemical shifts which were sufficient for distinguishing between *meso*- and *rac*-**12** whereas the Cp-hydrogen resonances were not markedly separated (see Figure 1). The opposite was true for the ^{13}C-NMR spectra. Here the Cp-carbon signals were slightly different in [D$_6$]benzene solution [*rac*-**12**: δ = 108.8, 114.2, 114.6, 115.0 (CH), 140.4 (*ipso*-C); *meso*-**12**: δ = 109.4, 113.9, 114.7 (double intensity), 140.4], whereas the substituent signals were not differentiated at 4.7 Tesla [δ = 47.4 (Cp-CH[B]), 30.8 (*C*HMe$_2$), 23.6, 24.5 (CH$_3$)].

The hydroboration of [CpCH=C(CH$_3$)Ph]$_2$ZrCl$_2$ (**9c**) with the 9-BBN reagent required 9 days at 60°C to become sufficiently complete. In this case, four chirality centers were newly formed per molecule if both C=C bonds of the starting material were utilized in the addition reaction. However, the well defined stereoelectronics of the hydroboration reaction (strict 1,2-*cis* addition under kinetic control) together with the practically complete regioselectivity [hydride addition only to the =C(CH$_3$)Ph terminus of the C=C bond within the limits of the ^{1}H-NMR detection] made the stereochemical outcome of the **9c** + 9-BBN reaction quite simple: only two diastereoisomers were formed. These products (**13a**, **13b**) were obtained in a ca. 1:1 ratio in a combined yield of ≈50%.



9c (1R*, 2S*, 1'R*, 2'S*) (1R*, 2S*, 1'S*, 2'R*)
13a/b (1:1)

Fractional crystallization from CH$_2$Cl$_2$ gave one of the diastereomers with >99:1 isomeric purity (checked by ^{1}H NMR). From the remaining solution the other isomer could be obtained only admixed with the less soluble component (5:95). The two diastereomers could readily be distinguished by their ^{1}H- and ^{13}C-NMR spectra. However, their absolute assignment, i.e. which were the *erythro*- [rel. configuration: 1*R**,2*S**,1′*S**,2′*R**] or *threo*- [1*R**,2*S**,1′*R**,2′*S**] form, remained unclear (see below).

Propene Polymerization Reactions

There remained the problem of the relative stereochemical assignment of the diastereoisomers **13a**, **13b** (which is *threo*, which *erythro*) and **12** (which is *rac*, which is *meso*), respectively. For making this decision we wanted to look for the ability of the **13**- or **12**-derived homogeneous metallocene/alumoxane Ziegler-type catalysts[15] for transferring their inherent chirality information to a growing polypropylene chain[16]. For the *rac-/meso*-**12**-derived catalysts any notable amount of isotactic polypropylene portions formed by "enantiomorphic site control" (characterized by regimes containing only singular stereochemical mistakes, i.e. exhibiting the mmmr, mmrr, and mrrm pentades in a 2:2:1 intensity relation) would reveal the chiral nature of active metallocene catalyst[17] and distinguish the *rac*-**12** from the achiral *meso*-**12** catalyst precursor. Similarly, a significant difference of the polypropylene portions formed by enantiomorphic site control could potentially be used to distinguish the *erythro*- from the *threo*-**13** isomer.

We therefore produced an active polymerization catalyst from the isomerically pure complex **13b** by treating it in toluene/propene solution ($\approx 1:1$) at -50°C with a large excess of oligomeric methylalumoxane (molar Al/Zr ratio $\approx$ 1000). Polypropylene was formed and isolated. The catalyst activity at -50°C was ca. 130 g polymer/g [Zr] · h. It had a molecular mass of $\bar{M}_\eta \approx 15000$. The similarly prepared catalyst derived from **13a** was slightly less reactive (-50°C: activity 35 at Al/Zr $\approx$ 1800). The stereochemical characterization of the polypropylene product was achieved by means of ^{13}C-NMR methyl pentade analysis[18]. The ^{13}C-NMR methyl signal region of both polymers is shown in Figure 2. Both polymers are very similar and very near to atactic. Therefore, a relative stereochemical assignment of the catalyst precursors **13a** and **13b** could not be derived from this type of experiment.

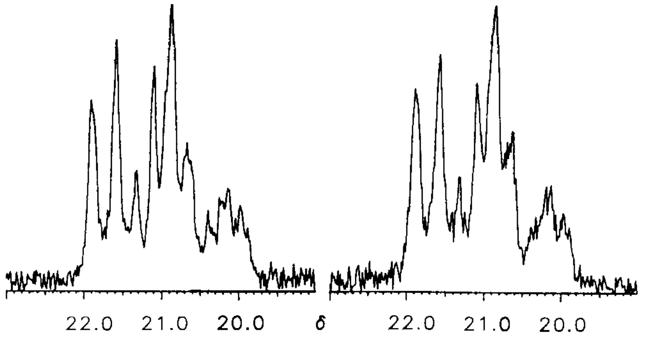


Figure 2. Comparison of the ^{13}C-NMR methyl resonances of the polypropylenes formed at methylalumoxane-activated **13a**- (left) and **13b**-derived (right) homogeneous Ziegler-type catalysts

This was different for the catalyst systems derived from the [CpCH(BC$_8$H$_{14}$)CH(CH$_3$)$_2$]ZrCl$_2$ complexes **12**. We first carried out propene polymerization reactions at -50°C with the achiral *meso*-**12**-derived catalyst system. Two experiments were performed by using increasing amounts of the methylalumoxane activator/cocatalyst (for details see Table 1). The polypropylene products formed (PP4 and PP5) were very similar. ^{13}C-NMR methyl pentade analysis revealed that almost completely atactic polypropylene was obtained in each case. By a detailed statistical analysis[19] some residual stereochemical "chain end control"[20] was found to a rather small extend to correlate with the observed intensities of the resolved pentade signals [see Figure 3, observed/calculated relative intensities from left to right: mmmm [σ^4] 0.22/0.23; mmmr [$\sigma^3(1-\sigma)$] 0.21/0.20; rmmr [$\sigma^2(1-\sigma)^2$] 0.06/0.05; mmrr [$2\sigma^2(1-\sigma)^2$] 0.09/0.09; mmrm + rmrr [$2\sigma^3(1-\sigma) + 2\sigma(1-\sigma)^3$] 0.27/0.24; rmrm [$2\sigma^2(1-\sigma)^2$] 0.09/0.09; rrrr [$(1-\sigma)^4$] 0.01/0.01; mrrr [$2\sigma(1-\sigma)^3$] 0.03/0.04; mrrm [$\sigma^2(1-\sigma)^2$] 0.03/0.05; where σ denotes the probability of formation of an m-diad at the active site under "chain end control"]. σ Values of 0.66 and 0.69 for PP4 and PP5, respectively, indicated the statistical distributions of very short isotactic block sequences of average lengths $\langle m \rangle_{n\sigma}$ around 3 [$\langle m \rangle_{n\sigma} = 1/(1-\sigma)$].

