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Preparation and Catalytic Application of a Novel Very Rigid Group 4 Ansa-Metallocene System

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Abstract: Treatment of 2,5-hexandione with cyclopentadiene in the presence of pyrrolidine yields the corresponding bisfulvene (**5**) that has been converted to the [4-cyclopentadienyliden-4,7,7-trimethyl-4,5,6,7-tetrahydroindenyl]ligand system, isolated as the dilithio compound **8**. Subsequent reaction with the group 4 metal halides MCl_4 (M = Ti, Zr, Hf) gives the rigid ansa-metallocene dichlorides **9a-c**. Their reaction with methyllithium yields the corresponding dimethyl-ansa-metallocenes **10a-c**. Complexes **9a-c** and **10a-c** were characterized by X-ray diffraction. The zirconium and hafnium systems all exhibit very low D1-M-D2 angles (D1 and D2 denote the centroids of the Cp-ring systems) at around 116°. Consequently the homogeneous metallocene/methylalumoxane Ziegler-type catalyst systems derived from the zirconium complex **9b** produce low molecular weight propene oligomers (in contrast to high molecular weight polypropylene formed at the titanium containing **9a**/MAO catalyst system), which is probably due to an electronic control of the $k_{propagation}/k_{termination}$-ratio of the propene polymerization process. It is forseeable that such ansa-metallocene derived catalyst systems favouring the formation of low molecular weight products instead of high molecular weight polyolefins will find increasing applications in organic synthesis.

Group 4 bent metallocene complexes have provided the basis for a very important recent catalyst development. Activated by excess methyl alumoxane (MAO) they provide extremely active homogeneous Ziegler-type catalyst systems for the production of α-olefin polymers.[1] The use of rigid ansa-metallocene frameworks allowed for a very effective means of controlling the activity and stereoselectivity of the α-olefin polymerization process and has contributed very essentially to the current state of homogeneous Ziegler-type bent metallocene catalyst application in α-olefin polymerization. Brintzinger's (ethylenbisindenyl)MX_2 systems deserve to be especially mentioned in this regard along with some more recent developments using CR_2 or SiR_2 groups bridging between the Cp-type ligands at the bent metallocene wedge.[2]

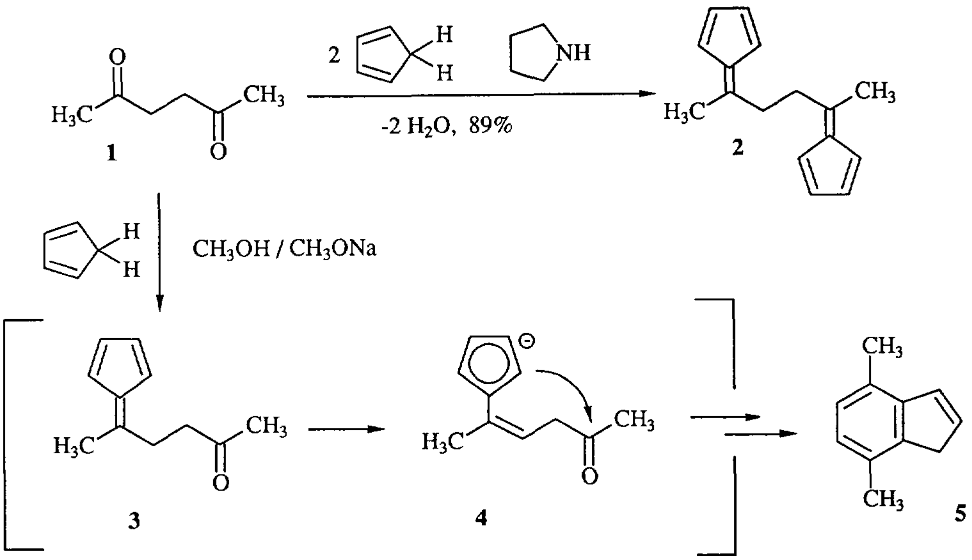
The ansa-metallocene frameworks are commonly employed as rigid templates allowing the attachment of sterically active substituents to control the catalyst action. Often, an additional electronic component brought about by the special features of the ansa-system is introduced to the very metallocene system. Such electronic components of catalyst performance are often masked by the obvious and apparently dominant sterical influences of substituents and groups attached to the ansa-metallocene backbone. Nevertheless, electronic control of some specific catalyst features can become important and even dominating with specific ligand types. We have recently designed a synthesis of a very rigid novel ansa-metallocene type where the catalyst action may be governed to a great extent by electronic features introduced to the metallocene system by the specific nature of the rigid ring-annulated C_1-bridged bis-cyclopentadienyl ligand system.[3] Some details concerning the preparation, the structural properties and the catalyst action of our novel group 4 ansa-metallocene systems will be described in this account.

Synthesis of the New Ansa-Metallocene Systems

There are two different principal synthetic protocols for converting ketones (or aldehydes) to fulvenes. The original fulvene preparation developed by Thiele at the turn of the century utilizes a strong base in a protic solvent (e.g. $NaOCH_3$ in CH_3OH) to condense the organic carbonyl compound with cyclopentadiene.[4] A method originating from the work of Stone and Little takes advantage of the dual function of pyrrolidine to serve as a carbonyl activating agent (by means of iminium salt formation) and as a base to effect fulvene formation.[5] It is evident from many examples in the literature that these two methods complement each other very nicely.

