Group 4 ansa-metallocene Ziegler catalysts derived from trans-1,2-cycloalkylene-bis(indenyl)- and -bis(tetrahydroindenyl)MCl$_2$ systems: structural and reactivity studies [1]

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Abstract

A series of trans-1,2-cycloalkylene-bridged bis(indenyl)MCl$_2$ complexes (M = Ti, Zr, Hf) with bridging hydrocarbyl moieties ranging from five- to eight-membered rings, and their corresponding bis(tetrahydroindenyl)MCl$_2$ complexes were prepared. In each case a mixture of two racem-like (rl, rl') and one meso-like (ml) diastereoisomers was obtained. Chromatographic separation and recrystallization gave the pure ansa-bis(tetrahydroindenyl)TiCl$_2$ complexes **7a-ml, 7b-rl, 7b-ml**, and **7c-ml** with bridging cyclopentylene, cyclohexylene, and cycloheptylene moieties, respectively, that were characterized by X-ray diffraction. Activation of the Ti-, Zr-, and Hf-complexes with methylalumoxane gave active homogeneous Ziegler catalysts that were employed in propene polymerization reactions. In each case the meso-like diastereoisomers were practically inactive compared to the isomeric racem-like systems, as could be expected from the pronounced shielding of the metal center observed in the X-ray crystal structure analyses of the meso-like trans-1,2-cycloalkylene-bis[1-(4,5,6,7-tetrahydroindenyl)]TiCl$_2$ complexes. © 1997 Elsevier Science S.A.

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1. Introduction

The homogeneous Group 4 metallocene Ziegler catalysts are receiving an ever increasing attention lately [1]. Their performance as selective α-olefin polymerization catalysts depends very critically on the structure of the bent metallocene framework. For practical applications, where stereochemical control is essential, mostly ansa-metallocene systems are used [2]. Some efforts have been made to further improve the original Brintzinger ansa-metallocenes, the ethylene-bis(indenyl)- and -bis(tetrahydroindenyl)MX$_2$ systems [3] (see also Ref. [4]), by making them conformationally still more rigid. It was thought that this might be achieved by making the ethylene bridge of the ansa-metallocene system part of a carbocyclic or heterocyclic ring system [5,6] (for a discussion of the conformational properties of ansa-metallocene complexes see e.g. Ref. [7]; see also Ref.

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[1] Dedicated to Professor Hans J. Schäfer on the occasion of his 60th birthday.

[8]). As it turned out this did not in a general way lead to a markedly improved catalyst performance, but, as shown by Rieger and coworkers [6,7], surprisingly opened a substantial reactivity gap between (the stereoselective) racem-like diastereomeric systems and their (unselective) meso-like congeners. It was demonstrated for the singular example of the trans-1,2-cyclohexylene-bis(indenyl)ZrCl$_2$/methylalumoxane (MAO) catalyst system that the reactivity difference between the respective diastereomers was so pronounced that it was not necessary to remove the undesired meso-like isomer to obtain a highly isotactic polypropylene product. At the time when this observation was reported we had almost completed a similar study using the complete series of fused ring ansa-zirconocenes and selected examples of the corresponding ansa-titanocenes with annulated ring sizes ranging from five to eight [9]. This investigation provided a broader view of the reactivity and selectivity pattern of such systems. We also were able to obtain several of the cycloalkylene-bis(tetrahydroindenyl) titanocene dichloride catalyst precursors isomerically pure and characterized them by X-ray

diffraction, which gave us a basis for understanding the marked differences in catalyst behavior between the diastereomeric ansa-metallocene Ziegler systems.

2. Results and discussion

2.1. Synthesis of the metallocene complexes

The synthesis of the series of ring-fused ansa-metallocenes was carried out conventionally. The cycloalkenes were trans-dihydroxylated and then the diols converted to their ditosylates (1a–d). The tosylates 1 were then treated with a little over two molar equivalents of indenyl lithium. Usually the substitution reaction required several days in tetrahydrofuran at reflux temperatures to go to completion. In each case the 3-substir··· 1 cycloalkylene-bridged indene systems (2) we·ε ʰʊ̣ained. Subsequent deprotonation was achieved by ɑreatment with n-butyl lithium. The corresponding trans-1,2-bis(lithioindenylidene) cycloalkanes (3a–d) were isolated in good yields as oils and characterized by ^{1}H and ^{13}C NMR spectroscopy (for detail see Section 3). For the purpose of comparison (see below) we have also prepared the corresponding ligand system 3e by the same method starting from 1,2-propandiol (see Scheme 1).

The cycloalkylene-bridged bis-indenyl lithium reagents 3a–d were reacted with ZrCl₄·2THF in refluxing tetrahydrofuran (24 h). This gave rise in each case to the formation of a mixture of three diastereomeric ansa-metallocene complexes due to the presence of two homochiral stereogenic centers at the trans-cycloalkylene unit (relative stereochemistry R*,R*) and two newly formed planar chiral 1-substituted (inde-nyl)transition metal complex moieties. Thus, two of the ansa-metallocene diastereomers are characterized by stereochemical descriptors (R*,R*,p-R*,p-R*) and (R*,R*,p-S*,p-S*) respectively. Their metallocene

M = Zr, n = 1-4: 4a-d
M = Ti, n = 1-3: 6a-c
M = Hf, n = 2, 3: 8b,c

M = Zr, n = 1-4: 5a-d
M = Ti, n = 1-3: 7a-c
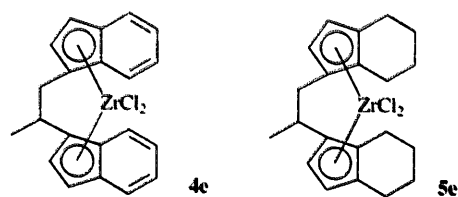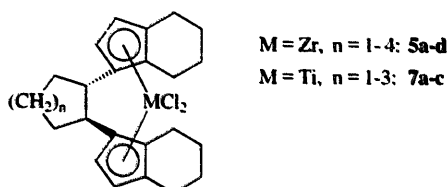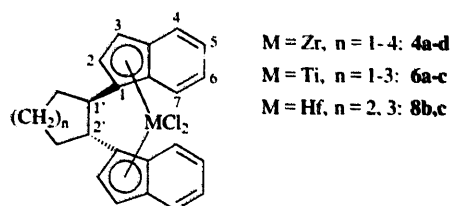
Scheme 2.

configuration is as in a rac-ansa-metallocene, and hence we have termed these isomers racem-like [i.e. 4a–d (rl) and 4a–d (rl')]. The remaining diastereoisomer has the relative configuration of (R*,R*,p-R*,p-S*); it consequently is termed meso-like [i.e. 4a–d (ml)] (for related stereochemical situations encountered at metallocene systems see e.g. Ref. [10]).

A closely related situation is found when the reagent 3e is reacted with zirconium-tetrachloride. Again, a mixture of three diastereoisomers is formed, two of which are racem-like [4e (rl), 4e (rl') with relative configurations (R*,p-R*,p-R*) and (R*,p-S*,p-S*) respectively] and the third is meso-like [4e (ml), (R*,p-R*,p-S*)] (see Scheme 2).

A statistical rl:rl':ml diastereomeric ratio is expected to be obtained in the ansa-metallocene formation unless
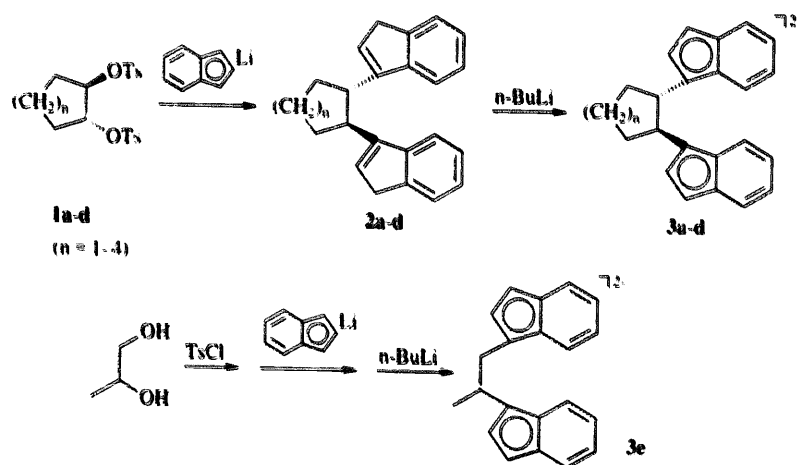
Scheme 1.

Table I

Diastereomeric ratios (rl:rl':ml) of the two racem-like and the meso-like diastereomeric Group 4 ansa-metallocenes as they were obtained directly from the syntheses

Compound	M	Yield (%)	M.p. (decomp., °C)	rl:rl':ml
4a	Zr	47	145	19:13:68
4b	Zr	44	~190	25:25:50
4c	Zr	60	174	25:15:60
4d	Zr	53	141	17:13:70
4e	Zr	86	163	40:14:44
8b	Hf	65	152	23:17:60
8c	Hf	54	155	16:3:81
6a	Ti	42	180	42:2:56
6b	Ti	30	216	15:11:74
6c	Ti	48	224	30:7:63

special stereochemically controlling factors are present. As can be seen from Table 1 in the case of the cycloalkylene-bis(1-indenyl)zirconium dichloride complexes 4a–d diastereomeric ratios close to statistical have indeed been obtained, although there seems to be a tendency to a slightly favored formation of the meso-like isomers in several cases. This is also observed in the ansa-hafnocene complexes 8b and 8c, that were prepared analogously. The ansa-zirconocene dichloride complex 4e seems to represent an example with a slightly different tendency of diastereoisomer formation. A markedly larger amount of one of the racem-like isomers is obtained, at the expense of the meso-like form. In all cases the racem-like and meso-like diastereoisomers could readily be distinguished by their ^{1}H and ^{13}C NMR spectra due to their characteristic molecular symmetry properties. Thus each of the C_2-symmetric racem-like diastereomers exhibits only a pair of indenyl 2- and 3-CH sets of signals, whereas the lower symmetry (C_1) of the meso-like forms gives rise to four such methine resonances (for details see Section 3).

Catalytic hydrogenation (H$_2$/Pt/CH$_2$Cl$_2$) [11] of 4a–e gave the corresponding ansa-alkylene-bis[1-(4,5,6,7-tetrahydroindenyl)]ZrCl$_2$ complexes in good yield. The diastereomeric ratio was, of course, not changed during this procedure except for close to negligible alterations caused by the work-up procedure.