Table 1. Propene polymerization with *rac*- and *meso*-**12**/(MeAlO)$_x$ catalysts

Polymer	PP1	PP2	PP3	PP4	PP5
Catalyst	*rac*	*rac*	*rac/meso* (1:1)	*meso*	*meso*
mg cat.	10.3	18.7	20.0	17.4	12.9
mmol cat.	0.016	0.029	0.031	0.027	0.020
g cocat.	2.3	1.8	1.3	1.2	1.5
mmol cocat.	39.6	31.0	22.3	20.8	25.9
Al/Zr[a]	2475	1070	720	770	1295
Temp. [°C]	−50	−50	−50	−50	−50
Reaction time [h]	12	11	7	6.5	6.5
g PP produced	1.6	3.0	2.1	0.9	1.8
Activity[b]	92	103	104	55	154
$\bar{M}_\eta$	25000	–	52000	16500	27000
ω	0.32	0.30	0.16	0.00	0.00
α	0.94	0.95	[c]	–	–
σ	0.72	0.70	0.73	0.66	0.69
$\langle m \rangle_n\alpha$	15.7	19.1	[c]	–	–
$\langle m \rangle_n\sigma$	3.40	3.30	3.70	2.90	3.20

[a] Al/Zr = mmol [AlMeO]/mmol [(RCp)$_2$ZrCl$_2$]. — [b] Activity given in g PP/g [Zr] · h · bar. — [c] Not calculated.

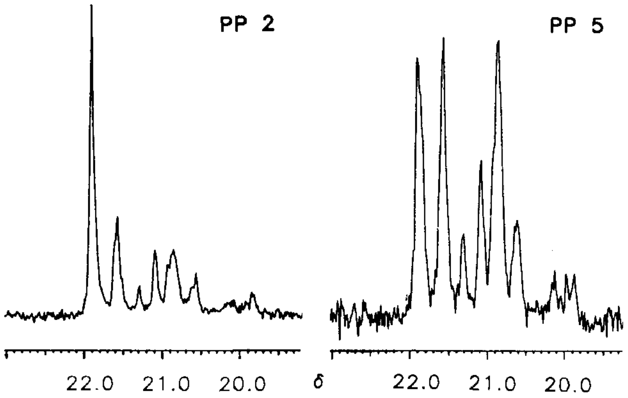


Figure 3. ^{13}C-NMR methyl resonances of polypropylene samples PP2 and PP5 obtained from catalysts derived from *rac*-**12** (left) and *meso*-**12** (right) at -50°C

The *rac*-**12**/alumoxane catalyst system was equally active at -50°C (see Table 1). It produced a polymer (polypropylene samples PP1 and PP2) that was stereochemically rather different from that formed at the *meso*-**12**-derived catalyst. As is evident from the ^{13}C-NMR methyl region of an example (PP2, see Figure 3, left side), an isotactic polypropylene was formed at the active catalyst derived from *rac*-**12**. The obtained spectrum could not be adequately reproduced by using a single statistical parameter[20] (i.e. either σ for pure chain end control or α for enantiomorphic site control). We had to apply a combination of both statistical descriptors plus a factor describing their relative weight [ω giving the partition at the polymer chain being due to the stereocontrol exerted by the chiral metal center, (1 − ω) the residual effective control of the chiral chain end; it should be noted that both influences are not independent of each other but occurring combined similar to the effect of double stereodifferentiation in conventional organic synthesis[19]]. For our specific example of the *rac*-**12**-derived catalyst system, the NMR spectra could be adequately reproduced by assuming ca. 30% enantiomorphic site control as opposed to ω = 0 for the diastereomeric *meso*-**12**/$(\mathrm{MeAlO})_x$ catalyst (see above) [e.g. PP2: ω = 0.30; α = 0.95 (probability that an *R*-controlling site produces an *R*-configurated center under enantiomorphic site control); σ = 0.70; $\langle m\rangle_{n\sigma} \approx 3$; $\langle m\rangle_{n\alpha} = [1 - 2\alpha(1 - \alpha)/\alpha(1 - \alpha)] \approx 19$]. For this example the following observed/calculated ^{13}C-NMR methyl resonance intensities were obtained [the respective calculation of the relative intensities due to enantiomorphic site control (ω) is given in parentheses]: with $\beta = \alpha(1 - \alpha)$: mmmm $(1 - 5\beta + 5\beta^2)$ 0.40/0.40; mmmr $(2\beta - 6\beta^2)$ 0.16/0.17; rmmr (β^2) 0.04/0.03; mmrr $(2\beta - 6\beta^2)$ 0.09/0.09; mmrm + rmrr $(2\beta^2 + 2\beta^2)$ 0.17/0.17; rmrm $(2\beta^2)$ 0.08/0.06; rrrr (β^2) 0.01/0.01; mrrr $(2\beta^2)$ 0.03/0.03; mrrm $(\beta - 3\beta^2)$ 0.03/0.04.

The observation of an effective chirality transfer in one case (*rac*-**12**) and the complete absence of enantiomorphic site control in the other (*meso*-**12**) under otherwise nearly identical reaction conditions allowed us to distinguish between the chiral and achiral metallocene catalyst precursors by means of the stereochemical analysis of the obtained polypropylene and thus to assign the *rac*- and *meso*-**12** diastereoisomers as described and used above.

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Experimental

Reactions with organometallic compounds were carried out in inert atmosphere using Schlenk techniques (argon) or in a glove box (nitrogen). Solvents were dried and distilled under argon prior to use. – NMR: Bruker WP 200 SY [^{1}H, 200 MHz; ^{13}C, 50 MHz; ^1J(C,H) coupling constants (Hz) are given in parentheses]. – IR: Nicolet 5DXC FT. – MS: Varian MAT CH7 and Finnigan 8200 MAT (exact mass). – Melting points (uncorrected): sealed glass capillaries. – Elemental analyses: Institut für Anorganische Chemie der Universität Würzburg. – Butadiene – magnesium[8], the fulvenes 7[12,21], and methylalumoxane[15] were prepared according to literature procedures.

(2-Propenyl)cyclopentadienyllithium (**2**): To a solution of cyclopentadienylsodium (31.0 g, 0.35 mol) in 500 ml of tetrahydrofuran 42.5 g (0.35 mol) of allyl bromide was added at −20°C. The mixture was stirred at −20°C for 24 h. Then 200 ml of a saturated aqueous ammonium chloride solution was added. The organic phase was separated and extracted four times with 100 ml of H_2O to remove the THF solvent. The remaining organic layer was dried with sodium sulfate and fractionated by vacuum distillation to yield 11.3 g (0.11 mol) of allylcyclopentadiene (mixture of isomers, b.p. 27 – 31°C/12 mbar). Methyllithium (60 ml of a 2 M ethereal solution, 0.12 mol) was added dropwise at 0°C to a solution of this product in ether. Stirring was continued at ambient temp. for 4 h. The resulting precipitate was recovered by filtration and washed with 50 ml of ether to yield 11.2 g (29%) of **2**. – ^{1}H NMR ([D_6]benzene/[D_8]THF, 4:1): δ = 3.32 [d, 2H, ^3J(H,H) = 6.9 Hz, $\mathrm{CpC}H_2\mathrm{CH{=}CH_2}$], 4.96 – 5.00 and 5.08 – 5.17 (2 m, 1H each, $\mathrm{CH{=}C}H_2$), 5.59 and 5.67 (2 m, 2H each, Cp), 6.06 – 6.27 (m, 1H, $\mathrm{C}H\mathrm{{=}CH_2}$). – ^{13}C NMR ([$D_6$]benzene/[$D_8$]THF, 4:1): δ = 35.3 (124, $\mathrm{CpCH_2}$), 103.1 (161, Cp), 103.6 (160, Cp), 112.6 (155, $\mathrm{CH{=}}C\mathrm{H_2}$), 118.0 (RCp, *ipso*-C), 141.0 (152, $\mathrm{CpCH_2}C\mathrm{H{=}}$).