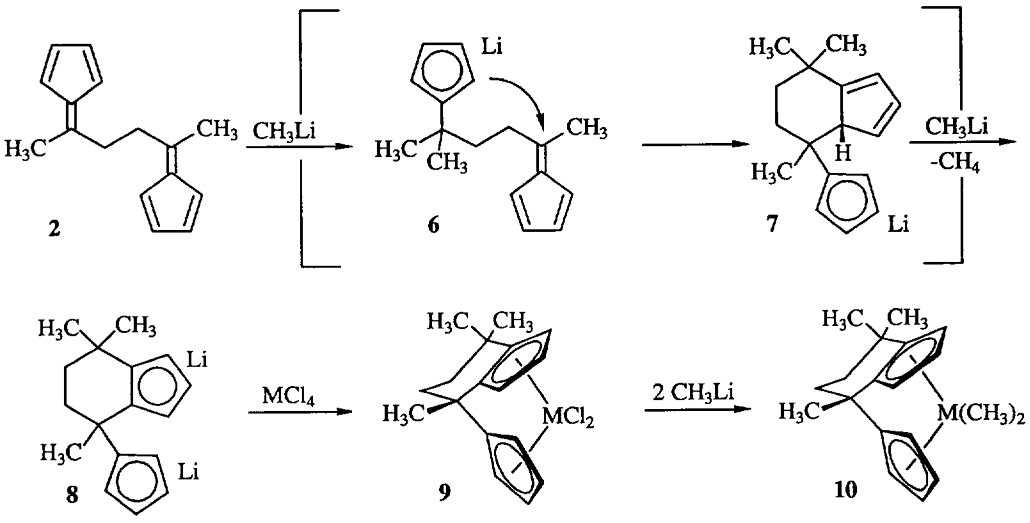
In the reaction of 1,4-diketones the application of the Thiele and Stone/Little methods, respectively, gives rise to the formation of two very different products. Treatment of 2,5-hexandione **1** with cyclopentadiene in methanol in the presence of 2.5 molar equiv. of sodium methoxide at ambient temperature gave exclusively 4,7-dimethyl indene (**5**) that was isolated in 84% yield. Under these preparative conditions, the intramolecular condensation step starting from the intermediate **3** is apparently faster than the introduction of the second fulvene unit. Under "Thiele-conditions" ring-closing condensation is a rather general reaction of internally enolizable aliphatic and aromatic 1,4-dicarbonyl compounds and a large variety of substituted indenes has been prepared this way.[6]

Scheme 1



In contrast, the bisfulvene **2** [3,7] was obtained and isolated in 89% yield when 2,5-hexandione (**1**) was treated with two molar equiv. of cyclopentadiene in methanol at 0°C in the presence of 1.5 molar equiv. of pyrrolidine. The bridged annulated bis-cyclopentadienyl ligand system (**8**) was constructed by reacting the bisfulvene **2** with 2.2 molar equiv. of methyllithium in ether. Presumably, one equiv. of the methylanion-nucleophile adds to an exocyclic fulvene sp^2-carbon atom to initiate a cyclization reaction sequence similar to that discussed in our indene synthesis (see Scheme 1 and above).[8] This would yield a Cp-substituted tetrahydroisoindene isomer (**7**) as an reactive intermediate that is unstable in the basic reaction medium and is rapidly deprotonated to give **8**. The dilithio ansa-metallocene reagent [**8** • diethylether] was isolated (89% yield) and characterized. Its reaction with the group 4 metal halides MCl_4 (M = Ti, Zr, Hf) furnished the corresponding ring-annulated ansa-metallocenes **9(a-c)**.

Scheme 2



[M = Ti(a), Zr(b), Hf(c)]

The [4-cyclopentadienyliden-4,7,7-trimethyl-4,5,6,7-tetrahydroindenyl]ligand system (**8**) contains a center of chirality and a prochiral disubstituted cyclopentadienyl ring. Attachment of a group 4 transition metal center to the latter generates a second element of chirality, here an element of planar chirality. Of the two possible diastereomers resulting from such a stereochemical situation only one can be realized in a mononuclear bent metallocene complex. Employing the stereochemical metallocene notation introduced by Schlögl and later amended by Brintzinger[9] the only possible diastereomer is characterized by a relative stereochemical descriptor R*,p-R*. Practical synthesis just had to assure that suitable reaction conditions were found to allow the synthesis of the mononuclear target molecules and sufficiently suppress the formation of the easily formed mixtures of oligomeric organometallic products. This was difficult, but eventually we succeeded in preparing the complexes **9a-c** in low but reproducible yields (13-18%).

Complexes **9a-c** were isolated as crystalline solids and characterized by X-ray diffraction (see below). NMR spectra in solution revealed the presence of the chiral metallocene framework. Thus the corresponding zirconium complex **9b** exhibits seven separated ^{13}C NMR cyclopentadienyl methine resonances at δ 125.9, 123.6, 117.9, 116.0, 110.3, 107.3, 105.8 in addition to three quarternary cyclopentadienyl carbon signals (δ 137.7, 121.3, 113.7).

Each of the complexes **9a-c** was treated with methyllithium in ether (two molar equiv.) to give the corresponding dimethyl-ansa-metallocene derivatives **10a-c** in 50-80% yield. The chirality of the ansa-metallocene backbone causes a diastereotopic differentiation of the σ-ligands attached at the central metal center. Therefore, all these complexes exhibit 1:1 pairs of ^{1}H NMR σ-methyl ligand resonances. These appear markedly shifted to lower δ values on going from the titanium complex **10a** (δ –0.05 and –0.06) to zirconium (**10b**: δ –0.26, –0.34) and hafnium (**10c**: δ –0.44, –0.49).

