Synthesis, Structural and Chemical Characterization of Unsaturated C_4- and C_{10}-Bridged Group-4 *ansa*-Metallocenes Obtained Through a Ring-Closing Olefin Metathesis Reaction

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Bis[(5-hexenyl)cyclopentadienyl]zirconium dichloride (**3**) underwent ring-closure olefin metathesis with loss of ethylene when treated with 10 mol % of the $[Cl_2(PCy_3)_2Ru{=}CHPh]$ catalyst in refluxing dichloromethane, to yield the large *ansa*-zirconocene complex [dec-5-ene-1,10-diylbis(η^5-cyclopentadienyl)]$ZrCl_2$ (*trans*-**4**). Characterization by NMR and by X-ray diffraction revealed that the isolated complex contained a *trans*-C=C double bond inside the *ansa* bridge. Similarly, bis[(allyl)cyclopentadienyl]$ZrCl_2$ (**7**) gave the *ansa*-metallocene [but-2-ene-1,4-diylbis(η^5-cyclopentadienyl)]zirconium dichloride (*cis*-**8**) when treated with the same ruthenium metathesis catalysts (10 mol %) under similar conditions, except that a *cis*-C=C double bond was now found to be present (shown by NMR and X-ray diffraction). The *cis*-**8** complex was used as a homogeneous Ziegler–Natta catalyst for ethylene polymerization [after activation of the metallocene dichloride **8** with MAO (methylalumoxane) or treatment of the corresponding dimethylmetallocene complex **9** with $B(C_6F_5)_3$]. Complex **8** was also converted into a mixture of (*s*-*cis*- and *s*-*trans*-η^4-butadiene)-*ansa*-metallocene complexes (*s*-*cis*-**15**/*s*-*trans*-**15** = 4:5) by treatment with (butadiene)magnesium. The C=C double bond of *cis*-**8** could be hydroborated with 9-BBN or with the $H{-}B(C_6F_5)_2$ reagent. $Li^+[B(C_6F_5)_4^-]$ added to *cis*-**8** to yield an interesting solid-state chain structure in which the $[Zr]Cl_2$ unit and the *o*-/*m*-F pairs of two $-C_6F_5$ groups were found to be in contact with the central lithium cation in a distorted octahedral coordination environment (as shown by X-ray diffraction).

Introduction

ansa-Metallocenes of the Group 4 metals have become of great importance, especially as components of homogeneous Ziegler−Natta catalyst systems.[1] Their synthesis in most cases involves nucleophilic substitution routes with Cp-anion equivalents and the respective bis(electrophile) of the bridging unit to build up the ligand framework before it is attached to the transition metal atom. This synthetic scheme has been followed in many cases, providing the ubiquitous *ansa*-metallocenes with small bridging units (e.g. SiR_2, $CH_2{-}CH_2$ etc.)[2−6] as well as the few examples of "large *ansa*-metallocenes" so far described in the literature.[7−10] A sizeable number of alternatives of linked bis(Cp) ligand syntheses has been reported in the literature,[11−19] but only very few in which selective organic transformations were carried out by coupling functional groups at the Cp ligands at the Group 4 metallocene stage.[20,21]

The C=C double bonds of alkenyl side chains at the Cp rings are functional groups compatible with many Group 4 metallocene features, and are easily introduced.[8,9,22−25] Modern variants of the olefin metathesis reaction, employing defined molecular Group 6 or Group 8 alkylidene complexes, can efficiently use alkenyl functional groups for carbon−carbon coupling.[26−28] Intramolecular variants ("ring-closure metathesis", RCM) has become an especially useful tool in organic synthesis.[29−36] We have employed such an olefin metathesis reaction for the intramolecular C−C coupling of bis[(ω-alkenyl)cyclopentadienyl]$ZrCl_2$ complexes to yield the respective C=C unsaturated *ansa*-metallocene complexes. Two representative examples are described, including their structural characterization and some chemical features of these easily available new systems.[37]

Results and Discussion

Synthesis and Characterization of the *ansa*-Metallocenes

Bis[(5-hexen-1-yl)cyclopentadienyl]zirconium dichloride (**3**) was prepared by a procedure analogous to that described by us in the literature: treatment of Cp−sodium