Bis[η^5-(2-propenyl)cyclopentadienyl]zirconium Dichloride (**3a**): A solution of 8.92 g (79.5 mmol) of the lithium reagent **2** in 150 ml of THF was added dropwise at 0°C to a suspension of 8.62 g (37.0 mmol) of zirconium tetrachloride in 20 ml of toluene. Stirring was continued for 2 h at room temp. and then the solvent removed at −10°C in vacuo. The residue was dissolved in 150 ml of CH_2Cl_2 and the precipitated LiCl filtered off. The filtrate was concentrated in vacuo to ca. 5 ml. Then 50 ml of pentane was added. The resulting precipitate was recovered by filtration and dried in vacuo (**3a**, 9.1 g, 66%); m.p. 90 – 91°C. – ^{1}H NMR ([D]chloroform): δ = 3.26 (m, 4H, $\mathrm{CpC}H_2\mathrm{CH{=}}$), 4.86 – 4.97 (m, 4H, $\mathrm{CH{=}C}H_2$), 5.66 – 5.87 (m, 2H, $\mathrm{C}H\mathrm{{=}CH_2}$), 6.07 and 6.21 (2 m, 4H each, Cp). – ^{13}C NMR ([D]chloroform): δ = 34.0 (128, $\mathrm{CpCH_2CH{=}}$), 112.3 (172, Cp), 116.1 (155, $\mathrm{CH{=}}C\mathrm{H_2}$), 116.2 (172, Cp), 132.3 (RCp, *ipso*-C), 135.7 (155, $C\mathrm{H{=}CH_2}$). – IR (KBr): $\tilde{\nu}$ = 3108, 3092, 2977, 1637 (C=C), 988, 909 (=CH_2) cm^{-1}.

$C_{16}H_{18}Cl_2Zr$ (372.4) Calcd. C 51.59 H 4.87
Found C 50.21 H 4.97

Bis[η^5-(2-propenyl)cyclopentadienyl]hafnium Dichloride (**3b**): The synthesis was carried out as described for **3a** starting from 6.29 g (56.1 mmol) of **2** and 8.98 g (28.0 mmol) of $HfCl_4$ and employing 100 ml of THF and 40 ml of toluene. The metallocene dihalide **3b** was obtained in 87% yield (11.2 g) as a white powder, m.p. 79 – 80°C. – ^{1}H NMR ([D]chloroform): δ = 3.43 (m, 4H, $\mathrm{CpC}H_2\mathrm{CH{=}}$), 4.99 – 5.10 (m, 4H, $\mathrm{CH{=}C}H_2$), 5.80 – 6.00 (m, 2H, $\mathrm{C}H\mathrm{{=}CH_2}$), 6.10 and 6.21 (2 m, 4H each, Cp). – ^{13}C NMR ([D]chloroform): δ = 34.2 (129, $\mathrm{CpCH_2CH{=}}$), 111.2 (175, Cp), 115.2 (176, Cp), 116.5 (155, $\mathrm{CH{=}}C\mathrm{H_2}$), 130.6 (RCp, *ipso*-C), 136.2 (155, $C\mathrm{H{=}CH_2}$). – IR (KBr): $\tilde{\nu}$ = 3112, 3079, 2978, 1637 (C=C), 988, 908 (=CH_2) cm^{-1}.

$C_{16}H_{18}Cl_2Hf$ (459.69) Calcd. C 41.80 H 3.94
Found C 41.43 H 4.03

[η^5-(2:5 – 7-η-Heptentriyl)cyclopentadienyl][η^5-(2-propenyl)cyclopentadienyl]zirconium (**5a**): A mixture of **3a** (2.79 g, 7.49 mmol) and butadiene – magnesium (1.67 g, 7.49 mmol) was suspended at −78°C in 150 ml of precooled toluene. The slurry was allowed to slowly warm to room temp. during 12 h. The resulting red-brown suspension was concentrated in vacuo, the residue suspended in 50 ml of toluene and the suspension filtered. The clear red filtrate was concentrated in vacuo to a volume of ca. 5 ml. Pentane (15 ml) was added and the precipitate recovered by filtration to give **5a** (2.0 g, 75%); m.p. 170°C (dec.). – ^{1}H NMR ([D_6]benzene): heptentriyl: δ = 2.25 and 3.40 [m and pseudo t, 1H each, $\mathrm{CpC}H_2\mathrm{CH(Zr)}$], −0.05 [m, 1H, $\mathrm{CpCH_2C}H\mathrm{(Zr)}$], 2.60 and 2.70 [2 m, 1H each, $\mathrm{CH(Zr)C}H_2\mathrm{CH_2}$], 1.75 and 2.35 [2 m, 1H each, $\mathrm{CH(Zr)CH_2C}H_2$], 3.96 (m, 1H, $\mathrm{CH_2C}H\mathrm{CHCH_2}$), 5.00 (m, 1H, $\mathrm{CH_2CHC}H\mathrm{CH_2}$), 1.33 and 2.05 (2 m, 1H each, $\mathrm{CH_2CHCHC}H_2$); 2-propenyl: δ = 2.91 (m, 2H, $\mathrm{CpC}H_2\mathrm{CH{=}}$), 4.90 – 5.00 (m, 2H, $\mathrm{CH_2CH{=}C}H_2$), 5.65 – 5.90

(m, 1H, $CH_2CH{=}CH_2$); cyclopentadienyl: δ = 4.28, 4.82, 5.10–5.40 (8 m, 8H). The ^1H-NMR signal assignments are based on difference NOE data obtained from a solution of **5a** in $[D_6]$benzene at 300 K. – ^{13}C NMR ($[D_6]$benzene): heptentriyl: δ = 27.8 [127, $CpCH_2CH(Zr)$], 5.40 [128, $CpCH_2\text{-}\mathit{CH}(Zr)$], 52.0 [121, $CH(Zr)\mathit{CH}_2CH_2$], 34.0 [127, $CH(Zr)CH_2\mathit{CH}_2$], 104.4 (146, $CH_2\mathit{CH}CHCH_2$), 124.2 (147, $CH_2CH\mathit{CH}CH_2$), 37.8 (dd, 150, 146, $CH_2CHCH\mathit{CH}_2$); 2-propenyl: δ = 34.6 (127, $Cp\mathit{CH}_2CH{=}$), 115.2 (156, $CH_2CH{=}\mathit{CH}_2$), 138.0 (153, $CH_2\mathit{CH}{=}CH_2$); cyclopentadienyl: δ = 96.2, 99.6, 103.0, 104.8, 105.1, 105.2, 105.5, 106.3; 101.9 (s); 118.9 (s). – IR (KBr): $\tilde{\nu}$ = 3101, 3077, 2966, 1637 (C=C), 992, 907 ($=CH_2$) cm^{-1}. – Exact mass (EI): calcd. for $C_{20}H_{24}Zr$ 354.9120, found 354.9114 [M^+ (^{90}Zr)].