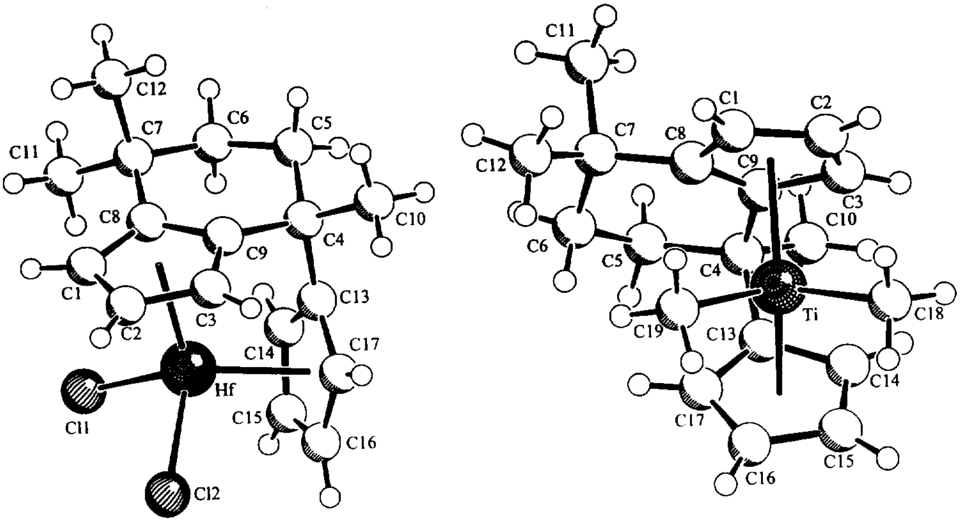
X-ray Crystal Structure Analyses

The ansa-metallocene dichlorides **9a-c** and the corresponding dimethylmetallocenes **10a-c** were characterized by X-ray diffraction. The zirconium complex **9b** is a typical member of the series. It exhibits a tetrahydroindenyl ligand bearing three methyl substituents that is fused to a cyclopentadienyl ligand at carbon atom C4. The annulated six-membered ring system adopts a typical cyclohexene-type half-chair conformation with a pronounced axial/equatorial positional differentiation of methyl groups at C7 and also of the substituents at C4, here with the η^5-cyclopentadienylidene ligand being attached axially.

Both substituted cyclopentadienyl systems in **9b** are η^5-coordinated to zirconium. However, tucking the large zirconium metal center into the fused C_1-bridged bis-cyclopentadienyl ligand system has led to several marked distortions. Inside the tetrahydroindenyl Cp-system there are three rather long zirconium to carbon contacts at 2.577(3) Å (Zr-C1), 2.527(2) Å (Zr-C2), and 2.538(3) Å (Zr-C8), whereas two Zr-C(sp^2) interactions are much shorter: 2.438(2) Å (Zr-C9), 2.418(2) Å (Zr-C3). Similarly, in the monosubstituted Cp-ring the Zr-C(Cp) distances in proximity to the ring junction are short [2.46(1): Zr-C17, 2.444(3) Zr-C13, 2.464(2) Zr-C14] whereas the distal Zr-C(Cp) bonds are longer [2.553(3) Å, Zr-C16; 2.553(4) Å, Zr-C17]. Carbon center C4 connects the two η^5-Cp-type ring systems in the C_1-bridged ansa-metallocene complex **9b** [C9-C4: 1.521(4) Å, C13-C4: 1.533(4) Å]. The substituents at both Cp-rings of the ansa-metallocene are markedly oriented outside the Cp-ring planes. The C(sp^2)-C(sp^3) linkages at the tetrahydroindenyl part are bent *toward* the metal center by ca. 15° (averaged value, see Table 1), at the Cp-section the bending angle is ca. 19°. This allows the angle between the Cp-planes (71.4°) to be far smaller than the corresponding angle at the bridging carbon center [C9-C4-C13 = 99.9(2)°]. It is the soft potential of such angular distortions that makes this set of carbon angles not very much suited to characterize and determine the ligand influence on the electronic properties of the metal inside the bent metallocene system. For principal reasons the D1-Zr-D2 angle (with D1 and D2 denoting the centroids of the Cp-ring systems) is a much better and very consistent descriptor for this purpose. In complex **9b** the D1-Zr-D2 angle is 116.3°. The Cl1-Zr-Cl2 angle in **9b** is 98.3°.

In the dimethyl-ansa-zirconocene derivative **10b**, the CH_3-Zr-CH_3 angle (C18-Zr-C19) is 99.6(1)°. In this complex, the angle between the Cp-planes is 72.1°. The D1-Zr-D2 angle in **10b** is 115.8° which is (within the accuracy limits of the method) almost identical to that found in the metallocene dichloride **9b**.

Figure 1. Views of the molecular geometry of the ansa-hafnocene dichloride complex **9c** (left) and the ansa-titanocene dimethyl complex **10a** (right) with atom numbering scheme.



The angles of 116.3° and 115.8° in the ansa-metallocene complexes **9b** and **10b**, respectively, to our knowledge are the smallest D1-Zr-D2 angles observed for zirconocene complexes so far. Typically, zirconocene Cp-centroid-Zr-Cp-centroid angles are around 130° and thus are more than 10° larger than found here. Brintzinger's (ethylene-bistetrahydroindenyl)zirconium dichloride complex exhibits a D-Zr-D angle of 125.2°, i.e. ca. 9° larger than found in the **9b**/**10b** series. Razawi's fluorenyl-derived C_1-bridged ansa-zirconocenes to our knowledge have exhibited the lowest D1-Zr-D2 angles so far. At ~118.0° they are much smaller than those of the C_2-bridged "Brintzinger-ansa-zirconocenes",[10] but are still markedly larger than the very small D1-Zr-D2 angles observed for the new [4-(η-cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]zirconium complexes.