The preparation of the ansa-titanocene complexes was carried out by reacting the deprotonated ligand systems 3a–c with TiCl$_3$, followed by oxidation using FeCl$_3$ [12]. The ansa-cycloalkylene-bis(indenyl)titanium dichlorides were then directly hydrogenated to give the corresponding bis(tetrahydroindenyl)TiCl$_2$ systems 7a–c in good yield after filtration through a short column of deactivated (silanated) silica gel. The rl:rl':ml diastereomeric ratios were found to be in a similar range as observed for the related zirconium complexes. Only

7a seems to be a notable exception exhibiting a relatively large content of one of the racem-like forms (see Table 1).

In the case of the zirconium and hafnium complexes our attempts to separate the isomers and obtain some of the ansa-metallocene diastereomerically pure have so far been without success. In contrast, chromatography at silanated silica gel provided us with pure samples of several of the major ansa-cycloalkylene-bis(tetrahydro-indenyl)titanocene dichloride complexes as single pure diastereoisomers. Thus, chromatography of the 7a (rl:rl':ml = 42:2:56) mixture with petrol–dichloromethane 10:1 furnished the pure major isomers 7a-rl (R_f = 0.41) and 7a-ml (R_f = 0.26). From the meso-like isomer, single crystals suitable for an X-ray crystal structure determination were obtained (see below). Similarly, the pure meso-like isomer and one of the racem-like isomers were isolated in sizeable quantities (see Section 3) by chromatography of the 7b mixture of diastereoisomers [see Table 1; R_f = 0.23 (7b-ml), 0.39 (7b-rl)]. In this case single crystals of both the major racem-like and the meso-like forms, that were suited for the X-ray crystal structure analysis, could be obtained by recrystallization from dichloromethane. Partial chromatographic separation of the 7c isomers was achieved similarly. Here the 7c-ml diastereomer was obtained pure (and as single crystals), whereas a 90:10 enriched 7c-rl–7c-rl' mixture was only obtained after chromatography and repeated recrystallization.

2.2. X-ray crystal structure analyses of the ansa-titanocene complexes

X-ray crystal structure analyses were carried out with the meso-like ansa-titanocene complexes 7a-ml and 7c-ml, and with the pair of racem-like and meso-like isomers 7b-rl and 7b-ml. In all these complexes the titanium center attains the usual pseudotetrahedral coordination geometry [13]. The Ti–Cp(centroid) distances are in the range between 2.05 Å and 2.10 Å, which is similar to that observed for the parent compounds ethylene-bis(tetrahydroindenyl)TiCl$_2$ (*meso*-9: 2.08 Å, *rac*-9: 2.10 Å) [14]. The racem-like complex 7b-rl is C_2-symmetric. The Ti–Cl distance is 2.3396(10) Å [15] and the Cl–Ti–Cl angle 94.71(6)°. The corresponding 7b-ml isomer shows very similar essential bonding features: Ti–Cl(1) = 2.360(2) Å, Ti–Cl(2) = 2.315(2) Å, Cl(1)–Ti–Cl(2) 94.35(7)°, Cp(centroid)–Ti–Cp(centroid) 129.3° (7b-rl: 129.0°). The structural similarity is much more pronounced for the 7b-rl–7b-ml pair than for the *rac*-9–*meso*-9 pair of the 'Brintzinger-ansa-titanocenes' (Cp(centroid)–Ti–Cp(centroid): 128.5°, 129.5°; Cl–Ti–Cl: 96.36°, 92.7°; α (angle between the planes of the annulated Cp-ring systems) 57.6°, 58.0° [14]. This may indicate that the annulated six-membered ring system
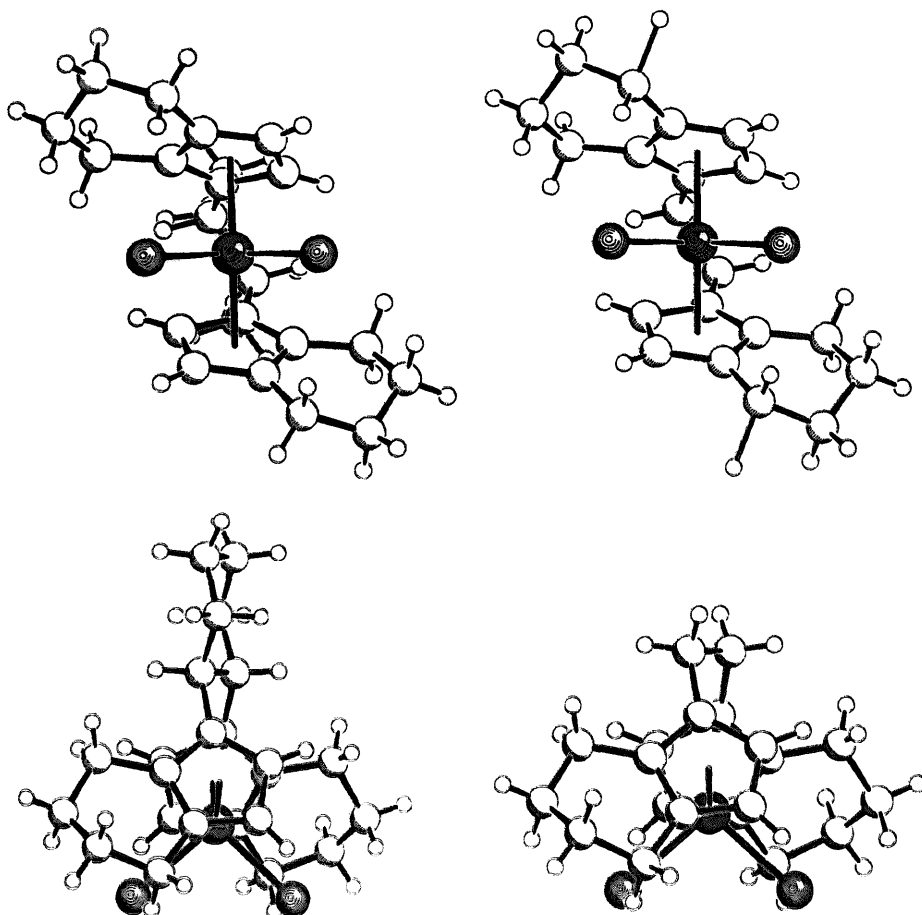
Fig. 1. Two projections of the molecular geometries of the ansa-titanocene dichlorides **7b-rl** (left) and *rac*-**9**, showing their close structural similarity.

indeed makes the ansa-metallocene more rigid. It appears that the residual conformational flexibility that is still featured with the unsubstituted ethylene-bridge, and thus allows for the differences in structural detail observed of the *rac*-**9**=*meso*-**9** pair, is lost upon introduction of the bridging ring systems, which leads to a remarkable similarity of the essential structural data in the complexes **7b-rl** and **7b-ml**. Nevertheless, there is a

remarkable structural similarity between the parent 'Brintzinger-complex' *rac*-**9** [14] and its cyclohexylene-bridged relative **7b-rl**. This very close structural relation is visualized in Fig. 1.

In the three meso-like complexes **7a–c-ml** the annulated tetrahydroindenyl six-membered ring systems are arranged in such a way that they perfectly shield one of the Ti=Cl moieties from above and below (see Fig. 2).

Table 2
Selected structural parameters of ansa-titanocene dichlorides

Compound	Ti–C(1) (Å)	Ti–C(2) (Å)	Cl–Ti–Cl (deg)	Ti–D (Å) [a]	D–Ti–D (deg)	α (deg) [b]
7a-ml	2.3586(8)	2.3162(8)	93.98(3)	2.095/2.101	130.3	57.7
7b-ml	2.360(2)	2.315(2)	94.35(7)	2.084/2.090	129.3	59.0
7b-rl	2.3396(10)	—	94.71(6)	2.102	129.0	57.1
7c-ml	2.356(4)	2.313(4)	95.0(2)	2.050/2.083	128.7	59.0
meso-**9** [c]	2.34(1)	2.35(2)	92.7(4)	2.076/2.081	129.5	58.0
rac-**9** [d]	2.3479(8)	—	96.36(2)	2.096	128.5	57.6

[a] D = Cp(centroid).
[b] Angle between the planes of the annulated Cp-ring systems.
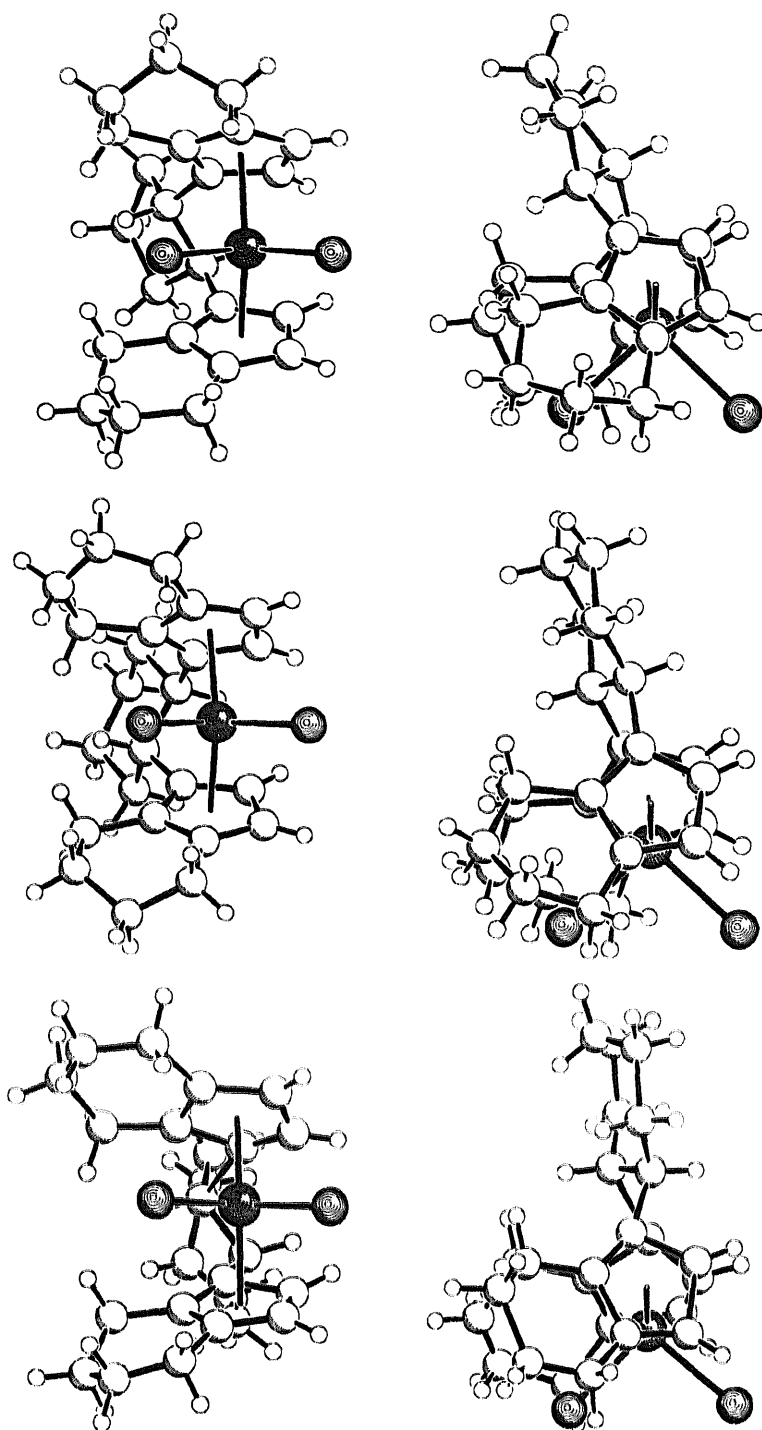[c] Data taken from Ref. [11].
[d] Data taken from Ref. [14].