[η⁵-(2:5–7-η-Heptentriyl)cyclopentadienyl][η⁵-(2-propenyl)cyclopentadienyl]hafnium (**5b**) was prepared analogously to **5a** by treating 4.28 g (9.31 mmol) of **3b** with 2.07 g (9.31 mmol) of butadiene–magnesium in 100 ml of toluene. A yield of 3.0 g (73%) of **5b** was obtained, m.p. 190°C (dec.). – ^1H NMR ($[D_6]$benzene): heptentriyl: δ = 2.22 and 3.54 [m and pseudo t, 1H, each, $Cp\text{-}\mathit{CH}_2CH(Hf)$], –0.11 [m, 1H, $CpCH_2C\mathit{H}(Hf)$], 2.58 and 3.17 [2 m, 1H each, $CH(Hf)C\mathit{H}_2CH_2$], 1.68 and 2.70 [2 m, 1H each, $CH(Hf)CH_2C\mathit{H}_2$], 4.14 (m, 1H, $CH_2C\mathit{H}CHCH_2$), 5.00 (m, 1H, $CH_2CHC\mathit{H}CH_2$), 1.19 and 1.80 (2 m, 1H each, $CHCHC\mathit{H}_2$); 2-propenyl: δ = 2.92 (m, 2H, $CpC\mathit{H}_2CH{=}$), 4.90–4.99 (m, 2H, $CH_2CH{=}C\mathit{H}_2$), 5.65–5.86 (m, 1H, $CH_2C\mathit{H}{=}CH_2$); cyclopentadienyl: δ = 4.32 (m, 1H), 4.78 (m, 2H), 5.08–5.19 (m, 3H), 5.29 (m, 1H), 5.37 (m, 1H). – ^{13}C NMR ($[D_6]$benzene): heptentriyl: δ = 27.3 [130, $Cp\mathit{CH}_2CH(Zr)$], 7.6 [125, $CpCH_2\mathit{CH}(Zr)$], 52.7 [124, $CH(Zr)\mathit{CH}_2CH_2$], 33.3 [126, $CH(Zr)CH_2\mathit{CH}_2$], 104.4 ($CH_2\mathit{CH}CHCH_2$, signal coinciding with Cp resonances), 123.8 (144, $CH_2CH\mathit{CH}CH_2$), 35.2 (dd, 153, 143, $CH_2CHCH\mathit{CH}_2$); 2-propenyl: δ = 34.5 (127, $Cp\mathit{CH}_2CH{=}$), 115.2 (155, $CH_2CH{=}\mathit{CH}_2$), 138.0 (153, $CH_2\mathit{CH}{=}CH_2$); cyclopentadienyl: δ = 94.7, 98.2, 102.0, 104.4 (double intensity); 105.1 (CpCH and *ipso*-C), 105.6, 106.1, 117.7 (s). – IR (KBr): $\tilde{\nu}$ = 3102, 3077, 2973, 1637 (C=C), 991, 908 ($=CH_2$) cm^{-1}. – Exact mass (EI): calcd. for $C_{20}H_{24}Hf$ 444.1346, found 444.1346 [M^+ (^{180}Hf)].

$C_{20}H_{24}Hf$ (442.9) Calcd. C 54.24 H 5.46
Found C 52.12 H 5.55

Reaction of 6,6-Pentamethylenefulvene (**7a**) *with Phenyllithium:* The solution of **7a** (0.75 g, 5.13 mmol) in 10 ml of ether was cooled to 0°C. A 0.8 M ethereal phenyllithium solution (7.7 ml, 6.15 mmol) was added dropwise with stirring. After 3 h at room temp. the mixture was filtered and the filtrate concentrated in vacuo to give 0.50 g (43%) of the addition product **6**. The substituted cyclopentadienyllithium compound was only characterized by its ^1H-NMR spectrum in $[D_6]$benzene/$[D_8]$THF (4:1): δ = 1.55, 1.85 and 2.45 (3 m, 10H, CH_2), 5.88 and 5.99 (2 pseudo-t, 2H each, Cp), 7.05 (m, 1H), 7.23 (m, 2H), 7.57 (m, 2H, Ph).

(1-Cyclohexen-1-yl)cyclopentadienyllithium (**8a**): The solution of lithium diisopropylamid (LDA, 3.90 g, 36.4 mmol) in 300 ml of THF was cooled to –78°C. A solution of 6.43 g (44.0 mmol) of 6,6-pentamethylenefulvene (**7a**) in 30 ml of ether was added. The mixture was allowed to warm to room temp. and then stirred for an additional 20 h. The solvent was removed in vacuo, the residue suspended in 100 ml of ether and the resulting solid recovered by filtration and dried in vacuo to yield 5.6 g (83%) of the **8a**. – ^1H NMR ($[D_6]$benzene/$[D_8]$THF, 4:1): δ = 1.64–1.70 (m, 4H, CH_2), 2.17 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 5.77 and 5.95 (2 m, 2H each, Cp), 5.81 (m, 1H, $CpC{=}C\mathit{H}{-}CH_2$). – ^{13}C NMR ($[D_6]$benzene/$[D_8]$THF, 4:1): δ = 23.9 (124, CH_2), 24.3 (126, CH_2), 26.3 (124, CH_2), 28.4 (126, CH_2), 100.7 (159, Cp), 103.8 (159, Cp), 112.1 (152, $CpC{=}\mathit{CH}CH_2$), 122.9 (RCp, *ipso*-C, 135.3 ($Cp\mathit{C}{=}CHCH_2$).

Bis[η⁵-(1-cyclohexen-1-yl)cyclopentadienyl]zirconium Dichloride (**9a**): A solution of **8a** (5.59 g, 36.7 mmol) in 100 ml of THf was added at 0°C to a suspension of $ZrCl_4(thf)_2$ (5.52 g, 16.0 mmol) during 30 min. Stirring was continued for 12 h at ambient temperature. Then the solvent was removed in vacuo. The orange residue was taken up in 200 ml of dichloromethane and filtered. The filtrate was concentrated in vacuo to a volume of ca. 10 ml. Then 50 ml of pentane was added to precipitate the product. The resulting solid was recovered by filtration, washed twice with pentane (20-ml portions each), and dried in vacuo; yield 5.4 g (74%) of **8a**; m.p. 156–158°C. – ^1H NMR ([D]chloroform): δ = 1.50–1.64 (m, 8H, CH_2), 2.09–2.19 (m, 8H, CH_2), 6.09 (m, 2H, $CpC{=}C\mathit{H}$), 6.15 and 6.29 (2 m, 4H each, Cp). – ^{13}C NMR ([D]chloroform): δ = 22.4 (127, CH_2), 22.9 (127, CH_2), 25.9 (127, CH_2), 27.1 (126, CH_2), 112.6 (173, Cp), 114.6 (175, Cp), 126.8 (153, $CpC{=}\mathit{C}H$), 130.5 (s); 133.2 (s). – IR (KBr): $\tilde{\nu}$= 3105, 2931, 1636 (C=C), 841 s (=C–H) cm^{-1}.

$C_{22}H_{26}Cl_2Zr$ (452.55) Calcd. C 58.38 H 5.79
Found C 58.14 H 5.95

(2-Methyl-1-propenyl)cyclopentadienyllithium (**8b**): A solution of LDA (4.42 g, 41.3 mmol) in 300 ml of THF was cooled to –78°C. A solution of 6-isopropylfulvene (**7b**, 7.02 g, 58.4 mmol) in 20 ml of ether was added dropwise during 0.5 h, and then the mixture was warmed to room temp. and stirred for an additional 22 h. The solvent was removed in vacuo and the residue suspended in 50 ml of ether. The suspension was rapidly stirred for 2 h until a fine precipitate was obtained. The solid was recovered by filtration and dried in vacuo to give 4.9 g (94%) of **8b**. – ^1H NMR ($[D_6]$benzene/$[D_8]$THF, 4:1): δ = 1.84 and 1.96 [2 s, 3H each, $=C(CH_3)_2$], 5.84 and 5.93 (2 m, 2H each, Cp), 6.26 (s, 1H, $CpC\mathit{H}{=}$). – ^{13}C NMR ($[D_6]$benzene/$[D_8]$THF, 4:1): δ = 20.1 (125, CH_3), 27.5 (127, CH_3), 104.2 (160, Cp), 105.4 (160, Cp), 119.5 [$CH{=}\mathit{C}(CH_3)_2$], 120.3 (RCp, *ipso*-C), 124.7 (145, $Cp\mathit{C}H{=}$).