The structures of the hafnium compounds **9c** and **10c** are very similar to the analogous ansa-zirconocenes, as expected. The bonds to hafnium are slightly shorter, as usual[11], and so the hafnium atom fits a little better into the narrow ansa-ligand wedge. Consequently, the D1-Hf-D2 angle of **9c** is a little larger at 117.1° as compared to the Zr compound **9b** (116.3°). This effect is increased upon going to the titanium complexes. The D1-Ti-D2 angle in the ansa-titanocene dichloride **9a** is 120.9°, in the corresponding dimethyl-ansa-titanocene **10a** it is 121.0°. This is identical as observed in (methylenbiscyclopentadienyl)$TiCl_2$.[12] Even titanocene dichloride exhibits only a slightly larger D-Ti-D angle at 124°.[10] We conclude, that the angular distortions in the titanocene series are not very pronounced and hence there should not be a great change in catalyst properties upon replacing e.g. Cp_2TiCl_2 for the ansa-titanocene dichloride **9a** as a component in homogeneous Ziegler-type catalyst systems. On the contrary, the novel [4-(η-cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]ligand system seems to be stereoelectronically effective in the corresponding zirconium and hafnium complexes. The marked reduction of the D1-M-D2 opening angle relative to the less strained reference compounds (see above[10]) may substantially influence the bonding features

Table I Selected bond lengths (Å) and angles (deg) of the ansa-metallocene complexes **9a-c** and **10a-c**.

compound (MX_2)	**9a** ($TiCl_2$)	**9b** ($ZrCl_2$)	**9c** ($HfCl_2$)	**10a** ($TiMe_2$)	**10b** ($ZrMe_2$)	**10c** ($HfMe_2$)
M-C1	2.482(2)	2.577(2)	2.558(7)	2.476(3)	2.597(2)	2.574(4)
M-C2	2.413(2)	2.527(3)	2.503(7)	2.402(3)	2.529(2)	2.512(4)
M-C3	2.291(2)	2.418(2)	2.414(7)	2.310(2)	2.444(2)	2.431(4)
M-C8	2.436(2)	2.538(3)	2.527(6)	2.458(2)	2.573(2)	2.561(4)
M-C9	2.328(2)	2.438(2)	2.428(6)	2.340(2)	2.464(2)	2.453(3)
M-C13	2.336(2)	2.444(3)	2.436(7)	2.338(2)	2.452(2)	2.444(4)
M-C14	2.351(2)	2.464(2)	2.438(7)	2.350(3)	2.510(2)	2.461(4)
M-C15	2.445(3)	2.553(4)	2.533(7)	2.450(3)	2.593(2)	2.560(4)
M-C16	2.446(3)	2.553(3)	2.548(7)	2.459(3)	2.583(2)	2.573(4)
M-C17	2.349(2)	2.46(1)	2.459(7)	2.369(2)	2.475(2)	2.495(4)
C4-C9	1.522(3)	1.521(4)	1.518(9)	1.516(3)	1.533(3)	1.534(5)
C4-C13	1.533(3)	1.533(4)	1.534(10)	1.529(3)	1.529(3)	1.532(5)
M-C1(1)/Cl8	2.362(1)	2.448(1)	2.401(2)	2.163(3)	2.266(3)	2.242(4)
M-C1(2)/C19	2.331(1)	2.427(1)	2.421(2)	2.153(3)	2.270(3)	2.241(4)
C7-C8-C9	122.6(2)	123.0(3)	123.3(6)	122.2(2)	122.8(2)	122.7(3)
C8-C9-C4	121.5(2)	121.9(2)	121.0(6)	121.8(4)	121.9(2)	121.8(3)
C9-C4-C13	97.1(2)	99.9(2)	100.5(5)	99.0(2)	101.1(1)	100.8(3)
C1(1)/C18-M-C1(2)/C19	95.3(1)	98.3(1)	96.79(7)	94.4(1)	99.6(1)	97.5(2)
D1-M-D2	120.9	116.3	117.1	121.0	115.8	116.4
Cp(A)-Cp(B)	67.3	71.4	69.8	66.6	72.1	61.0
C2-C1-C8-C7	-167.0	166.6	167.0(7)	-166.3(3)	-166.5	-166.5(4)
C3-C9-C8-C7	169.3	-168.4	-168.5(6)	167.5(2)	167.4	167.7(2)
C2-C3-C9-C4	-161.4	162.1	160.7(7)	-158.3(2)	159.6	-159.3(4)
C1-C8-C9-C4	162.1	-162.5	-161.4(6)	159.1(2)	160.6	159.9(3)
C16-C17-C13-C4	161.4	-162.3	-160.8(7)	-158.8(2)	162.7	-160.4(4)
C15-C14-C13-C4	-160.0	160.7	158.8(7)	160.1(2)	-161.1	162.1(3)

X-ray crystal structure analysis:

9a: a=9.233(2), b=10.543(1), c=16.665(1) Å, β=105.62(1)°, $P2_1/n$(No.14), R=0.033, R_w=0.042
9b: a=9.230(2), b=10.724(2), c=16.902(4) Å, β=105.06(2)°, $P2_1/n$(No.14), R=0.023, R_w=0.030
9c: a=9.220(1), b=10.718(1), c=16.920(2) Å, β=105.13(1)°, $P2_1/n$(No.14), R=0.035, wR^2=0.089
10a: a=7.552(2), b=16.919(1), c=12.822(2) Å, β=94.92(2)°, $P2_1/n$(No.14), R=0.054, wR^2=0.165
10b:a=7.656(1), b=16.886(2), c=13.034(1) Å, β=94.66(1)°, $P2_1/n$(No.14), R=0.027, wR^2=0.039
10c: a=7.628(2), b=16.818(3), c=12.910(3) Å, β=94.80(3)°, $P2_1/n$(No.14), R=0.025, wR^2=0.068