Fig. 2. Two projections of the molecular geometries of the meso-like ansa-titanocene dichloride complexes 7a-ml (top), 7b-ml (center), and 7c-ml (bottom).

This sterical influence even shows up clearly in the Ti–Cl distances (Table 2). The Ti–Cl bond inside the 'tetrahydroindenyl sandwich' is markedly shorter (by about 0.04 Å) in each case. This rigid arrangement of the shielding annulated cyclohexene ligand moieties is likely to make the corresponding sectors in the active Ziegler catalysts derived from these systems inaccessible for both the incoming monomer (e.g. propene, see

below) and the growing polymer chain. It appears that the increased rigidity of the framework, introduced by the cycloalkylene connection, holds the tetrahydroindenyl six-membered rings consequently in a perfect shielding position in the meso-like complexes, which results in a dramatically reduced catalytic activity of the Ziegler catalysts derived from these diastereoisomers (see for a comparison Ref. [16]). The shielding is

marginally reduced on going from a five-membered bridge (**7a-ml**) through the six- to the seven-membered ring bridged system (**7c-ml**, see Fig. 2). In contrast, the racem-like ansa-metallocene system **7b-rl** shows no special or increased shielding of sectors at the front side of the bent metallocene wedge as compared to its parent compound *rac*-9 (see above).

2.3. Propene polymerization reactions

The ansa-metallocenes were activated by treatment with a large excess of MAO (Al/M ratios varied between 500–5000). Mostly the polymerization reactions were carried out in dilute toluene solution under 1.4 bar of propene. Under these conditions the racem-like ansa-titanocene complex **7a-rl** featured a propene polymerization activity of $a = 100$ g polypropylene/(g[Ti]h bar) at $0\,°C$. The obtained polymer is isotactic (^{13}C NMR methyl pentade analysis: enantiomorphic site control, 94% mmmm) [17] (also, for the statistical treatment of the obtained NMR data see Ref. [18]) and has a molecular weight of $\overline{M}_\eta \approx$ 32 000. Thus the rigidity of the **7a-rl** framework has lead to a slightly better catalyst performance as compared to the *rac*-9 reference ($a = 40$, 86% mmmmm, $\overline{M}_\eta \approx 13\,000$ at $-8\,°C$ [19]). As expected the corresponding meso-like ansa-titanocenes **7a-ml** and **7b-ml** showed no propene polymerization activity when activated by treatment with MAO. The **7c-ml**/MAO catalyst produced ca. 100 mg of a slightly isotactic polypropylene at $25\,°C$ (59% mmmm; $a = 26$). This is about the same isotacticity as was obtained in the propene polymerization reaction employing the 90% enriched **7c-rl** isomers ($a = 350$, 63% mmmm). So it cannot be excluded that the small observed **7c-ml** catalytic activity actually may have originated from a small **7c-rl** contamination.

We conclude that the diastereomeric cycloalkylene-fused ansa-titanocene complexes indeed exhibit an enormous difference in Ziegler catalyst activities. The racem-like systems show a normal activity towards propene polymerization, whereas the corresponding meso-like systems appear to be inactive. From the obtained structural information it seems likely that this large difference in reactivity at the active catalyst stage is mainly due to a very effective shielding of two C_s-symmetry related sectors above and below the bent metallocene σ-plane by the annulated tetrahydroindenyl six-membered rings, rigidly held in their position by the conformationally rather inflexible backbones of these very metallocenes.

Unfortunately, the corresponding racem-like and meso-like ansa-zirconocene dichloride diastereoisomers were not obtained as pure diastereoisomers. We have, however, obtained three mixtures of different composition of the *trans*-1,2-cycloheptylene-bis[1-(4,5,6,7-tetra-

Table 3

A comparison of the propene polymerization activities (in kg polymer/(g[Zr]h bar)) of the ansa-zirconocene dichloride/MAO Ziegler catalysts [a] in toluene solution at various temperatures

Metallocene	$-15\,°C$	$0\,°C$	$25\,°C$	$50\,°C$	$75\,°C$
4a	0.24	0.38	4.6	10.5	14.2
4b	0.36	1.13	9.4	22.1	24.8
4c	0.19	0.47	5.5	13.7	22.4
4d	0.11	0.21	1.3	3.3	2.4
4e	0.19	0.90	14.9	31.4	59.0
5a	0.04	0.18	0.74	6.5	8.9
5c	0.06	0.46	2.1	8.9	18.1
5e	0.56	0.76	5.4	27.8	36.4

[a] In each case the original mixture of the two racem-like and the meso-like isomers were used (see Table 1).

hydroindenyl)]ZrCl₂, **5c**. Fractionating crystallization of the original 25:15:60 mixture of the **5c-rl**, **5c-rl′**, and **5c-ml** isomers gave a mixture that was enriched in the meso-like form (12:7:81 ratio) plus a fraction that was depleted in this isomer (32:18:50). These three mixtures were employed in separate propene polymerization experiments (MAO activated, Al:Zr ≈ 600, $25\,°C$ in toluene solution at 1.4 bar propene pressure). All three experiments produced almost identical polypropylene samples ($\overline{M}_\eta \approx 17\,000$, isotactic, enantiomorphic site control, ca. 95% mmmm), but with very different activities [$a = 750$ g polypropylene/(g[Zr]h bar) with the 12:7:81 rl:rl′:ml mixture; $a = 1500$ (25:15:60); $a = 2200$ (32:18:50)]. This indicates that the meso-like cycloalkylene-fused ansa-metallocene catalyst system also in the case of zirconium is practically inactive in propene polymerization as compared to the racem-like diastereoisomers. Therefore, the series of ansa-zirconocene complexes **4** and **5** was employed as catalysts in homogeneous MAO-activated propene polymerization reactions as mixtures of the three diastereoisomers directly as they were obtained from the synthesis (see above and Table 1). This provided some information about systematic trends of essential features of these

Table 4

A comparison of the isotacticities (% mmmm [a]) of polypropylene formed at the ansa-zirconocene dichloride/MAO catalysts in toluene at various temperatures [b]

Metallocene	$-15\,°C$	$0\,°C$	$25\,°C$	$50\,°C$	$70\,°C$
4a	93	91	90	86	83
4b	>95	95	94	92	77
4c	93	93	91	87	78
4d	89	89	84	79	56
4e	>95	95	95	90	76
5a	95	95	94	89	79
5c	>95	>95	95	82	43
5e	>95	>95	94	81	63

[a] Determined by ^{13}C NMR pentade analysis.
[b] See footnote a in Table 3.

Table 5
Molecular weights ($\overline{M}_\eta \times 1000$) of the polypropylenes formed at the ansa-zirconocene dichloride/MAO Ziegler catalysts in toluene solution at various temperatures [a]

Metallocene	−15 °C	0 °C	25 °C	50 °C	70 °C
4a	75	51	28	11	3.8
4b	62	42	26	7	2.8
4c	69	38	24	7	2.8
4d	62	35	24	10	5
4e	94	55	28	7	4
5a	33	25	9	5	3.3
5c	45	27	16	2.6	1.4
5e	54	44	15	6	1.6

[a] See footnote a in Table 3.

polymerization reactions in dependence of the size of the fused cycloalkylene ring system. For the purpose of a comparison the simple acyclic systems 4e and 5e were included in this systematic study as a reference. The trends of several characteristic features of the propene polymerization reactions (isotacticities, molecular weights, polymerization activity, and their temperature dependence) are summarized in Tables 3–5.

The data featured in Table 3 to Table 5 show that the differences in Ziegler catalyst performance among the 4a–d/MAO (and their respective tetrahydroindenyl offsprings 5) are marginal. There appears to be a slight trend indicating that the six-membered annulated system 4b represents the optimum in the series. This is certainly true for the stereoselectivity and probably also holds for the activity values. However, it has to be stressed that the differences in these respective numbers are rather small. It seems to be evident from the data given in the tables that the catalyst performance in general seems to fall slightly off towards the eight-membered ring system (4d), although the open-chain ansa-metallocene references (4e, 5e) (for related systems see Ref. [20]) are better with regard to catalyst activities and stereoselectivities (under analogous conditions the original 'Brintzinger-system' rac-9/MAO gave at 25 °C a polypropylene sample showing 94% mmmm, $a = 8.7$, $\overline{M}_\eta = 27\,000$). Only at the highest polymerization temperatures did the small ring fused ansa-zirconocene dichloride/MAO catalysts seem to give rise to slightly higher isotacticities, a trend that is even more pronounced when the polymerization reactions are carried out in liquid propene under 'technical conditions'. [2]

In comparing the activity data one must bear in mind that only the racem-like isomers of the systems 4a–d and 5a,c appear to serve as the active components in these catalyst systems. Since these represent only the

minor isomers of these complexes obtained from the direct syntheses, the actual activity values must probably be regarded to be about two to four times higher, which brings them in close proximity to the open chain references (4e, 5e). However, as a separation of the respective isomers has turned out to be impractical, the use of the cycloalkylene-bridged ansa-metallocenes does probably not offer any advantage over the simple ansa-metallocene catalyst precursors described in the literature [1–4]. However, these systems may provide a simple entry into optically active ansa-metallocenes (via their optically pure trans-1,2-alkandiol-precursors), whose catalytic and stoichiometric use in organic synthesis is foreseeable [21] (see also Ref. [22]).

Eventually, the hafnium system 8b (23:17:60 mixture) was also tested in a propene polymerization reaction. As expected, the catalyst activity was low ($a = 67$ g polypropylene/(g [Hf] h bar) at 25 °C) and an isotactic polypropylene was obtained ($> 95\%$ mmmm, $\overline{M}_\eta = 46\,000$).