Bis[η⁵-(2-methyl-1-propenyl)cyclopentadienyl]zirconium Dichloride (**9b**): A solution of 4.91 g (38.9 mmol) of **8b** in 100 ml of THF was added dropwise at 0°C to a suspension of $ZrCl_4(thf)_2$ (5.45 g, 15.8 mmol) in 30 ml of toluene. The resulting yellow solution was stirred for 15 h at room temperature. Then the solvent was removed in vacuo. The viscous residue was taken up in 100 ml of pentane and the solution again concentrated in vacuo. Then the solid was suspended in 200 ml of dichloromethane and the suspension filtered. The filtrate was concentrated in vacuo to a volume of ca. 50 ml and then kept for several h at –30°C to allow for crystallization of the product. The crystalline solid was recovered by filtration and dried in vacuo. Yield of **9b** 4.2 g (66%), m.p. 177–179°C. – ^1H NMR ([D]chloroform): δ = 1.90 [d, 6H, $^4J(H,H)$ = 1.4 Hz, CH_3], 1.91 [d, 6H, $^4J(H,H)$ = 1.7 Hz, CH_3], 6.06 (m, 2H, $CpC\mathit{H}{=}$), 6.29 and 6.34 (2 m, 4H each, Cp). – ^{13}C NMR ([D]chloroform): δ = 20.1 (125, CH_3), 27.2 (124, CH_3), 118.5 (156, $Cp\mathit{C}H{=}$), 114.3 (175, Cp), 116.4 (175, Cp), 128.5 [$CpCH{=}\mathit{C}(CH_3)_2$], 137.9 (RCp, *ipso*-C). – IR (KBr): $\tilde{\nu}$ = 3206, 2967, 1658 (C=C), 840 cm^{-1}.

$C_{18}H_{22}Cl_2Zr$ (400.5) Calcd. C 53.98 H 5.53
Found C 53.73 H 5.55

6-(1-Phenylethyl)fulvene (**7c**): 2-Phenylpropionaldehyde (40.3 g, 0.30 mol) and cyclopentadiene (52.9 g, 0.80 mol) were dissolved in 300 ml of methanol. Then pyrrolidine (24.9 g, 0.35 mol) was slowly added at 0°C. The mixture was then stirred for 90 min at room temp., then hydrolyzed with glacial acetic acid (21.0 g, 0.35 mol) at 0°C. The product was given to a mixture of ether/H_2O (100 ml each). The organic layer was separated and the aqueous layer extracted with two 50-ml portions of ether. The combined organic solutions were washed with 100 ml of brine and then dried with sodium sulfate. The solvent was removed in vacuo (water aspirator) and the remaining product distilled to give 13.0 g of **7c** (24%), b.p. 90–93°C (1 mbar). – ^{1}H NMR ([D$_6$]benzene): δ = 1.24 (d, 3H, CH$_3$), 3.94 [m, 1H, *C*H(Ph)CH$_3$], 6.18 (m, 2H), 6.42 (m, 1H), 6.56 (m, 2H), 6.99–7.16 (m, 5H, Ph). – ^{13}C NMR ([D$_6$]benzene): δ = 21.4 (127, CH$_3$), 40.9 [130, *C*H(Ph)CH$_3$], 119.6 (162) and 126.7 (162, cyclopentadiene), 126.6 (162), 127.5 (157), 128.9 (159, Ph), 131.4 (166) and 133.9 (164, cyclopentadiene), 144.3 (s), 144.7 (s), 145.7 [155, C=*C*HCH(Ph)CH$_3$]. – IR (film): $\tilde{\nu}$ = 3071, 3027, 2968, 1644 (C=C), 1473, 1077, 886, 765 cm^{-1}.

$C_{14}H_{14}$ (182.25) Calcd. C 92.26 H 7.74 Found C 92.38 H 7.75

[(E)-2-Phenyl-1-propenyl]cyclopentadienyllithium (**8c**): **7c** (5.58 g, 30.6 mmol) was added dropwise during 30 min to a solution of LDA (3.28 g, 30.6 mmol) in 100 ml of THF at –78°C. The solution was allowed to warm to room temp. and was stirred for 12 h. The solvent was removed in vacuo. The viscous red residue was taken up in 100 ml of ether and the solution rapidly stirred for 3 h. The white solid obtained was recovered by filtration and dried in vacuo to give 3.6 g of **8c** (65%). – ^{1}H NMR ([D$_6$]benzene/[D$_8$]THF, 4:1): δ = 2.38 [d, 3H, ^1J(H,H) = 0.72 Hz, CH$_3$], 6.09 and 6.28 (2 m, 2H each, Cp), 6.98 (m, 1H, Ph), 7.11–7.18 (m, 3H, Ph and CpC*H*=), 7.47 (m, 2H, Ph). – ^{13}C NMR ([D$_6$]benzene/[D$_8$]THF, 4:1): δ = 17.9 (125, CH$_3$), 105.9 (160, Cp), 107.5 (159, Cp), 119.6 (RCp, *ipso*-C), 121.4 [CH=*C*(Ph)CH$_3$], 124.3 (160, Ph), 125.1 (157, Ph), 128.2 (158, Ph and CpCH=), 147.2 (Ph, *ipso*-C).

Bis{η^5-[(E)-2-phenyl-1-propenyl]cyclopentadienyl}zirconium Dichloride (**9c**): A solution of **8c** (3.60 g, 19.8 mmol) in 100 ml of THF was added dropwise at 0°C during 1 h to a suspension of ZrCl$_4$(thf)$_2$ (3.42 g, 9.90 mmol) in 40 ml of toluene. The mixture was then stirred for 2 d at room temperature. The solvent was removed in vacuo. The residue was taken up in 50 ml of CH$_2$Cl$_2$ and filtered. The clear filtrate was concentrated in vacuo to a volume of ca. 25 ml and then the product crystallized at –30°C. Filtration yielded 4.1 g (79%) of **9c**, m.p. 169–170°C. – ^{1}H NMR ([D]chloroform): δ = 2.29 [d, 6H, ^4J(H,H) = 1.3 Hz, CH$_3$], 6.38 (m, 4H, Cp: C*H*–CH–C–R), 6.51 (2 m, 4H, Cp: CH–C*H*–C–R), 6.59 (bs, 2H, CpC*H*=), 7.20–7.45 (2 m, 10H, Ph). The stereochemical assignment (*E* isomer) was based on NOE-difference spectra of **9c** in [D$_6$]benzene solution at 300 K. – ^{13}C NMR ([D]chloroform): δ = 18.3 (127, CH$_3$), 114.6 (175, Cp), 116.9 (175, Cp), 120.8 (155, CpCH=), 126.1 (158) and 127.5 (160, Ph), 128.2 (RCp, *ipso*-C), 128.4 (159, Ph), 139.4 [CH=*C*(Ph)CH$_3$], 143.5 (Ph, *ipso*-C). – IR (KBr): $\tilde{\nu}$ = 3104, 3083, 3047, 3028, 2957, 1597 (C=C), 841 (=CH) cm^{-1}.