Programs used: SHELX-86, SHELX-93, SCHAKAL-92. Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD 58408, 58712, and 401266-401268, the names of the authors, and the journal citation.

at the metal center. Hoffmann and Lauher carried out the general orbital analysis of bent metallocene complexes in 1976 and described the very pronounced dependence of the bent metallocene valence orbital energies on the D-M-D angle.[13] Decreasing this angle, qualitatively has the consequence of decreasing the stability of σ-bonds to zirconium in the bent metallocene ligand environment. Among these, zirconium to carbon σ-bonds are more effected than zirconium-hydrogen bonds. Consequently, closing the D1-Zr-D2 angle by ligand construction — as this has been achieved in the complexes **9b** and **10b** (and to a similar extent in their hafnium analogues as well) — could increase the probability of the β-hydride elimination step leading to increased chain termination and transfer at the homogeneous Ziegler-type α-olefin polymerization catalysts derived from these systems. Such an effect should be absent or much less pronounced with the analogous titanium systems.

Catalytic α-Olefin Coupling

The ansa-metallocene dichlorides **9a-c** were employed as components to generate homogeneous Ziegler-type catalysts for propene polymerization reactions. The transition metal compounds were dissolved in toluene and activated by treatment with a large excess of methylalumoxane. Propene was added at various chosen temperatures and polymerized at that temperature for a given time. The mixture was then quenched and the polymer isolated.

At -50°C the ansa-titanocene derived catalyst system **9a**/MAO produces high molecular weight polypropylene (PP1, $\overline{M}_\eta$ = 670000) with a catalyst activity of a ≈ 300 [g polymer / g [Ti] • h]. The stereochemistry of the polymer formed was determined by ^{13}C NMR methyl pentade analysis combined with a statistical treatment as described previously.[14] At –50°C the stereocontrol of the CC-coupling process is almost exclusively taking place by the influence of the polymer chain end. The probability (σ) of formation of a meso dyad (m) in the chain end controlled process forming the polypropylene PP1 is $\sigma = 0.78$. With increasing temperature the formed polypropylene is less isotactic (see Table II). Moreover, the overall stereocontrol becomes more complicated. At –30°C there is a clear indication that there is also transfer of the chirality information from the chiral metallocene backbone taking place (enantiomorphic site control, meso-probability factor α) in addition to the chain end stereocontrol. Such double stereodifferentiation type stereocontrol is frequently encountered in metallocene based catalytic α-olefin polymerization.[15] The proportion of enantiomorphic site control (ω) is increased with increasing temperature but overall the polymers are rapidly approaching an atactic situation. With the titanocene derived **9a**/MAO catalyst the activity increases and the molecular weight of the polymer decreases with increasing temperature as is often observed with such metallocene Ziegler-type catalyst systems.[16]

The corresponding ansa-zirconocene dichloride derived **9b**/MAO catalyst system has very different polymerization characteristics. As usual, the propene polymerization activity rapidly increases with temperature (see Table II) but the molecular weights of the products are much lower than those from the Ti-catalyzed process. The $\overline{M}_\eta$-values are unusually low for α-olefin coupling products formed at a zirconocene/methylalumoxane catalyst system. As discussed in the preceeding chapter, this probably reflects the unusual electronic situation at the ansa-zirconocene framework of **9b** and may potentially be due to a dominating electronic control of the polymerization process.[17] At

Table II. Propene polymerization with ansa-metallocene derived **9**/MAO catalyst systems.

polymer	metallocene		T(°C)	Al:Zr	activity^a	$\overline{M}_\eta$	ω^b	α^b	σ^b
PP1	**9a**	Ti	-50	626	300	670000	--	--	0.78
PP2	**9a**	Ti	-30	659	650	220000	0.39	0.88	0.66
PP3	**9a**	Ti	-11	659	1100	27000	0.45	0.77	0.66
PP4	**9a**	Ti	0	569	1300	10000	c	c	c
PP5	**9b**	Zr	-50	706	17	25000	d	-	0.30
PP6	**9b**	Zr	-30	706	330	13000	d	-	0.32
PP7	**9b**	Zr	-5	706	1500	1900	d	-	0.34
PP8	**9c**	Hf	0	865	41	850	c	c	c

[a] in g polymer/g[M] • h; [b] for definition of these statistical parameters see text; [c] not determined; [d] no mmmm ^{13}C NMR methyl pentade signal observed.

–5°C a product with an averaged $\overline{M}_\eta$ of only 1900 is obtained. At room temperature, a mixture of oligomers was isolated from the propene coupling reaction at the **9b**/MAO catalyst with a distribution exhibiting its maximum at n = 6 (determined by GC/MS and by ^{13}C NMR end group analysis). In this case, the isolated toluene solvent fraction contained a sizable amount of dimers and trimers, that were, however, not isolated.

The propene CC-coupling process at the **9b**/MAO catalyst exhibits some uncommon stereochemical characteristics. The stereocontrol is largely temperature independent and in each case a slightly syndiotactic polypropylene is obtained. It is noteworthy that the mmmm ^{13}C NMR methyl pentade signal is absent and that the pentade resonances having a high r content show increased intensities. σ-Values between 0.30 and 0.34 were obtained from the statistical analysis. This is probably one of the rare catalyst systems being able to produce slightly syndiotactic polypropylene by a chain end stereocontrolled process.[18] The ansa-hafnocene derived **9c**/MAO catalyst produces similar low molecular weight propene-oligomers (0°C: $\overline{M}_\eta \approx 850$), albeit with a much lower catalyst activity. The polymer is atactic.