3. Experimental section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents) were dried and distilled prior to use. Instruments used for characterization include Bruker WP 200 SY and AC 200 P NMR spectrometers (^{1}H: 200 MHz, ^{13}C: 50 MHz), Nicolet 5 DXC FT-IR spectrometer, Finnigan MAT 312 and Varian MAT CH7 MS-spectrometers (70 eV), Foss-Heraeus CHN-Rapid (CH elemental analyses), DuPont 910 DSC. Silica gel was silanated by adding trichloromethylsilane to 0.063 mm silica gel (Merck) in cyclohexane. X-ray crystal structure analyses: Enraf Nonius CAD4 diffractometer; programs used: SHELX 86, SCHAKAL. Propene polymerization reactions and polymer analyses were carried out analogously as previously described by us [10]. 1,2-Diol starting materials and their respective tosylates or mesylates were prepared by standard literature procedures. For clarity the two racem-like metallocene isomers are marked A and B, and the meso-like metallocene diastereomer is marked C in the description of the NMR spectra of these respective compounds. A non-systematic atom numbering scheme is used throughout Section 3, denoting the cycloalkylene carbon centers as 1' to n', while numbering the indene framework in the usual way (i.e. 1 to 9).

3.1. Preparation of the trans-1,2-bis(indenyl)cycloalkanes, general procedure

n-Butyl lithium (105 mmol) in n-hexane is added dropwise to a solution of 100 mmol of indene in 100 ml

of THF. The mixture is then stirred for 2 h at ambient temperature. At 0 °C a solution of 45 mmol of the ditosylate of the respective 1,2-cycloalkane diol, dissolved in 150 ml of THF, is added. The mixture is stirred for 5 h at ambient temperature and then refluxed at 50 °C for 3 - 4 days. The mixture is hydrolyzed with 150 ml of water, and 150 ml of ether is added. The organic phase is separated and washed with water (3 ×). The combined aqueous layers are extracted with ether (2 × 50 ml). The combined ethereal phases are dried (Na$_2$SO$_4$), and the solvent is removed in vacuo. Oily products are purified by column chromatography, solids by recrystallization.

3.1.1. trans-1,2-Bis(3-indenyl)cyclopentane 2a

Indenyl lithium was formed by treatment of 43.6 g (0.38 mol) of indene in 300 ml of THF with 225 ml of a 1.6 M solution of n-butyl lithium in n-hexane. trans-1,2-Cyclopentylen-bis(p-toluolsulfonate) (1a, 62.0 g, 0.15 mol), dissolved in 300 ml of THF, was added and the reaction mixture refluxed for 72 h, then hydrolyzed and extracted with ether to give 2a as a viscous oil, yield 35 g (78%). For characterization an aliquot was purified by chromatography (silica gel, ether–pentane 5:1). ^{1}H NMR (CDCl$_3$): δ = 1.80–2.21 (m, 6H, 3'-, 5'-H); 3.40 (m, 4H, 1-H); 3.62 (m, 2H, 1'-, 2'-H); 6.29 (m, 2H, 2-H); 7.11–7.63 (m, 8H, 4- to 7-H). ^{13}C NMR (CDCl$_3$): δ = 24.8 (–CH$_2$, C-4'); 32.8 (CH$_2$, C-3', -5'); 38.0 (=CH$_2$, C-1); 43.4 (=CH, C-1', C-2'); 119.9, 124.1, 124.7, 126.2, 126.8 (=CH, C-2, -4 to -7); 145.3, 145.8, 147.9 (=C, C-3, -8, -9). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3052, 2957, 2868, 1607, 1464, 1402, 973, 775, 714. MS (EI, 70 eV): m/z (%) = 298 (M$^+$, 18), 182 (38), 120 (56), 105 (100), 84 (78), 77 (66), 67 (84). Anal. calcd. for C$_{23}$H$_{22}$ (298.43) C, 92.60; H, 7.43; found: C, 92.10; H, 7.81.

3.1.2. trans-1,2-Bis(3-indenyl)cyclohexane 2b

Indene (28.9 g, 0.25 mol), dissolved in 200 ml of THF, was treated with 138 ml of n-butyl lithium solution in hexane (0.22 mol) at 0 °C. After 3 h a solution of trans-1,2-cyclohexylen-bis(p-toluolsulfonate) 1b (42.5 g, 0.10 mol) in 200 ml of THF was added. Work-up after 72 h of reflux and recrystallization from acetone yielded 9.4 g (30% of 2b as a solid, m.p. 146 °C. ^{1}H NMR (CDCl$_3$): δ = 1.51 (m, 4H); 1.88; 2.20 (each m, each 2H); 3.10 (m, 6H, 1-, 1'-, 2'-H); 6.02 (br s, 2H, 2-H); 7.12 (t, 2H, 5-H, $^3J_{HH}$ = 7.3 Hz); 7.25 (t, 2H, 6-H, $^3J_{HH}$ = 7.3 Hz); 7.36 (d, 2H, 4-H, $^3J_{HH}$ = 7.2 Hz); 7.43 (d, 2H, 7-H, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR (CDCl$_3$): δ = 26.8, 34.4, 37.7 (–CH$_2$, C-1, -3', -4', -5', -6'); 40.6 (=CH, C-1', -2'); 118.9, 123.6, 124.1, 125.7, 126.6 (=CH, C-2, -4 to -7); 144.7, 145.3, 148.2 (C-indene, C-3, -8, -9). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3065, 2923, 2882, 1604, 1457, 1390, 972, 767, 718. MS (EI, 70 eV): m/z (%) = 312 (M$^+$, 35), 196 (100), 115 (70), 81 (50), 77

(30). Anal. calcd. for C$_{24}$H$_{24}$ (312.45) C, 92.26; H, 7.74; found: C, 92.06; H, 7.69.

3.1.3. trans-1,2-Bis(3-indenyl)cycloheptane 2c

Treatment of 43.9 g (0.10 mol) of the ditosylate 1c in 200 ml THF with 30 g (0.25 mol) of indenyl lithium, in situ generated in 250 ml of THF, at 0 °C, followed by 48 h reflux at 50 °C and work-up as described above gave 13.7 g (42%) of 2c, m.p. 105 °C. ^{1}H NMR CDCl$_3$): δ = 1.50–2.08 (m, 10H, 3'- to 7'-H); 3.11 (m, 4H, 1-H); 3.38 (m, 2H, 1'-, 2'-H); 6.11 (br s, 2H, 2-H); 7.00–7.47 (m, 8H, 4- to 7-H). ^{13}C NMR (CDCl$_3$): δ = 27.1, 30.2, 32.9 (–CH$_2$, C-3' to -7'); 37.8 (–CH$_2$, C-1); 42.0 (–CH, C-1', -2'); 119.3, 123.4, 124.5, 126.0, 126.3 (–CH, C-2, C-arom.); 145.1, 145.7, 149.3 (–C, C-3, C-arom.). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3052, 2930, 2855, 1607, 1464, 1402, 1027, 973, 782, 721. MS (EI, 70 eV): m/z (%) = 326 (M$^+$, 28), 210 (74). 167 (85), 141 (100), 128 (95), 115 (87). Anal. calcd. for C$_{25}$H$_{26}$ (326.48) C, 91.97; H, 8.03; found: C, 91.76; H, 8.24.

3.1.4. trans-1,2-Bis(3-indenyl)cyclooctane 2d

Treatment of 34.9 g (0.30 mol) of indene in 200 ml of THF with 175 ml of a 1.6 M n-butyl lithium solution (0.28 mol) in hexane followed by reaction with 59.0 g (0.13 mol) of the ditosylate 1a in 300 ml of THF (60 h reflux) gave 32.9 g (72%) of 2d. Part of the product was purified by chromatography at silica gel (ether–petrol 10:1) for characterization. ^{1}H NMR (CDCl$_3$): δ = 1.47–2.21 (m, 12H, 3'- to 8'-H); 3.10 (m, 2H, 1'-, 2'-H); 3.42 (m, 4H, 1-H); 6.23 (br s, 2H, 2-H); 7.11–7.61 (m, 8H, 4- to 7-H). ^{13}C NMR (CDCl$_3$): δ = 25.3, 29.1, 30.3 (=CH$_2$, C-3' to -8'); 35.4 (=CH, C-1', -2'); 36.7 (=CH$_2$, C-1); 118.2, 122.8, 123.4, 124.7, 124.8 (=CH, C-2, C-arom.); 137.8, 147.2, 150.0 (=C, C-3, C-arom.). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3052, 2916, 2861, 1614, 1464, 1389, 775, 727. MS (EI, 70 eV): m/z (%) = 340 (M$^+$, 20), 167 (64), 141 (100), 128 (96), 115 (92), 67 (79). Anal. calcd. for C$_{26}$H$_{28}$ (340.51) C, 91.71; H, 8.29; found: C, 91.32; H, 8.18.

3.1.5. 2-Bis(3-indenyl)propane 2e

27.9 g (0.24 mmol) of indene in 200 ml of THF was treated with 132 ml (0.22 mol) of a 1.6 M n-butyl lithium solution in hexane, followed by addition of 38.5 g (0.10 mol) of the ditosylate 1e in 250 ml of THF. Work-up after 48 h at 50 °C yielded 18.0 g (66%) of 2e as a pale yellow oil. ^{1}H NMR (CDCl$_3$): δ = 1.24 (d, 3H, 3'-H, $^3J_{HH}$ = 6.5 Hz); 2.60–3.08 (m, 3H, 1'-, 2'-H); 3.22 (s, 4H, 1-H); 6.16 (m, 2H, 2-H); 7.05–7.55 (m, 8H, H-4, -7). ^{13}C NMR (CDCl$_3$): δ = 19.8 (–CH$_3$, C-3'); 31.1 (–CH, C-2'); 34.2 (–CH$_2$, C-1'); 37.6, 37.7 (–CH$_2$, C-1); 119.3, 119.6, 124.0, 124.8, 126.2, 126.3, 126.6, 128.3, 128.8, 133.1 (–CH, C-2, C-arom.); 143.2, 144.8, 145.1, 145.2, 146.0, 150.1 (–C, C-3, C-arom.). IR(NaCl): $\tilde{\nu}$ (cm^{-1}) = 3059, 2971, 2923, 2854, 1696,

1607, 1457, 1396, 775, 721. MS (EI, 70 eV): m/z (%) = 272 (M^+, 18), 156 (39), 142 (76), 128 (100), 105 (96), 77 (98). Anal. calcd. for $C_{21}H_{20}$ (272.39) C, 92.60; H, 7.40; found: C, 92.55; H, 7.70.