$C_{28}H_{26}Cl_2Zr$ (524.6) Calcd. C 64.10 H 4.99
Found C 63.67 H 4.98

[(Z)-1-Phenyl-1-propenyl]cyclopentadienyllithium (**8d**): A solution of 6-ethyl-6-phenylfulvene (**7d**) in 20 ml of THF was added to a solution of LDA (3.69 g, 59.4 mmol) in 20 ml of THF at –78°C. The solution was then stirred for 20 h at room temperature. The solvent was removed in vacuo and the residue suspended in 200 ml of ether. The resulting precipitate was recovered by filtration and dried in vacuo. Yield of **8d**: 9.5 g (85%). – ^{1}H NMR ([D$_6$]benzene/[D$_8$]THF, 4:1): δ = 1.75 [d, 3H, ^3J(H,H) = 7.0 Hz, =CHC*H*$_3$], 5.97 (bs, 4H, Cp), 6.03 (q, 1H, =C*H*–CH$_3$), 7.15 (m, 1H), 7.29 (m, 2H) and 7.44 (m, 2H, Ph). – ^{13}C NMR ([D$_6$]benzene/[D$_8$]THF, 4:1): δ = 15.2 (125, =CH–*C*H$_3$), 103.6 (160, Cp), 104.4 (160, Cp), 110.9 (152, =*C*HCH$_3$), 123.2 (RCp, *ipso*-C), 126.0 (160), 127.7 (158) and 130.4 (158, Ph), 141.9 [Cp*C*(Ph)=], 143.8 (Ph, *ipso*-C).

Bis{η^5-[(E)-1-phenyl-1-propenyl]cyclopentadienyl}zirconium Dichloride (**9d**): A solution of **8d** (4.08 g, 21.6 mmol) in 80 ml of THF was added dropwise to a suspension of ZrCl$_4$(thf)$_2$ (3.74 g, 10.8 mmol) in 30 ml of toluene at 0°C. The mixture was then stirred for 10 h at room temperature. The solvent was removed in vacuo and the residue extracted with 100 ml of dichloromethane. Lithium chloride was removed by filtration and the filtrate concentrated in vacuo to a volume of ca. 20 ml. Pentane (10 ml) was added and the product allowed to crystallize at –30°C during several h. Complex **9d** was recovered by filtration and dried in vacuo. Yield 4.2 g (74%), m.p. 122 to 124°C. – ^{1}H NMR ([D]chloroform): δ = 1.58 (d, 6H, =CHC*H*$_3$), 6.03 (m, 8H, Cp), 6.16 (q, 2H, =C*H*–CH$_3$), 7.05–7.35 (m, 10H, Ph). The stereochemical assignment (CH$_3$ and Ph *cis*-positioned at the C=C bond) was based on the NOE difference spectra of **9d** in [D]chloroform at 300 K. – ^{13}C NMR ([D]chloroform): δ = 15.2 (127, CH$_3$), 113.5 (174, Cp), 114.5 (175, Cp), 126.9 (153, =*C*HCH$_3$), 127.3 (160), 128.3 (160) and 129.7 (159, Ph), 132.9 (RCp, *ipso*-C), 134.8 [Cp*C*(Ph)=], 138.3 (Ph, *ipso*-C). – IR (KBr): $\tilde{\nu}$ = 3118, 3101, 3019, 2970, 1598 (C=C), 824, 816 cm^{-1}.

$C_{28}H_{26}Cl_2Zr$ (524.6) Calcd. C 64.10 H 5.00
Found C 63.94 H 5.09

Bis{η^5-[3-(9-borabicyclo[3.3.1]non-9-yl)propyl]cyclopentadienyl}zirconium Dichloride (**10a**): To a solution of **3a** (1.12 g, 4.59 mmol) in 80 ml of toluene was added a solution of 9-borabicyclo[3.3.1]nonane (9-BBN) in 30 ml of THF. The solution was kept at room temp. for 12 h. Then the clear solution was concentrated in vacuo to a volume of ca. 40 ml. The mixture was kept at –30°C for several hours during which time small white needles of **10a** were obtained. Filtration gave 2.7 g (95%) of **10a**, m.p. 146–148°C. – ^{1}H NMR ([D$_6$]benzene): δ = 1.17 [m, 4H, CH$_2$B(C*H*)$_2$], 1.36 [t, 4H, ^3J(H,H) = 7.2 Hz, CH$_2$C*H*$_2$B(CH)$_2$], 1.59–1.87 (m, 28H, 12 × CH$_2$ of 9-BBN and CpCH$_2$C*H*$_2$), 2.75 [t, 4H, ^3J(H,H) = 7.5 Hz, CpC*H*$_2$CH$_2$], 5.87 and 6.01 (2 m, 4H each, Cp). – ^{13}C NMR ([D$_6$]benzene): δ = 23.6 (129, 4 × CH$_2$ of 9-BBN), 26.3 (126, CpCH$_2$*C*H$_2$), 28.3 [CH$_2$*C*H$_2$B(CH)$_2$, broadened by the adjacent boron nucleus], 31.4 [129, CH$_2$B(*C*H)$_2$, broadened by the adjacent boron nucleus], 33.5 (126, 8 × CH$_2$ of 9-BBN), 33.6 (126, Cp-*C*H$_2$CH$_2$), 111.8 (173, Cp), 117.1 (173, Cp), 134.7 (RCp, *ipso*-C). – IR (KBr): $\tilde{\nu}$ = 3104, 2923, 847, 815, 710 cm^{-1}. – MS (EI): *m/z* (%) = 614 [M$^+$] (11), 579 (3), 493 (5), 398 (6), 265 (89), 225 (21), 121 (42), 41 (100).

$C_{32}H_{48}B_2Cl_2Zr$ (616.4) Calcd. C 62.34 H 7.85
Found C 61.85 H 7.67

Bis{η^5-[3-(9-borabicyclo[3.3.1]non-9-yl)propyl]cyclopentadienyl}hafnium Dichloride (**10b**): The synthesis of **10b** was carried out analogously to **10a** by treating **3b** (0.69 g, 1.50 mmol) with 9-BBN (0.37 g, 3.00 mmol) in 25 ml of toluene. Complex **10b** (1.0 g, 96%) was obtained as a white microcrystalline solid; m.p. 130–132°C. – ^{1}H NMR ([D$_6$]benzene): δ = 1.17 [m, 4H, CH$_2$B(C*H*)$_2$], 1.36 [t, 4H, ^3J(H,H) = 7.3 Hz, CH$_2$C*H*$_2$B(CH)$_2$], 1.58–1.87 (m, 28H, 12 × CH$_2$ of 9-BBN and Cp-CH$_2$C*H*$_2$), 2.77 [t, 4H, ^3J(HH) = 7.5 Hz, CpC*H*$_2$CH$_2$], 5.70 and 5.91 (2 m, 4H each, Cp). – ^{13}C NMR ([D$_6$]benzene): δ = 23.6 (127, 4 × CH$_2$ of 9-BBN), 26.5 (127, CpCH$_2$*C*H$_2$), 28.2 [CH$_2$*C*H$_2$B(CH)$_2$, broadened by the adjacent boron nucleus], 31.4 [CH$_2$B(*C*H)$_2$, broadened by the adjacent boron nucleus], 33.5 (128, 8 × CH$_2$ of 9-BBN and Cp*C*H$_2$CH$_2$), 110.7 (175, Cp), 115.8 (173, Cp), 132.7 (RCp, *ipso*-C). – IR (KBr): $\tilde{\nu}$ = 3107, 2925, 1213, 849, 817, 711 cm^{-1}.