Conclusions

Treatment of the bisfulvene **5** with methyllithium provides an easy access to the novel ansa-group 4 metallocenes **9**. These C_1-bridged ansa-metallocene complexes are unusually rigid. Especially the incorporation of the larger group 4 metals zirconium and hafnium leads to a very specific ligand distortion which is characterized by a marked decrease of the D1-M-D2 angles as compared to a great variety of reference metallocenes. This specific opening of the bent metallocene bite is probably going along with a strong electronic change of the energetics of the σ-ligand bonds at the bent metallocene. As a consequence, the chain termination step during polypropylene formation at the bent metallocene/MAO catalysts via β-hydride elimination is becoming increasingly favoured. We consider this means of an electronic influence of the catalyst performance as important: this effect may help to convert the homogeneous bent metallocene/MAO polymerization catalysts eventually into novel catalytic systems useful for olefin coupling in organic monomer synthesis, i.e. change the preferred products formed from high molecular weight polymeric materials to monomeric olefin cyclization or coupling products. We regard this as a very significant field of potential future application of the increasingly important family of group 4 metallocene derived homogeneous Ziegler-type catalyst systems. Our study shows that low molecular weight products are formed at these novel electronically modified catalyst systems and ways toward effective stereocontrol also seem possible. So the scene is set for a rapid development of such bent metallocene derived catalyst systems for applications in selective organic synthesis.

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Experimental Section

Reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. All solvents were dried and distilled under argon prior to use. For a more detailed description of general experimental conditions including a listing of spectrometers used see ref. 15. Propene polymerizations were carried out as previously described.[15] The procedures used for polymer characterization were recently described in detail.[15]

2,5-Bis(2,4-cyclopentadien-1-yliden)hexane **2**. 2,5-Hexandione (**1**, 11.0 g, 96.3 mmol) and 12.7 g (193 mmol) of cyclopentadiene were dissolved at 0°C in 60 ml of methanol. Pyrrolidine (8.6 g, 121 mmol) was added and the mixture stirred for 90 min at 0°C. Glacial acetic acid (5 ml) and water (50 ml) were added. The mixture was extracted with pentane (2 x 70 ml), the combined organic phases washed with brine and dried over $MgSO_4$. Removal of the solvent in vacuo gave the bisfulvene **2** (18.0 g, 89% yield) as a viscous oil. Anal. Calcd. for $C_{16}H_{18}$ (210.3) C 91.37, H 8.63; found C 90.81, H 8.68. ^1H NMR ($CDCl_3$): δ 6.56-6.55 (br.m, 8H, cyclopentadienylidene CH), 2.82 (s, 4H, CH_2) 2.30 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 151.5, 143.2 (C), 131.4 (double intensity) 120.9, 120.2 (CH), 36.9 (CH_2), 21.1 (CH_3). IR (NaCl): $\tilde{\nu}$ 3100, 3068, 2988, 2963, 2908, 1637, 1470, 1434, 1368, 1088, 858, 764 cm^{-1}.

4,7-Dimethylindene **5**. Sodium (19.6 g, 855 mmol) was dissolved in 200 ml of methanol. At 0°C 33.9 g (513 mmol) of freshly distilled cyclopentadiene and then 39.0 g (342 mmol) of 2,5-hexandione were added dropwise. The mixture was stirred for 2 h at room temperature. Then 100 ml of water and 200 ml of ether were added. The organic phase was separated, washed with brine and dried over anhydrous magnesium sulfate. Solvent was removed in vacuo and the product **5** isolated by fractional distillation (bp. 65°C, 0.1 mbar) as a colorless oil, 41.4 g (84% yield). ^1H NMR ($CDCl_3$): δ 7.25, 7.16 (AX, ^3J = 7.6 Hz, 2H, 5-H, 6-H), 7.23 (m, 1H, 3-H), 6.78 (dt, ^3J (2-H, 3-H) = 5.6 Hz, ^3J (2-H, 1-H) = 1.9 Hz, 1H, 2-H), 3.49 (dd, ^3J (1-H, 2-H) = 4.0 Hz, ^4J (1-H, 3-H) = 2.0 Hz, 2H, 1-H), 2.68, 2.57 (s, each 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 143.1, 142.1, 130.0 (double intensity) (C4, C7, C8, C9), 133.1, 130.5, 127.5, 125.7 (C2, C3, C5, C6), 38.1 (C1), 18.3, 18.2 (CH_3).

Dilithio[4-(η^5-cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)] **8**. Ethereal methyllithium (62.4 ml of a 1.60 M solution, 99.8 mmol) was added dropwise to a solution of the bisfulvene **2** (10.0 g, 47.5 mmol) in 150 ml of ether with stirring at 0°C. The mixture was stirred for 24 h at room temperature. The resulting precipitate was isolated, washed with pentane and dried to yield 13.2 g of the etherate of the dilithio reagent **8**. A ^1H NMR spectrum of the product was monitored (d_6-benzene/d_8-THF, 9:1): δ 5.82, 5.67, 5.45, 4.98 (br. m, 7H, CH), 2.10-1.85 (br.m, 4H, CH_2), 1.52, 1.45, 1.25 (3 br.s, 9H, CH_3). The product was used without further characterization in the reactions with the metal halides.