3.2. Preparation of the trans-1,2-cycloalkylen-bis(1-indenyllithium) compounds 3, general procedure

100 mmol of the substituted indene starting material is dissolved in 100 ml of THF. At 0 °C 105 mmol of n-butyl lithium in n-hexane (1.6 M) is slowly added. The mixture is stirred for 4 h at room temperature. The product has precipitated during that period of time and is collected by filtration, washed with pentane (2 × 100 ml) and dried in vacuo. Characterization is carried out by NMR spectroscopy in benzene-d_6-THF-d_8.

3.2.1. trans-1,2-Cyclopentylen-bis(1-indenyllithium) 3a

Treatment of 10.0 g (33.5 mmol) of 2a in 100 ml of THF with 46.1 ml (73.7 mmol) of 1.6 M n-butyl lithium in hexane gave 9.6 g (92%) of 3a. ^{1}H NMR (benzene-d_6-THF-d_8 20:1): δ = 1.79–2.75 (m, 6H, 3'-, 4'-, 5'-H); 4.19 (m, 2H, 1'-, 2'-H); 6.11 (d, 2H, 2-H, $^3J_{HH}$ = 3.2 Hz); 6.90 (m, 6H, 3-, 5-, 6-H); 7.61 (d, 2H, 4H, $^3J_{HH}$ 8.1 Hz); 7.92 (d, 2H, 7-H, $^3J_{HH}$ = 8.1 Hz).

3.2.2. trans-1,2-Cyclohexylen-bis(1-indenyllithium) 3b

Analogously as described above 12.0 g (38.4 mmol) of 2b in 100 ml of THF was treated with 52.8 ml (84.5 mmol) of a 1.6 M n-butyl lithium solution in hexane to yield 11.0 g (89%) of 3b. ^{1}H NMR (benzene-d_6-THF-d_8 20:1): δ = 1.65–2.35 (m, 8H, 3'- to 6'-H); 3.67 (m, 2H, 1'-, 2'-H); 5.80 (d, 2H, 2-H, $^3J_{HH}$ = 3.2 Hz); 6.57–6.77 (m, 6H, 3-, 5-, 6-H); 7.30, 7.77 (each d, 2H, 4-, 7-H, $^3J_{HH}$ = 8.0 Hz). ^{13}C NMR (benzene-d_6-THF-d_8 20:1): δ = 28.8, 38.8 (–CH_2, C-3', -4', -5', -6'); 44.4 (–CH, C-1', -2'); 90.0 (–CH, C-3); 112.2 (–CH, C-2); 114.2, 118.4, 119.9 (–CH, C-4 to -7); 111.8, 124.7, 128.3 (–C, C-1, -8, -9).

3.2.3. trans-1,2-Cycloheptylen-bis(1-indenyllithium) 3c

Treatment of 14.0 g (42.9 mmol) of 2c in 100 ml of THF with 59 ml (94.4 mmol) of a 1.6 M n-butyl lithium solution in hexane analogously as described above gave 12.9 g (89%) of 3c. ^{1}H NMR (benzene-d_6-THF-d_8 20:1): δ = 1.81–2.38 (m, 10H, 3'- to 7'-H); 4.03 (m, 2H, 1'-, 2'-H); 5.93 (d, 2H, 2-H, $^3J_{HH}$ = 3.2 Hz); 6.80–7.00 (m, 6H, 3-, 5-, 6-H); 7.49 (d, 2H, 4-H, $^3J_{HH}$ = 8.0 Hz); 7.91 (d, 2H, 7H, $^3J_{HH}$ = 8.0 Hz). ^{13}C NMR (benzene-d_6-THF-d_8 20:1): δ = 27.6, 29.4, 38.3 (–CH_2, C-3' to -7'); 46.0 (–CH, C-1', -2'); 89.0 (–CH, C-3); 111.8, 114.8, 115.3, 118.8, 120.3 (–CH, C-2, C-4 to -7); 114.6 (–C, C-1); 124.2, 124.4 (–C, C-8, -9).

3.2.4. trans-1,2-Cyclooctylen-bis(1-indenyllithium) 3d

Analogously as described above 14.0 g (41.1 mmol) of 2d in 100 ml of THF was treated with 56.5 ml

(90.4 mmol) of 1.6 M butyl lithium solution in hexane to yield 12.9 g (89%) of 3d. ^{1}H NMR (benzene-d_6-THF-d_8 20:1): δ = 1.80–2.58 (m, 12H, 3'- to 8'-H); 3.69 (m, 2H, 1'-, 2'-H); 6.18 (d, 2H, 2-H, $^3J_{HH}$ = 3.1 Hz); 6.76 (d, 2H, 3-H, $^3J_{HH}$ = 3.1 Hz); 7.00 (m, 4H, 5-, 6-H); 7.80 (m, 4H, 4-, 7-H).

3.2.5. trans-1,2-Propylen-bis(1-indenyllithium) 3e

5.0 g (18.4 mmol) of 2e was treated with 24.2 ml (38.7 mmol) of 1.6 M n-butyl lithium in hexane analogously as described above to give 4.8 g (96%) of 3e. ^{1}H NMR (benzene-d_6-THF-d_8 20:1): δ = 1.73 (d, 3H, 3'-H, $^3J_{HH}$ = 6.8 Hz); 3.45 (m, 2H, 1'-H); 3.96 (m, 1H, 2'-H); 5.74 (d, 1H, 2- or 2*-H, $^3J_{HH}$ = 3.1 Hz); 5.82 (d, 1H, 2- or 2*-H, $^3J_{HH}$ = 3.1 Hz); 6.39 (d, 1H, 3- or 3*-H, $^3J_{HH}$ = 3.1 Hz); 6.52 (d, 1H, 3- or 3*-H, $^3J_{HH}$ = 3.1 Hz); 6.82 (d, 2H, 4-, 7- or 4*-, 7*-H; $^3J_{HH}$ = 8.0 Hz); 6.85; 7.42 (each m, each 2H, 5-, 6-, 5*-, 6*-H); 7.77 (d, 2H, 4-, 7- or 4*-, 7*H; $^3J_{HH}$ = 8.0 Hz). ^{13}C NMR (benzene-d_6-THF-d_8 20:1): δ = 15.4 (–CH_3, C-3'); 34.5 (–CH_2, C-1'); 36.8 (–CH, C-2'); 89.4, 89.5 (–CH, C-3, -3*); 106.0, 111.3 (–C, C-1, -1*); 110.9, 113.0, 115.5, 115.7, 115.8, 115.9, 118.9 (double intensity), 120.5, 120.6 (–CH, C-2, -2*, -4 to -7, -4* to -7*); 124.3, 124.8, 127.1, 128.3 (–C, C-8, -9, -8*, -9*).

3.3. Preparation of the ansa-zirconocene dichlorides 4, general procedure

Two reagent solutions are prepared, one by dissolving 10 mmol of $ZrCl_4 \cdot 2THF$ in 100 ml of THF and another by dissolving the trans-1,2-cycloalkylen-bis(1-indenyllithium) compound (10 mmol) in 100 ml of THF. From two dropping funnels these two solutions are dropped slowly and simultaneously into a Schlenk-flask stirred for 5 h at room temperature and then stirred at reflux temperature (~ 50 °C) for another 24 h. Solvent is then removed in vacuo. The diastereomeric ratio is determined from an aliquot by ^{1}H NMR spectroscopy. The remainder of the product is washed with pentane (2 × 50 ml), dissolved in dichloromethane (100 ml) and filtered from the precipitated lithium chloride. Solvent was removed from the clear filtrate and the product dried in vacuo.

3.3.1. [trans-1,2-Cyclopentylen-bis(η⁵-1-indenyl)]zirconium dichloride 4a

Analogously as described above 4.0 g (12.9 mmol) of the lithium compound 3a was reacted with 4.9 g (12.9 mmol) of $ZrCl_4 \cdot 2THF$ to yield 2.8 g (47%) of 4a, m.p. 145 °C (decomp.). The diastereomeric ratio (racem-like A:racem-like B:meso-like C) was determined by integration of the respective indenyl 2-H and 3-H ^{1}H NMR resonances (A:B:C = 19:13:68). ^{1}H NMR ($CDCl_3$): δ = 1.51–2.40 (m, 18H, 3'-, 4'-, 5'-H); 4.04 (m, 6H, 1'-, 2'-H); 6.03 (d, 0.7H, 2/3-H^B, $^3J_{HH}$ = 3.3 Hz); 6.18 (d, 1.1H, 2/3-H^A, $^3J_{HH}$ = 3.3 Hz); 6.42

(d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz); 6.57 (d, 0.7H, 2/3-H^B, $^3J_{HH}$ = 3.3 Hz); 6.37 (d, 1.1H, 2/3-H^A, $^3J_{HH}$ = 3.3 Hz); 6.44 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz); 6.71 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz); 6.88 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz), 7.00–7.92 (m, 24H, 4- to 7-H). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3073, 2957, 2875, 1464, 1396, 1348, 1259, 775, 755. Anal. calcd. for C$_{23}$H$_{20}$Cl$_2$Zr (458.54) C. 60.25; H, 4.40; found: C, 60.99; H, 4.97.

3.3.2.   [trans-1,2-Cyclohexylen-bis(η^5-1-indenyl)]zirconium dichloride 4b

Analogously as described above 2.8 g (8.8 mmol) of the indenyl lithium reagent 3b was reacted with 3.3 g (8.8 mmol) of ZrCl$_4$ · 2THF to give 1.8 g (44%) of 4b (A:B:C ratio 25:25:50), m.p. 185–195 °C (decomp.). ^{1}H NMR (CDCl$_3$): δ = 1.00–2.35 (m, 24H, 3'- to 6-'H); 3.37–4.16 (m, 6H, 1'-, 2'-H); 5.98, 6.38, 6.48, 6.57, 6.71, 6.84 (each d, 8H, 2/3-H, $^3J_{HH}$ = 3.3 Hz); 6.25 (d, 4H, 2/3-H, $^3J_{HH}$ = 3.3 Hz); 6.97–7.96 (m, 24H, 4- to 7-H). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3063, 2923, 2858, 1445, 803, 741. Anal. calcd. for C$_{24}$H$_{22}$Cl$_2$Zr (472.57) C, 61.00; H, 4.69; found: C, 59.11; H, 5.01.