$C_{32}H_{48}B_2Cl_2Hf$ (703.7) Calcd. C 54.61 H 6.87
Found C 54.22 H 7.26

{η^5-[3-(9-Borabicyclo[3.3.1]non-9-yl)propyl]cyclopentadienyl}-[η^5-(2:5–7-η-heptentriyl)cyclopentadienyl]zirconium (**11a**): To a solution of **5a** (0.60 g, 1.69 mmol) in 5 ml of toluene was added a solution of 9-BBN (0.20 g, 1.69 mmol) in 15 ml of toluene. The

orange solution was kept at room temp. for 24 h. The solvent was removed in vacuo and the viscous residue suspended in 20 ml of pentane. After several hours of rapid stirring the precipitate had solidifed to allow collection by filtration to give 0.70 g (90%) of **11a**, m.p. 200°C (dec.). – ^{1}H NMR ([D$_6$]benzene): δ = 0.05 [m, 1H, CpCH$_2$C*H*(Zr)], 1.18 [m, 2H, CH$_2$B(C*H*)$_2$], 1.30–1.46 [m, 3H, C*H*$_2$B(CH)$_2$ and 1H of CH(Zr)CH$_2$CH$_2$CHCHC*H*$_2$], 1.59–2.00 [m, 15H, 6 × CH$_2$ of 9-BBN, CpCH$_2$C*H*$_2$CH$_2$B and 1H of CH(Zr)CH$_2$C*H*$_2$CH], 2.06 [m, 1H of CH(Zr)CH$_2$CH$_2$CHCHC*H*$_2$], 2.23 (m, 2H, CpC*H*$_2$CH$_2$CH$_2$B), 2.39 and 3.45 [m and pseudo t, 1H each, CpC*H*$_2$CH(Zr)], 2.38 [m, 1H of CH(Zr)CH$_2$C*H*$_2$CH], 2.58–2.81 [m, 2H, CpCH$_2$CH(Zr)C*H*$_2$], 4.02 (m, 1H, CH$_2$C*H*CHCH$_2$), 4.31 (m, 1H, Cp), 4.90 (m, 1H, Cp), 4.95–5.15 (m, 1H, CH$_2$CHC*H*CH$_2$), 5.02 (m, 1H, Cp), 5.21 (m, 2H, Cp), 5.28 (m, 1H, Cp), 5.33 (m, 1H, Cp), 5.40 (m, 1H, Cp). – ^{13}C NMR ([D$_6$]benzene): δ = 5.5 [125, CpCH$_2$*C*H(Zr)], 23.6 (125, 2 × CH$_2$ of 9-BBN), 27.8 (127, CH$_2$), 27.9 (127, CH$_2$), 28.0 [CH$_2$CH$_2$B(CH)$_2$, broadened by the adjacent boron nucleus], 31.4 [CH$_2$B(*C*H)$_2$, broadened by the adjacent boron nucleus], 33.5 (126, 4 × CH$_2$ of 9-BBN), 33.9 (*C*H$_2$), 34.1 (*C*H$_2$), 37.7 (dd, 155, 146, CH$_2$CHCH*C*H$_2$), 52.0 [125, CpCH$_2$CH(Zr)*C*H$_2$], 96.2 (173, Cp), 99.6 (173, Cp), 102.1 (RCp, *ipso*-C), 103.1 (Cp), 104.4 (Cp and CH$_2$*C*HCHCH$_2$), 104.9 (Cp), 105.1 (Cp), 105.5 (Cp), 106.1 (Cp), 122.3 (RCp, *ipso*-C), 124.3 (147, CH$_2$CH*C*HCH$_2$). – IR (KBr): ṽ = 3100, 2962, 1262, 796 cm^{-1}. – Exact mass (EI): calcd. for C$_{28}$H$_{39}$BZr 476.2188, found 476.2184 [M$^+$ (^{90}Zr,^{11}B)].

{η^5-[3-(9-Borabicyclo[3.3.1]non-9-yl)propyl]cyclopentadienyl}[η^5-(2:5–7-η-heptentriyl)cyclopentadienyl]hafnium (**11b**): The synthesis of **11b** was performed as described for **11a** by treating **5b** (0.56 g, 1.26 mmol) with 9-BBN (0.15 g, 1.26 mmol) in 20 ml of toluene. The addition reaction was complete after 24 h. A 86% yield of **11b** (0.6 g) was obtained; m.p. 208°C (dec.). – ^{1}H NMR ([D$_6$]benzene): δ = 0.17 [m, 1H, CpCH$_2$C*H*(Hf)], 1.14–1.26 [m, 3H, CH$_2$B(C*H*)$_2$ and 1H of CH$_2$CHCHC*H*$_2$], 1.36 [m, 2H, CH$_2$C*H*$_2$B(CH)$_2$], 1.59–2.05 (m, 16H, 6 × CH$_2$ of 9-BBN, 1H of CH$_2$CHCHC*H*$_2$, 1H of C*H*$_2$CHCHCH$_2$ and CpCH$_2$C*H*$_2$CH$_2$B), 2.24 (m, 2H, CpC*H*$_2$CH$_2$CH$_2$B), 2.28 and 3.57 [m and pseudo-t, 1H each, CpC*H*$_2$CH(Hf)], 2.38 (m, 1H of C*H*$_2$CHCHCH$_2$), 2.66 and 3.19 [2 m, 1H each, CpCH$_2$CH(Hf)C*H*$_2$], 4.18 (m, 1H, CH$_2$C*H*CHCH$_2$), 4.35 (m, 1H, Cp), 4.83 (m, 1H, Cp), 4.92 (m, 1H, Cp), 4.98–5.12 (m, 1H, CH$_2$CHC*H*CH$_2$), 5.15 (m, 2H, Cp), 5.23 (m, 1H, Cp), 5.30 (m, 1H, Cp), 5.40 (m, 1H, Cp). – ^{13}C NMR ([D$_6$]benzene): δ = 7.6 [127, CpCH$_2$*C*H(Hf)], 23.6 (126, 2 × CH$_2$ of 9-BBN), 27.4 (CH$_2$), 27.8 (CH$_2$), 28.4 (CpCH$_2$CH$_2$*C*H$_2$B, broadened by the adjacent boron nucleus), 31.5 [CH$_2$B(*C*H)$_2$, broadened by the adjacent boron nucleus], 33.4 (CH$_2$), 33.5 (126, 4 × CH$_2$ of 9-BBN), 33.8 (CH$_2$), 35.2 (dd, 151, 144, CH$_2$CHCH*C*H$_2$), 52.7 [125, CpCH$_2$CH(Hf)*C*H$_2$], 94.7 (175, Cp), 98.2 (174, Cp), 102.2 (Cp), 104.2 (CH$_2$*C*HCHCH$_2$), 104.4 (Cp), 104.5 (Cp), 104.8 (Cp), 105.1 (RCp, *ipso*-C), 105.7 (2 × Cp), 121.0 (RCp, *ipso*-C), 123.8 (CH$_2$CH*C*HCH$_2$). – IR (KBr): ṽ = 3101, 2922, 1261, 794 cm^{-1}. – Exact mass (EI): calcd. for C$_{28}$H$_{39}$BHf 566.2615, found 566.2620 [M$^+$ (^{180}Hf,^{11}B)].