[4-(η^5-Cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]dichlorotitanium **9a**. A suspension of the dilithio compound **8** (5.46 g, 17.5 mmol) in 200 ml of toluene was cooled to -78°C. Titaniumtetrachloride (3.32 g, 17.5 mmol) was added. The dark red reaction mixture was stirred for 30 h at room temperature and then filtered. Solvent was removed from the clear filtrate and the residue washed repeatedly with pentane to give 1.85 g of the crude metallocene complex. This material was extracted continously with 100 ml of pentane for 2 d. Removal of the solvent gave 780 mg (13% yield) of **9a**, mp 259°C (DSC). Crystals of complex **9a** for the X-ray crystal structure analysis were obtained by recrystallization of a sample from methylene chloride. Anal. Calcd. for $C_{17}H_{20}Cl_2Ti$ (343.2) C 59.50, H 5.87; found C 59.54, H 5.97. ^1H NMR ($CDCl_3$): δ 7.05, 6.93, 6.79 (double intensity), 5.85, 5.80, 5.61 (m, 7H, CH), 2.45 (ddd, 1H, 5-H_{eq}), 2.31 (ddd, 1H, 5-H_{ax}), 1.91 (ddd, 1H, 6-H_{ax}), 1.69 (ddd, 1H, 6-H_{eq}; coupling constants: ^2J = 14.2 Hz, ^3J (ax,ax) = 13.8 Hz, ^3J (ax,eq) = 6.3/6.2, ^3J (eq,eq) = 2.8 Hz), 1.86, 1.25, 1.11 (s, each 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 142.3, 114.8, 106.9 (C), 134.1, 131.6, 126.3, 126.2, 113.6, 112.1, 111.1 (CH), 37.0, 33.7 (C4, C7), 35.3, 31.5 (CH_2), 35.4, 27.4, 25.5 (CH_3). IR (KBr): $\tilde{\nu}$ 3113, 3086, 3070, 2960, 2922, 1684, 1478, 1455, 1439, 1387, 1303, 1109, 1053, 823, 802, 740 cm^{-1}.

[4-(η^5-Cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]dichlorozirconium **9b**. Reaction of **8** (9.58 g, 30.7 mmol) with 7.50 g (32.2 mmol) of $ZrCl_4$ in 200 ml of toluene (50 h) analogously as described above gave 1.7 g (14 %) of **9b** as an amorpheous solid, m. p. 223°C (decomp. DSC). Recryst. from methylene chloride gave crystals for the X-ray crystal structure analysis. Anal. Calcd. for $C_{17}H_{20}Cl_2Zr$ (386.5) C 52.83, H 5.22; found C 52.35, H 5.19. ^1H NMR ($CDCl_3$): δ 6.71, 6.69, 6.51, 6.43, 6.05, 5.86, 5.71 (m, 7H, CH), 2.42 (ddd, 1H, 5-H_{eq}), 2.30 (ddd, 1H, 5-H_{ax}), 2.00 (ddd, 1H, 6-H_{ax}), 1.72 (ddd, 1H, 6-H_{eq}; coupling constants: ^2J = 14.8 Hz, ^3J (ax,ax) = 14.3 Hz, ^3J (ax,eq) = 6.0/5.6, ^3J (eq,eq) = 2.2 Hz), 1.83, 1.33, 1.10 (s, each 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 137.7, 121.3, 113.7 (C), 125.9, 123.6, 117.9, 116.0, 110.3, 107.3, 105.8 (CH), 37.6, 32.8 (C4, C7), 35.8, 32.0 (CH_2), 35.1, 27.7, 26.5 (CH_3). IR (KBr): $\tilde{\nu}$ 3105, 3084, 3073, 2969, 2957, 1653, 1477, 1456, 1368, 1105, 869, 741 cm^{-1}.

[4-(η^5-Cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]dichlorohafnium **9c**. Reaction of **8** (5.06 g, 16.2 mmol) with 5.19 g (16.2 mmol) of $HfCl_4$ in 200 ml of toluene analogously as described above gave 1.38 g (18 %) of **9c**, m. p. 200°C (decomp. DSC). Recryst. from methylene chloride gave single crystals for the X-ray crystal structure analysis. Anal. Calcd. for

$C_{17}H_{20}Cl_2Hf$ (473.7) C 43.10, H 4.26; found C 42.94, H 4.30. ^1H NMR ($CDCl_3$): δ 6.60, 6.42, 6.33, 5.96, 5.78, 5.62 (m, 7H, CH), 2.43 (ddd, 1H, 5-H_{eq}), 2.26 (ddd, 1H, 5-H_{ax}), 2.08 (ddd, 1H, 6-H_{ax}), 1.74 (ddd, 1H, 6-H_{eq}; coupling constants: ^2J = 14.4 Hz, ^3J (ax,ax) = 13.6 Hz, ^3J (ax,eq) = 5.5/5.9, ^3J (eq,eq) = 2.5 Hz), 1.83, 1.34, 1.12 (s, each 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 133.6, 122.4, 114.9 (C), 124.8, 122.2, 116.9, 115.3, 108.0, 105.6, 103.7 (CH), 36.8, 31.7 (C4, C7), 34.9, 31.7 (CH_2), 34.6, 26.7, 25.6 (CH_3). IR (NaCl): $\tilde{\nu}$ 3085, 3076, 2980, 2968, 2957, 2918, 1542, 1476, 1454, 1427, 1386, 1364, 1105, 1049, 827, 811, 792, 751 cm^{-1}.