3.3.3.   [trans-1,2-Cycloheptylen-bis(η^5-indenyl)]zirconium dichloride 4c

According to the general procedure as described above 6.6 g (19.4 mmol) of 3c was reacted with 7.3 g (19.4 mmol) of ZrCl$_4$ · 2THF to yield 5.7 g (60%) of 4c (A:B:C ratio 25:15:60), m.p. 174 °C (decomp.) ^{1}H NMR (CDCl$_3$): δ = 1.40 2.41 (m, 30H, 3'- to 7'-H); 3.82, 4.25 (each m, 6H, 1'-, 2'-H); 5.95 (d, 1.5H, 2/3H^A, $^3J_{HH}$ = 3.3 Hz); 6.18 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz); 6.22 (d, 0.9H, 2/3-H^B, $^3J_{HH}$ = 3.3 Hz); 6.36 (d, 1.5H, 2/3-H^A, $^3J_{HH}$ = 3.3 Hz); 6.44 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz); 6.53 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz); 6.72 (d, 0.9H, 2/3-H^B, $^3J_{HH}$ = 3.3 Hz); 6.84 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.3 Hz); 6.90–7.90 (m, 24H, 4- to 7-H). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3073, 2930, 2861, 1464, 1348, 809, 755. Anal. calcd. for C$_{25}$H$_{24}$Cl$_2$Zr (486.60) C, 61.71; H, 4.97; found: C, 60.99; H, 5.37. HRMS, calcd. 484.03022; found: 484.02866.

3.3.4.   [trans-1,2-Cyclooctylen-bis(η^5-1-indenyl)]zirconium dichloride 4d

Analogously as described above 5.4 g (15.3 mmol) of the lithium reagent 3d was reacted with 5.8 g (15.3 mmol) ZrCl$_4$ · 2THF to yield 4.1 g (53%) of the product 4d (A:B:C ratio 17:13:70), m.p. 141 °C (decomp.) ^{1}H NMR (CDCl$_3$): δ = 1.23–2.29 (m, 36H, 3'- to 8'-H); 4.31 (m, 6H, 1', 2'-H); 5.90 (d, 0.8H, 2/3-H^B, $^3J_{HH}$ = 3.2 Hz); 6.14 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.22 (d, 1.0H, 2/3-H^A, $^3J_{HH}$ = 3.2 Hz); 6.38 (d, 0.8H, 2/3-H^B, $^3J_{HH}$ = 3.2 Hz); 6.45 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.52 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.72 (d, 1.0H, 2/3-H^A, $^3J_{HH}$ = 3.2 Hz); 6.86 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.98–7.80 (m, 24H, 4- to 7-H). IR

(KBr): $\tilde{v}$ (cm^{-1}) = 3072, 2923, 2855, 1464, 1451, 1266, 809, 748. Anal. calcd. for C$_{26}$H$_{26}$Cl$_2$Zr (500.62) C, 62.38; H, 5.23; found: C, 63.99; H, 6.07

3.3.5.   [1,2-Propylen-bis(η^5-1-indenyl)]zirconium dichloride 4e

The reaction of 5.7 g (20.0 mmol) of the dilithio reagent 3e with 7.6 g (20.0 mmol) of ZrCl$_4$ · 2THF was carried out analogously as described in the general procedure (see above) to yield 7.4 g (86%) of the ansa-metallocene dichloride 4e, m.p. 163 °C (A:B:C isomer ratio: 40:16:44). ^{1}H NMR (CDCl$_3$): δ = 1.57, 1.59, 1.62 (each d, each 3H, 3'-H, $^3J_{HH}$ = 6.7 Hz); 3.20–4.68 (m, 3H, 1'-, 2'-H); 5.90 (d, 0.5 H, 2/3-H^B, $^3J_{HH}$ = 3.4 Hz); 6.04 (d, 1.2H, 2/3-H^A, $^3J_{HH}$ = 3.4 Hz); 6.11 (d, 1.2H, 2/3-H^A, $^3J_{HH}$ = 3.4 Hz); 6.19 (d, 0.5H, 2/3-H^B, $^3J_{HH}$ = 3.4 Hz); 6.32 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.4 Hz); 6.36 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.4 Hz); 6.38 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.4 Hz); 6.45 (d, 1.2H, 2/3-H^A, $^3J_{HH}$ = 3.4 Hz); 6.57 (d, 0.5H, 2/3-H^B, $^3J_{HH}$ = 3.4 Hz); 6.74 (d, 1.2H, 2/3-H^A, $^3J_{HH}$ = 3.4 Hz); 6.77 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.4 Hz); 6.90 (d, 0.5H, 2/3-H^B, $^3J_{HH}$ = 3.4 Hz); 6.97–8.00 (m, 8H, 4- to 7-H, 4'- to 7'-H). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3066, 2957, 2868, 1457, 1355, 809, 761. Anal. calcd. for C$_{21}$H$_{18}$Cl$_2$Zr (432.45) C, 58.33; H, 4.20; found: C, 58.98; H, 4.73. HRMS, calcd. 431.98195; found: 431.98323.

3.4.   Preparation of the ansa-bis(tetrahydroindenyl)zirconium dichlorides (5), general procedure

Catalytic hydrogenation of the ansa-bis(indenyl)zirconium dichlorides was carried out according to a related literature procedure [11]; to a solution of ca. 1 g of the ansa-bis(indenyl)ZrCl$_2$ complex in 60 ml of dichloromethane is added 50 mg of PtO$_2$. The suspension is then stirred in an autoclave for 7 h under 60 bar hydrogen pressure. The mixture is filtered and solvent is removed in vacuo. The residue is taken up in a minimum amount of dichloromethane and filtered through a short chromatography column of silanated silica gel with dichloromethane–petrol 5:1. Solvent is removed and the residue dried in vacuo. The diastereomeric A:B:C ratio is then determined by integration of the ^{1}H NMR tetrahydroindenyl 2-H and 3-H resonances.

3.4.1.   [trans-1,2-Cyclopentylen-bis(η^5-4,5,6,7-tetrahydroindenyl)zirconium dichloride 5a

Hydrogenation of 1.17 g (2.55 mmol) of 4a was carried out as described above to yield 1.11 g (94%) of 5a, m.p. 16. °C (decomp.), the isomer ratio after work-up is A:B:C = 24:12:64. ^{1}H NMR (CDCl$_3$): δ = 1.02–2.50 (m, 66H, 4 to 7-H, 3'-, 4'-, 5'-H); 3.01 (m, 6H, 1'-, 2'-H); 5.72 (d, 0.9H, 2/3-H^B, $^3J_{HH}$ = 3.2 Hz); 5.76 (d,

1.7H, 2/3-H^A, $^3J_{HH}$ = 3.2 Hz); 5.96 (d, 1.7H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.09 (d, 1.7H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.13 (d, 1.7H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.25 (d, 0.9H, 2/3-H^B, $^3J_{HH}$ = 3.2 Hz); 6.31 (d, 1.7H, 2/3-H^C, $^3J_{HH}$ = 3.2 Hz); 6.44 (d, 1.7H, 2/3-H^A, $^3J_{HH}$ = 3.2 Hz). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3080, 2943, 2875, 1464, 1266, 1102, 1027, 809, 741. Anal. calcd. for C$_{23}$H$_{28}$Cl$_2$Zr (466.60) C, 59.21; H, 6.05; found: C, 61.03; H, 6.57. HRMS, calcd. 466.06027; found: 466.05920.

3.4.2. [trans-1,2-Cyclohexylen-bis(η^5-4,5,6,7-tetrahydroindenyl)]zirconium dichloride 5b

Hydrogenation of 1.25 g (2.65 mmol) of **4b**, carried out analogously as described above, gave 1.20 g (97%) of **5b**, m.p. 120 °C. In this case a chromatographic purification was not necessary. A:B:C isomer ratio 25:25:50. ^{1}H NMR (CDCl$_3$): δ = 1.00–3.22 (m, 78H, 4- to 7-H, 1'- to 6'-H); 5.53 (d, 3H, 2/3-H^{A,B}, $^3J_{HH}$ = 3.0 Hz); 5.77 (d, 1.5H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.06 (d, 1.5H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.08 (d, 1.5H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.17 (d, 1.5H, 2/3-H^B, $^3J_{HH}$ = 3.0 Hz); 6.41 (d, 1.5H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.44 (d, 1.5H, 2/3-H^A, $^3J_{HH}$ = 3.0 Hz). ^{13}C NMR (CDCl$_3$): δ = 43.1, 43.6, 47.4, 48.2 (–CH, C-1', -2'); 103.6, 104.6, 110.6, 111.4, 115.9, 118.2, 121.3, 123.9 (–CH, C-2, -3); 119.9, 121.6, 125.5, 127.1, 129.8, 131.0, 132.0, 133.2, 134.2, 135.1, 136.1, 137.2 (C-indene, C-1, -8, -9). CH$_2$ signals strongly overlapping. IR (KBr): $\tilde{v}$ (cm^{-1}) = 3073, 2889, 2812, 1461, 1386, 798, 754. Anal. calcd. for C$_{24}$H$_{30}$Cl$_2$Zr (480.63) C, 59.98; H, 6.29; found: C, 61.42; H, 6.36.

3.4.3. [trans-1,2-Cycloheptylen-bis(η^5-4,5,6,7-tetrahydroindenyl)]zirconium dichloride 5c

Hydrogenation of 1.70 g (3.50 mmol) of **4c** yielded 1.56 g (91%) of **5c**, m.p. 155 °C. A:B:C = 25:15:60. ^{1}H NMR (CDCl$_3$): δ = 1.00–3.5 (2m, 84H, 4- to 7-H, 1'- to 7'-H), 5.45 (d, 1.5H, 2/3-H^A, $^3J_{HH}$ = 3.0 Hz); 5.50 (d, 0.9H, 2/3-H^B, $^3J_{HH}$ = 3.0 Hz); 5.68 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.01 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.05 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.14 (d, 1.5H, 2/3-H^A, $^3J_{HH}$ = 3.0 Hz); 6.39 (d, 1.8H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.42 (d, 0.9H, 2/3-H^B, $^3J_{HH}$ = 3.0 Hz). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3086, 2930, 2855, 1464, 1266, 1102, 1027, 802. Anal. calcd. for C$_{25}$H$_{32}$Cl$_2$Zr (494.66) C, 60.70; H, 6.52; found: C, 61.02; H, 6.77.

3.4.4. [trans-1,2-Cyclooctylen-bis(η^5-4,5,6,7-tetrahydroindenyl)]zirconium dichloride 5d

A suspension of 1.36 g (2.72 mmol) of **4d** in 70 ml dichloromethane was hydrogenated and worked up analogously as described above to yield 1.19 g (82%) of **5d**, m.p. 192 °C. A:B:C = 17:14:69. ^{1}H NMR (CDCl$_3$): δ = 1.05–3.40 (m, 90H, 4- to 7-H, 1'- to 8'-H), 5.43 (d, 0.8H, 2/3-H^B, $^3J_{HH}$ = 2.9 Hz); 5.48 (d, 1.0H, 2/3-H^A, $^3J_{HH}$ = 2.9 Hz); 5.66 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 2.9 Hz); 6.02

(d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 2.9 Hz); 6.08 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 2.9 Hz); 6.13 (d, 0.8H, 2/3-H^B, $^3J_{HH}$ = 2.9 Hz); 6.39 (d, 2.1H, 2/3-H^C, $^3J_{HH}$ = 2.9 Hz); 6.41 (d, 1.0H, 2/3-H^A, $^3J_{HH}$ = 2.9 Hz). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3068, 2923, 2855, 1464, 1457, 1259, 823, 761. Anal. calcd. for C$_{26}$H$_{34}$Cl$_2$Zr (508.68) C, 61.39; H, 6.74; found: C, 62.99; H, 7.07. HRMS, calcd. 506.10847; found: 506.10733.