Bis{η^5-[1-(9-borabicyclo[3.3.1]non-9-yl)-2-methylpropyl]cyclopentadienyl}zirconium Dichloride (**12**): 9-BBN (1.15 g, 9.40 mmol) and complex **9b** (1.88 g, 4.69 mmol) were mixed as solids. Toluene (20 ml) was added, and the mixture was kept in a sealed Schlenk tube at 55°C for 18 h. The resulting clear yellow solution was concentrated in vacuo to ca. half of its volume and then kept at –30°C for 2 d. The resulting white precipitate was collected by filtration and dried in vacuo to give 2.7 g (88%) of a 1:1 mixture of *rac*- and *meso*-**12**, m.p. 145–148°C. Three subsequent fractional crystallizations from 5 ml of toluene at 5°C gave the *meso*-**12** isomer >99:1 pure. The remaining mother liquor contained the complexes *meso*-**12**:*rac*-**12** in a ≈ 15:85 ratio. Crystallization at –15°C gave a sample of *rac*-**12** that had a >99:1 diastereomeric purity. – ^{1}H NMR ([D$_6$]benzene): *rac*-**12**: substituent: δ = 1.04 (d, 6H, CH$_3$), 1.20 (d, 6H, CH$_3$), 1.35 [m, 4H, CH$_2$B(C*H*)$_2$], 1.50–1.94 (2 m, 24H, 12 × CH$_2$ of 9-BBN), 2.48 [m, 2H, C*H*(CH$_3$)$_2$], 3.44 [d, 2H, ^3J(H,H) = 3.7 Hz, CpC*H*]; cyclopentadienyl: δ = 5.76 (m, 4H), 5.97 (m, 2H), 6.15 (m, 2H), *meso*-**12**: δ = 1.03 (d, 6H, CH$_3$), 1.19 (d, 6H, CH$_3$), 3.43 [d, 2H, ^3J(H,H) = 3.5 Hz, CpC*H*]. The remaining resonances could not be distinguished from those of *rac*-**12**. – ^{13}C NMR ([D$_6$]benzene): *rac*-**12**: substituent: δ = 23.5 (4C, CH$_2$, 23.6 (2C, CH$_3$), 24.5 (2C, CH$_3$), 30.8 [2C, *C*H(CH$_3$)$_2$], 32.8 [4C, CpCHB(*C*H)$_2$, broadened by the adjacent boron nucleus], 33.9 (4C, CH$_2$), 34.3 (4C, CH$_2$), 47.4 (2C, Cp*C*HB-, broadened by the adjacent boron nucleus); cyclopentadienyl: δ = 108.8 (2C), 114.2 (2C), 114.6 (2C), 115.0 (2C), 140.4 (2 *ipso*-C). *meso*-**12**: The substituent signals were identical with those of the *rac*-**12** diastereomer; cyclopentadienyl: δ = 109.4 (2C), 113.9 (2C), 114.7 (4C), 140.4 (2 *ipso*-C). – IR (KBr): ṽ = 3104, 2954, 2885, 809 cm^{-1}.

meso-**12**: C$_{34}$H$_{52}$B$_2$Cl$_2$Zr (644.5)	Calcd.	C 63.35	H 8.13
	Found	C 62.87	H 8.30

Bis{η^5-[1-(9-borabicyclo[3.3.1]non-9-yl)-2-phenylpropyl]cyclopentadienyl}zirconium Dichloride (**13**): A mixture of complex **9c** (2.66 g, 5.07 mmol) and 9-BBN (1.24 g, 10.1 mmol) was suspended in 50 ml of toluene and kept in a sealed Schlenk tube at 60°C. After 12 h a clear solution was obtained from which a light yellow solid began to precipitate. After 5 d another portion of 9-BBN (0.60 g) was added and heating at 60°C continued for another 4 d. The reaction mixture was then concentrated in vacuo, the residue dissolved in ca. 150 ml of warm dichlormethane and the solution kept for 3 d at –30°C. The resulting solid was recovered by filtration and dried in vacuo to give 2.1 g (53%) of the **13a**/**13b** 1:1 mixture; m.p. 208–209°C. Two consecutive fractionating crystallizations from 20 ml of CH$_2$Cl$_2$ at 5°C furnished a product containing >99:1 of the diastereoisomer **13a**. From the filtrate crystallization at –30°C gave a 5:95 mixture of **13a**/**13b**. ^{1}H NMR ([D]chloroform): diastereomer **13a**: δ = 1.03, 1.45 and 1.70 (3 m, 28H, 9-BBN), 1.32 [d, 6H, ^3J(H,H) = 7.0 Hz, CH(Ph)C*H*$_3$], 3.45 [m, 2H, C*H*(Ph)-CH$_3$], 3.82 [d, 2H, ^3J(H,H) = 8.7 Hz, CpC*H*], 6.02 (m, 2H, Cp), 6.20 (m, 4H, Cp), 6.43 (m, 2h, Cp), 7.13–7.24 (m, 10H, Ph); diastereomer **13b**: δ = 1.08 and 1.33–1.96 (2 m, 28H, 9-BBN), 1.30 [d, 6H, ^3J(H,H) = 7.0 Hz, CH(Ph)C*H*$_3$], 3.47 [m, 2H, C*H*(Ph)-CH$_3$], 3.75 [d, 2H, ^3J(H,H) = 8.1 Hz, CpC*H*], 6.03 (m, 2H, Cp), 6.12 (m, 2H, Cp), 6.21 (m, 2H, Cp), 6.38 (m, 2H, Cp), 7.13–7.28 (m, 10H, Ph). – IR (KBr): ṽ = 3106, 2949, 2888, 823, 811, 700 cm^{-1}. – Elemental analysis of the **13a**/**13b** 1:1 mixture.

C$_{44}$H$_{56}$B$_2$Cl$_2$Zr (768.6)	Calcd.	C 68.75	H 7.34
	Found	C 67.05	H 7.23

Propene Polymerization Reactions (General Procedure): A 500-ml two-necked Schlenk flask was charged with the methylalumoxane cocatalyst. Toluene (250 ml) was added and the solution cooled to –50°C. Propene (30–35 ml) was condensed into the solution. The mixture was then thermostated at the temp. selected for the polymerization reaction and the zirconium catalyst component added as a toluene solution. After the chosen reaction time, the polymerization was terminated by adding the reaction mixture to excess aqueous hydrochloric acid in methanol (500 ml). Excess propene was evaporated. The polymer was recovered from the toluene phase and additional ether extracts from the aqueous solution.

Selected details of the propene polymerization reactions with *rac*- and *meso*-**12**-derived catalysts are given in Table 1. Typical parameters of the propene polymerization reactions with the methylalumoxane/**13a**- and -[**13b**]-derived catalysts are as follows: mg (mmol) zirconium catalyst used: 9.22 (0.012), [18.4 (0.024)]; g (mmol) methylalumoxane cocatalyst used: 1.29 (22.4), [1.40 (24.1)]; Al/Zr ratio: ca. 1800 [ca. 1000]; reaction temperature: −50°C [−50°C]; reaction time: 9 h [7 h]; g polypropylene recovered: 0.35 [2.0]; activity: 35 [130]; $\bar{M}_\eta$: not determined [15000].

CAS Registry Numbers

1: 106-95-6 / **2**: 132408-80-1 / **3a**: 85500-11-4 / **3b**: 85500-12-5 / **5a**: 132487-97-9 / **5b**: 132438-31-4 / **6**: 126116-89-0 / **7a**: 3141-04-6 / **7b**: 13912-68-0 / **7c**: 132408-82-3 / **7d**: 78405-52-4 / **8a**: 132408-81-2 / **8b**: 132408-83-4 / **8c**: 132408-84-5 / **8d**: 132408-85-6 / **9a**: 121002-79-7 / **9b**: 132408-88-9 / **9c**: 132408-91-4 / **9d**: 132408-92-5 / **10a**: 132408-86-7 / **10b**: 132408-89-0 / **11a**: 132438-30-3 / **11b**: 132408-90-3 / *rac*-**12**: 132408-93-6 / *meso*-**12**: 132408-94-7 / **13a**: 132408-87-8 / **13b**: 132487-98-0 / $ZrCl_4$: 10026-11-6 / $HfCl_4$: 13499-05-3 / $Mg(C_4H_6)$: 70809-00-6 / $ZrCl_4(thf)_2$: 21959-01-3 / cyclopentadienylsodium: 4984-82-1 / 2-phenylpropionaldehyde: 93-53-8 / cyclopentadiene: 542-92-7 / propene: 115-07-1 / isotactic polypropylene: 25085-53-4

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1) Dedicated to Professor *Paul Binger* on the occasion of his 60th birthday.

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