[4-(η^5-Cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]dimethyltitanium **10a**. Methyllithium (0.85 ml of a 1.60 M ethereal solution, 1.36 mmol) was added dropwise at 0°C to a suspension of **9a** (234 mg, 0.68 mmol) in 30 ml of ether. The mixture was allowed to warm to ambient temperature and then stirred for another 4 h. Solvent was removed in vacuo and the residue extracted with pentane (2 x 20 ml). The combined pentane extracts were concentrated in vacuo and cooled to -25°C to yield 110 mg (54%) of crystalline **10a**, m. p. 113°C (decomp. DSC). Single crystals suited for the X-ray crystal structure analysis were obtained by additional recrystallization from pentane at –25°C. Anal. Calcd. for $C_{19}H_{26}Ti$ (302.3) C 75.49, H 8.67; found C 75.15, H 8.71. ^1H NMR ($CDCl_3$): δ 6.95 (fourfold intensity), 5.56, 5.18, 4.99 (m, 7H, CH), 2.07 (ddd, 1H, 5-H_{eq}), 2.95 (ddd, 1H, 5-H_{ax}), 1.60 (ddd, 1H, 6-H_{ax}), 1.48 (ddd, 1H, 6-H_{eq}; coupling constants: ^2J = 14.4 Hz, ^3J (ax,ax) = 14.4 Hz, ^3J (ax,eq) = 6.4/6.2, ^3J (eq,eq) = 3.2, ^4J = 0.5 Hz), 1.41, 1.14, 1.10 (s, each 3H, CH_3), -0.05, -0.06 (s, each 3H, Ti-CH_3). ^{13}C NMR ($CDCl_3$): δ 135.9, 112.4, 105.0 (C), 122.3, 120.4, 117.9, 115.5, 110.1, 109.5, 107.7 (CH), 36.7, 32.0 (C4, C7), 45.8, 41.8 (Ti-CH_3), 36.1, 32.1 (CH_2), 35.6, 27.5, 25.6 (CH_3). IR (KBr): $\tilde{\nu}$ 3096, 2961, 2929, 2869, 1471, 1455, 1434, 1378, 1358, 1103, 1049, 871, 801, 790, 745 cm^{-1}.

[4-(η^5-Cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]dimethylzirconium **10b**. Reaction of methyllithium (3.30 ml of a 1.60 M ethereal solution, 5.33 mmol) with **9b** (1.03 g, 2.66 mmol) in 50 ml of ether analogously as described above yielded 700 mg (76%) of **10b**, m. p. 114°C (decomp. DSC). Repeated recryst. of a sample from pentane at –25°C gave crystals suited for the X-ray crystal structure determination. Anal. Calcd. for $C_{19}H_{26}Zr$ (345.6) C 66.03, H 7.58; found C 65.76, H 7.52. ^1H NMR ($CDCl_3$): δ 6.54 (double intensity), 6.36 (double intensity), 5.89, 5.50, 5.32 (m, 7H, CH), 2.18 (ddd, 1H, 5-H_{eq}), 2.09 (ddd, 1H, 5-H_{ax}), 1.80 (ddd, 1H, 6-H_{ax}), 1.57 (ddd, 1H, 6-H_{eq}; coupling constants: ^2J = 14.0 Hz, ^3J (ax,ax) = 14.0 Hz, ^3J (ax,eq) = 5.3/5.9, ^3J (eq,eq) = 3.1 Hz), 1.53, 1.19, 1.12 (s, each 3H, CH_3), -0.26, -0.34 (s, each 3H, Zr-CH_3). ^{13}C NMR ($CDCl_3$): δ 135.0, 107.7, 106.8 (C), 116.6, 114.3, 111.7, 108.7, 107.9, 106.2, 103.9 (CH), 36.7, 32.0 (C4, C7), 36.3, 32.4 (CH_2), 35.1, 27.9, 26.7 (CH_3), 31.3 (double intensity, Zr-CH_3). IR (KBr): $\tilde{\nu}$ 3092, 2961, 2923, 2865, 1478, 1455, 1435, 1378, 1358, 1103, 1048, 862, 851, 788, 751 cm^{-1}.

[4-(η^5-Cyclopentadienyliden)-4,7,7-trimethyl-(η^5-4,5,6,7-tetrahydroindenyl)]dimethylhafnium **10c**. Reaction of methyllithium (1.10 ml of a 1.60 M ethereal solution, 1.77 mmol) with 420 mg (0.89 mmol) of $HfCl_4$ in 50 ml of ether analogously as described above yielded 254 mg (66%) of **10c**, m. p. 125°C (decomp. DSC). Recryst. of a sample from pentane at –25°C gave single crystals for the X-ray structure analysis. Anal. Calcd. for $C_{19}H_{26}Hf$ (432.9) C 52.72, H 6.05; found C 52.91, H 6.22. ^1H

NMR ($CDCl_3$): δ 6.50, 6.43, 6.28 (double intensity), 5.81, 5.45, 5.27 (m, 7H, CH), 2.22 (ddd, 1H, 5-H_{eq}), 2.07 (ddd, 1H, 5-H_{ax}), 1.90 (ddd, 1H, 6-H_{ax}), 1.61 (ddd, 1H, 6-H_{eq}; coupling constants: ^{2}J = 13.5 Hz, ^{3}J (ax,ax) = 13.5 Hz, ^{3}J (ax,eq) = 5.3/5.7, ^{3}J (eq,eq) = 3.0, ^{4}J = 0.6 Hz), 1.56, 1.21, 1.15 (s, each 3H, CH_3), -0.44, -0.49 (s, each 3H, Hf-CH_3). ^{13}C NMR ($CDCl_3$): δ 133.6, 116.7, 109.6 (C), 115.9, 113.4, 110.7, 108.2, 107.0, 105.3, 103.0 (CH), 36.8, 33.5 (Hf-CH_3), 36.3, 32.5 (CH_2), 36.8, 33.5 (C4, C7), 31.9 (double intensity, Hf-CH_3). IR (KBr): $\tilde{\nu}$ 3093, 2961, 2917, 2900, 2862, 1478, 1453, 1434, 1378, 1358, 1126, 1101, 1047, 871, 863, 790, 751 cm^{-1}.

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