3.4.5. [1,2-Propylen-bis(η^5-4,5,6,7-tetrahydroindenyl)]zirconium dichloride 5e

Hydrogenation of 1.18 g (2.73 mmol) of **4e**, carried out analogously as described above, yielded 1.15 g (96%) of **5e**, m.p. (133 °C) (decomp. > 194 °C). Chromatographic work-up was not necessary in this case; the A:B:C isomer ratio is 40:16:44. ^{1}H NMR (CDCl$_3$): δ = 1.24, 1.30, 1.33 (each d, 3H, 3'-H, $^3J_{HH}$ = 6.6 Hz); 1.57, 1.92, 2.50, 2.99 (each m, 54H, 1'-, 4- to 7-H); 3.61 (m, 3H, 2'-H); 5.52 (d, 1.2H, 2/3-H^A, $^3J_{HH}$ = 3.0 Hz); 5.59 (d, 1.2H, 2/3-H^A, $^3J_{HH}$ = 3.0 Hz); 5.60 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 5.61 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 5.83 (d, 0.4H, 2/3-H^B, $^3J_{HH}$ = 3.0 Hz); 6.05 (d, 1.2H, 2/3-H^A, $^3J_{HH}$ = 3.0 Hz); 6.14 (d, 0.4H, 2/3-H^B, $^3J_{HH}$ = 3.0 Hz); 6.19 (d, 0.4H, 2/3-H^B, $^3J_{HH}$ = 3.0 Hz); 6.23 (d, 12H, 2/3-H^A, $^3J_{HH}$ = 3.0 Hz); 6.41 (d, 0.4H, 2/3-H^B, $^3J_{HH}$ = 3.0 Hz); 6.43 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); 6.48 (d, 1.3H, 2/3-H^C, $^3J_{HH}$ = 3.0 Hz); IR (KBr): $\tilde{v}$ (cm^{-1}) = 3073, 2943, 2861, 1459, 1450, 1375, 802, 755. Anal. calcd. for C$_{21}$H$_{26}$Cl$_2$Zr (440.57) C, 57.25; H, 5.95; found: C, 56.63; H, 6.06.

3.5. Preparation of the ansa-bis(tetrahydroindenyl)titanocene dichloride complexes 7, general procedure

A solution of the cycloalkylene-bis(indenyllithium) reagent **3** (10.0 mmol) in 150 ml of THF is added dropwise to a suspension of 10.0 mmol of TiCl$_3$ in 100 ml of THF at ambient temperature. The mixture is stirred for 2 h at room temperature, then refluxed (50 °C) for 12 h. The mixture is cooled to room temperature and then charged with 1.7 g (10.5 mmol) of FeCl$_3$ in 50 ml of THF. After 5 h solvent is removed in vacuo. The residue is taken up in dichloromethane and washed with water (3 × 100 ml). The organic phase is dried (MgSO$_4$) and the solvent is removed in vacuo. The residue is recrystallized from dichloromethane–pentane. The resulting ansa-bis(indenyl)TiCl$_2$ complexes **6** were still not pure (see below) and were, therefore, directly subjected to subsequent catalytic hydrogenation without further spectroscopic characterization: a suspension of ca. 1 g of the respective crude product **6**, prepared as described above, is hydrogenated in 50 ml dichloromethane with 40 mg PtO$_2$ at 60 bar hydrogen pressure in an autoclave for 6 h at room temperature. The catalyst is removed by filtration and the solvent

evaporated in vacuo. The residue is taken up in dichloromethane and passed through a short silanated silica gel column. The A:B:C diastereomeric ratio is then determined by integration of the ^1H NMR signals of the 2-H and 3-H tetrahydroindenyl resonances. In some cases subsequent flash chromatography with petrol–dichloromethane 10:1 at silanated silica gel gave several of the pure diastereoisomers of 7.

3.5.1. [trans-1,2-Cyclopentylen-bis(η^5-4,5,6,7-tetrahydroindenyl)]titanium dichloride 7a

2.90 g (9.3 mmol) of the 1,2-cyclopentylen-bis(indenyllithium) reagent 3a was reacted with 1.43 g (9.3 mmol) of $TiCl_3$ analogously as described in the general procedure above. Oxidation, work-up and re-crystallization gave 1.7 g (44%) of the crude product 6a [anal. calcd. for $C_{23}H_{20}Cl_2Ti$ (415.2): C, 66.54; H, 4.86; found: C, 68.12; H, 5.05%] that was hydrogenated without further characterization. 1.5 g (3.61 mmol) of the crude titanium complex 6a was hydrogenated analogously as described above to yield 1.6 g (97%) of 7a, m.p. > 180 °C (decomp.). A:B:C isomer ratio 42:2:56. Subsequent flash chromatography (silanated silica gel, petrol–dichloromethane 10:1) gave 0.60 g of the pure racem-like diastereoisomer A ($R_f = 0.41$) and 0.75 g of the meso-like diastereomer C ($R_f = 0.26$). Racem-like form A: ^1H NMR ($CDCl_3$): $\delta = 1.52$ (m, 8H); 1.94 (m, 6H); 2.58 (m, 6H); 3.10 (m, 2H); 3.42 (m, 2H); 5.77 (d, 2H, 2/3-H, $^3J = 3.1$ Hz); 6.64 (d, 2H, 2/3-H, $^3J = 3.1$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 20.7$, 20.9, 22.9, 23.3, 26.2, 29.3 (–CH_2, C-4 to -7, -3', -4', -5'); 47.9 (–CH, C-1', -2'); 109.2, 126.7 (–CH, C-2, -3); 131.8, 133.1, 136.1 (–C, C-1, -8, -9). Meso-like form C: ^1H NMR ($CDCl_3$): $\delta = 1.41–2.70$ (m, 2H); 3.04 (m, 1H); 3.21 (m, 1H); 3.40 (m, 1H); 3.69 (m, 1H); 6.17 (d, 1H, 2/3-H, $^3J = 2.9$ Hz); 6.30 (d, 1H, 2/3-H, $^3J = 2.9$ Hz); 6.57 (d, 1H, 2/3-H, $^3J = 2.9$ Hz); 6.74 (d, 1H, 2/3-H, $^3J = 2.9$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 21.7$ (double intensity), 21.9, 22.0, 23.5, 24.2, 24.8, 25.3, 26.2, 26.8, 30.9 (–CH_2, C-4 to -7, -4' to -7', -3', -4', -5'); 49.3, 52.2 (–CH, C-1', -2'); 108.9, 114.7, 125.2, 130.2 (–CH, C-2, -3, -2', -3'); 126.4, 128.2, 131.5, 133.7, 136.1, 140.5 (–C, C-1, -8, -9, -1', -8', -9'). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3066, 2943, 2875, 1716, 1464, 1266, 911, 809. Anal. calcd. for $C_{23}H_{28}Cl_2Ti$ (423.26) C, 65.27; H, 6.68; found: C, 64.59; H, 6.62. Single crystals of the meso-like 7a diastereoisomer were obtained from dichloromethane.

X-ray crystal structure analysis of 7a-ml: formula $C_{23}H_{28}TiCl_2$, M = 423.25, 0.4 × 0.3 × 0.2 mm, a = 11.928(2), b = 10.414(1), c = 15.726(1) Å, β = 90.43(1)°, V = 1953.4(4) Å³, ρ_{calc} = 1.439 g cm⁻³, μ = 7.16 cm⁻¹, no absorption correction, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, ω–2θ scans, 8015 reflections collected ($\pm h$, $+k$, $\pm l$). [(sin θ)/λ]$_{max}$ = 0.62 Å⁻¹, 3964 independent and 2761

observed reflections [$I \leq 2\sigma(I)$], 235 refined parameters, R = 0.036, wR^2 = 0.086, max. residual electron density 0.62 (−0.24) e⁻ Å⁻³, hydrogen atoms calculated and riding.

3.5.2. [trans-1,2-Cyclohexylen-bis(η^5-4,5,6,7-tetrahydroindenyl)]titanium dichloride 7b

Analogously as described above 3.11 g (9.6 mmol) of 3b was reacted with 1.48 g (9.6 mmol) of $TiCl_3$. After oxidation and work-up, including recrystallization from dichloromethane–pentane 1.33 g (32%) of impure 6b [as judged from the C,H elemental analysis: calcd. for $C_{24}H_{22}Cl_2Ti$ (429.2) C, 67.16; H, 5.17; found: C, 71.59; H, 6.18%] was obtained, that was directly subjected to hydrogenation to yield 1.26 g (95%) of 7b as a red solid, m.p. > 216 °C (decomp.). A:B:C isomer ratio 15:11:74. Flash chromatography (silanated silica gel, petrol–dichloromethane 10:1) gave 0.69 g of the meso-like diastereomer ($R_f = 0.23$) and a small amount of one of the racem-like isomers ($R_f = 0.39$). NMR data of the racem-like forms A and B: ^1H NMR ($CDCl_3$): $\delta = 1.53$ (m, 8H); 1.83 (m, 8H); 2.32 (m, 1H); 2.46 (m, 2H); 2.58 (m, 2H); 2.81 (m, 2H); 3.08 (m, 1H); 3.25 (m, 2H); 5.41 (d, 2H, 2/3-H^A, $^3J = 2.2$ Hz); 5.50 (d, 2H, 2/3-H^B, $^3J = 2.2$ Hz); 6.39 (d, 2H, 2/3-H^A, $^3J = 2.2$ Hz); 6.62 (d, 2H, 2/3-H^B, $^3J = 2.2$ Hz); meso-like isomer C: ^1H NMR ($CDCl_3$): $\delta = 1.32–2.50$ (m, 18H); 2.58–3.37 (3m, 8H); 5.88 (d, 1H, 2/3-H, $^3J = 2.9$ Hz); 6.29 (d, 1H, 2/3-H, $^3J = 2.9$ Hz); 6.38 (d, 1H, 2'/3'-H, $^3J = 2.9$ Hz); 6.56 (d, 1H, 2'/3'-H, $^3J = 2.9$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 21.7$ (double intensity), 21.8, 21.9, 23.3, 24.3, 25.0, 25.1, 25.9, 26.2, 31.2, 35.9 (–CH_2, C-4 to -7, -4' to -7', C-3' to -6'); 44.3, 48.1 (–CH, C-1', -2'); 108.6, 114.6, 125.6, 131.3 (–CH, C-2, -3, -2', -3'); 126.7, 133.9 (double intensity), 134.4, 137.4, 140.7 (–C, C-1, -8, -9, -1', -8', -9'). IR (KBr): $\tilde{v}$ (cm^{-1}) = 3086, 2930, 2848, 1716, 1443, 1259, 1048, 816. Anal. calcd. for $C_{24}H_{30}Cl_2Ti$ (437.29) C, 65.92; H, 6.91; found: C, 66.70; H, 7.09. Recrystallization from dichloromethane gave single crystals of the meso-like isomer and one racem-like isomer of 7b.

X-ray crystal structure analyses analysis of 7b-ml: formula $C_{24}H_{30}TiCl_2$, M = 437.28, 0.4 × 0.3 × 0.2 mm, a = 12.550(1), b = 10.693(1), c = 15.692(1) Å, β = 90.24(1)°, V = 2106.6(3) Å³, ρ_{calc} = 1.379 g cm⁻³, μ = 6.67 cm⁻¹, no absorption correction, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, ω–2θ scans, 4839 reflections collected ($\pm h$, $-k$, $\pm l$). [(sin θ)/λ]$_{max}$ = 0.62 Å⁻¹, 4278 independent and 1844 observed reflections [$I \leq 2\sigma(I)$], 244 refined parameters, R = 0.057, wR^2 = 0.115, max. residual electron density 0.52 (−0.30) e⁻ Å⁻³, hydrogen atoms calculated and riding.

X-ray crystal structure analysis of 7b-rl: formula $C_{24}H_{30}TiCl_2$, M = 437.28, 0.5 × 0.5 × 0.3 mm, a = 11.458(2), b = 10.686(4), c = 17.810(5) Å, V =

2180.7(11) Å³, ρ_{calc} = 1.332 g cm⁻³, μ = 6.44 cm⁻¹, no absorption correction, Z = 4, orthorhombic, space group *Pbcn* (No. 60), λ = 0.71073 Å, ω–2θ scans, 4906 reflections collected ($\pm h$, $+k$, $-l$), [(sin θ)/λ]$_{max}$ = 0.62 Å⁻¹, 2223 independent and 1475 observed reflections [$I \le 2\sigma(I)$], 123 refined parameters, R = 0.041, wR^2 = 0.103, max. residual electron density 0.50 (−0.26) e⁻ Å⁻³, hydrogen atoms calculated and riding.

3.5.3. [trans-1,2-Cycloheptylen-bis(η^5-4,5,6,7-tetrahydroindenyl)]titanium dichloride 7c

Analogously as described above 2.50 g (7.4 mmol) of 3c was reacted with 1.14 g (7.4 mmol) of TiCl₃ to give 1.57 g (48%) of the crude ansa-metallocene product 6c [anal. calcd. for C₂₅H₂₄Cl₂Ti (443.3): C, 67.74; H, 5.46; found: C, 72.01; H, 5.62%], that was directly subjected to catalytic hydrogenation to give ca. 1.6 g (quant.) of 7c, m.p. > 224 °C (decomp.), A:B:C ratio 30:7:63. Flash chromatography (conditions see above) gave 0.42 g of a mixture of the racem-like isomers A and B (R_f = 0.42), from which further crystallization gave a 90% enriched sample of one of the racem-like forms (A), and 1.05 g of the meso-like isomer (R_f = 0.22) of 7e. NMR data of the racem-like isomer A: ¹H NMR (CDCl₃): δ = 1.58–2.07 (m, 18H); 2.25 (m, 2H); 2.43 (m, 2H); 2.60 (m, 2H); 3.11 (m, 2H); 3.26 (m, 2H); 5.46 (m, 2H, 2/3-H, ^3J = 2.2 Hz); 6.62 (d, 2H, 2/3-H, ^3J = 2.2 Hz). ¹³C NMR (CDCl₃): δ = 21.6, 21.8, 21.9, 23.8, 24.3, 26.6, 37.3 (−CH₂, C-4 to -7, -3' to -7'); 45.4 (−CH, C-1', -2'); 108.7, 128.1 (−CH, C-2, -3); 128.5, 136.2, 136.7 (−C, C-1, -8, -9); meso-like isomer C: ¹H NMR CDCl₃: δ = 1.53 (m, 8H); 1.78 (m, 8H); 1.98 (m, 4H); 2.29 (m, 4H); 2.61 (m, 2H); 3.25 (m, 1H); 3.50 (m, 1H); 5.77 (d, 1H, 2/3-H, ^3J = 2.9 Hz); 6.27 (d, 1H, 2/3-H, ^3J = 2.9 Hz); 6.30 (d, 1H, 2/3-H, ^3J = 2.9 Hz); 6.57 (d, 1H, 2/3-H, ^3J = 2.9 Hz). ¹³C NMR (CDCl₃): δ = 20.7, 20.7, 20.8, 21.0, 22.3, 23.4, 24.0, 24.3, 25.2, 25.2, 26.2, 32.2, 37.7 (−CH₂, C-4 to -7, -4* to -7*, -3' to -7'); 45.4, 48.3 (−CH, C-1', -2'); 107.1, 112.5, 124.6, 130.5 (−CH, C-2, -3, -2*, -3*); 124.6, 131.0, 133.1, 133.3, 136.3, 139.8 (−C, C-1, -8, -9, -1*, -8*, -9*). IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3086, 2936, 2861, 1498, 1464, 1437, 1048, 823. Anal. calcd. for C₂₅H₃₂Cl₂Ti (451.31) C, 66.53; H, 7.15; found: C, 68.63; H, 7.00. Single crystals of the meso-like 7c diastereoisomer were obtained from dichloromethane.

X-ray crystal structure analysis of 7c-ml: formula C₂₅H₃₂TiCl₂, M = 423.25, 0.3 × 0.15 × 0.15 mm, a = 11.179(3), b = 12.460(2), c = 15.735(5) Å, V = 2191.7(10) Å³, ρ_{calc} = 1.368 g cm⁻³, μ = 6.43 cm⁻¹, no absorption correction, Z = 4, orthorhombic, space group *Pna2₁* (No. 33), λ = 0.71073 Å, ω–2θ scans, 1954 reflections collected ($\pm h$, $+k$, $+l$), [(sin θ)/λ]$_{max}$ = 0.58 Å⁻¹, 1921 independent and 768 observed reflections [$I \le 2\sigma(I)$], 253 refined parameters, R = 0.063, wR^2 = 0.132, max. residual electron density 0.28

(−0.32) e⁻ Å⁻³, hydrogen atoms calculated and riding. Due to the poor crystal quality (weakly diffracting) the accuracy of this analysis is rather low.

3.6. Preparation of the ansa-cycloalkylen-bis(indenyl)hafnium dichlorides 8, general procedure

A solution of 5.0 mmol HfCl₄ · 2THF in 100 ml of THF and a solution of 2.5 mmol of the respective dilithium reagent 3 in 100 ml of THF are added dropwise simultaneously into 100 ml of THF at room temperature. The mixture is then stirred for 5 h at ambient temperature and then for 24 h at 50 °C. Solvent is removed in vacuo, the residue taken up in 100 ml of dichloromethane and the precipitated lithium chloride removed by filtration. Solvent is evaporated from the clear filtrate in vacuo and the remaining solid product washed with pentane.

3.6.1. [trans-1,2-Cyclohexylen-bis(η^5-1-indenyl)]hafnium dichloride 8b

Following the general procedure as described above 0.40 g (1.23 mmol) of 3b was reacted with 0.58 g (1.25 mmol) of HfCl₄ · 2THF to yield 0.45 g (65%) of 8b, m.p. 152 °C (decomp.), A:B:C isomer ratio 23:17:60. ¹H NMR (CDCl₃): δ = 1.30–2.23 (m, 24H); 3.80 (m, 6H); 5.85 (d, 1.0H, 2/3-H^B, ^3J = 3.3 Hz); 6.13 (d, 1.0H, 2/3-H^B, ^3J = 3.3 Hz); 6.15 (d, 1.8H, 2/3-H^C, ^3J = 3.3 Hz); 6.28 (d, 1.4H, 2/3-H^A, ^3J = 3.3 Hz); 6.34 (d, 1.8H, 2/3-H^C, ^3J = 3.3 Hz); 6.51 (d, 1.8H, 2/3-H^C, ^3J = 3.3 Hz); 6.59 (d, 1.4H, 2/3-H^A, ^3J = 3.3 Hz); 6.74 (d, 1.8H, 2/3-H^C, ^3J = 3.3 Hz); 6.91–7.60 (m, 18H), 7.78 (m, 6H). IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3079, 2930, 2855, 1468, 1457, 1273, 816, 741. Anal. calcd. for C₂₄H₂₂Cl₂Hf (559.83) C, 51.49; H, 3.96; found: C, 53.05; H, 4.05.

3.6.2. [trans-1,2-Cycloheptylen-bis(η^5-1-indenyl)]hafnium dichloride 8c

Analogously as described above 0.89 g (2.63 mmol) of 3c was treated with 1.23 g (2.65 mmol) of HfCl₄ · 2THF to give 0.81 g (54%) of 8c, m.p. 155 °C (decomp.), A:B:C ratio 16:3:81. ¹H NMR (CDCl₃): δ = 1.41–2.18 (m, 30H); 3.73 (m, 6H); 5.85 (d, 0.2H, 2/3-H^B, ^3J = 3.4 Hz); 6.10 (d, 2.4H, 2/3-H^C, ^3J = 3.4 Hz); 6.13 (d, 1.0H, 2/3-H^A, ^3J = 3.4 Hz); 6.26 (d, 0.2H, 2/3-H^B, ^3J = 3.4 Hz); 6.35 (d, 2.4H, 2/3-H^C, ^3J = 3.4 Hz); 6.45 (d, 2.4H, 2/3-H^C, ^3J = 3.4 Hz); 6.59 (d, 1.0H, 2/3-H^A, ^3J = 3.4 Hz); 6.72 (d, 2.4H, 2/3-H^C, ^3J = 3.4 Hz); 6.87–7.49 (m, 18H); 7.70 (m, 6H). IR (KBr): $\tilde{\nu}$ (cm⁻¹)

= 3069, 2930, 2855, 1464, 1459, 1396, 1348, 1259, 802, 741. Anal. calcd. for $C_{25}H_{24}Cl_2Hf$ (573.86) C, 52.33; H, 4.22; found: C, 53.78; H, 4.53.

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