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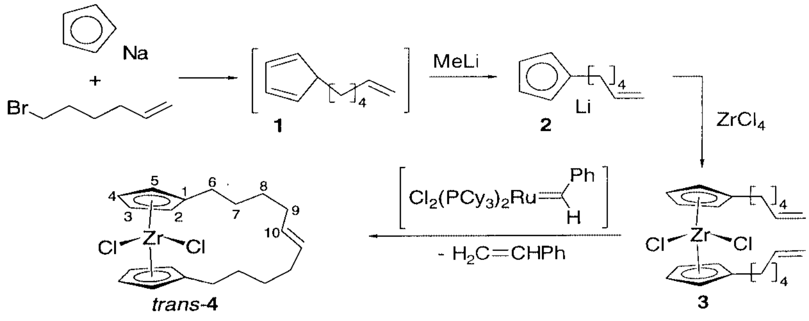


Scheme 1

with hexenyl bromide, followed by deprotonation (MeLi) and transmetallation furnished complex **3** in 38% yield (see Scheme 1).[8,22] Intramolecular olefin metathesis was carried out catalytically on **3** by treatment with 10 mol % of the "Grubbs catalyst" benzylidenedichlorobis(tricyclohexylphosphane)ruthenium.[38,39] In dilute solution, with use of a syringe pump for addition of **3** in dichloromethane to the metathesis catalyst, the reaction can largely be kept in the intramolecular regime. Crystallization from toluene gave the "large *ansa*-zirconocene dichloride complex" as a white crystalline solid in 25% yield.

Single crystals of **4** suitable for X-ray crystal structure analysis were obtained from [D$_6$]benzene at room temperature. The crystals were very thin needles, and the diffraction power was therefore weak, giving data of limited accuracy. The structure features an *ansa*-metallocene containing a *trans*-C=C double bond [C10−C11: 1.291(18) Å] in its centre. The large "13-membered" ring displays a crown-shaped conformation. The metallocene conformation is such that the bridging ring system is completely oriented toward a lateral sector of the bent metallocene wedge ["bis(lateral) *syn*" conformation, see Figure 1].[10,40,41] The zirconium atom in complex **4** is pseudotetrahedrally coordinated by the two η^5-Cp rings [Cp(centroid)−Zr: 2.193 and 2.216 Å, Cp(centroid)−Zr−Cp(centroid) angle 129.4°, Zr−Cl2 2.430(3) Å, Zr−Cl1 2.437(3) Å, Cl1−Zr−Cl2 angle: 98.2(1)°] in a largely unstrained fashion.

In the NMR spectra the signals of a major (> 95%) and a minor component could be seen. Whereas the minor compound has remained unidentified so far (it could be the *cis* isomer or an oligomer), the major product is likely to be identical to *trans*-**4** as identified by X-ray diffraction. This is indicated by the typical ^{13}C NMR shift of the allylic $-CH_2-CH=$ resonance (C-9) at $\delta = 31.9$ ppm [δ(C-10) = 131.5 ppm]. The remaining CH_2 shifts of the bridging hydrocarbyl chain are found at $\delta = 29.3$ (C-6), 26.4 (C-7) and 28.5 (C-8) ppm (for atom numbering scheme see Scheme 1). The corresponding ^{1}H NMR resonances occur at $\delta = 2.52$ (6-H), 1.22 (7-H), 1.30 (8-H), 2.01 (9-H) and 5.25 (olefinic 10-H) ppm.

The synthesis of bis(allylcyclopentadienyl)zirconium dichloride (**7**) was carried out analogously to the procedure described by us previously (Scheme 2).[22] The ring-closing metathesis reaction was carried out by treatment of **7** with $Cl_2(PCy_3)_2Ru=CHPh$ under high-dilution reaction conditions. Oligomeric by-products were removed by filtration and the product **8** was purified by fractional crystallization. Eventually, the isomerically pure complex *cis*-**8** was obtained as a colourless, crystalline material in ca. 50% yield.

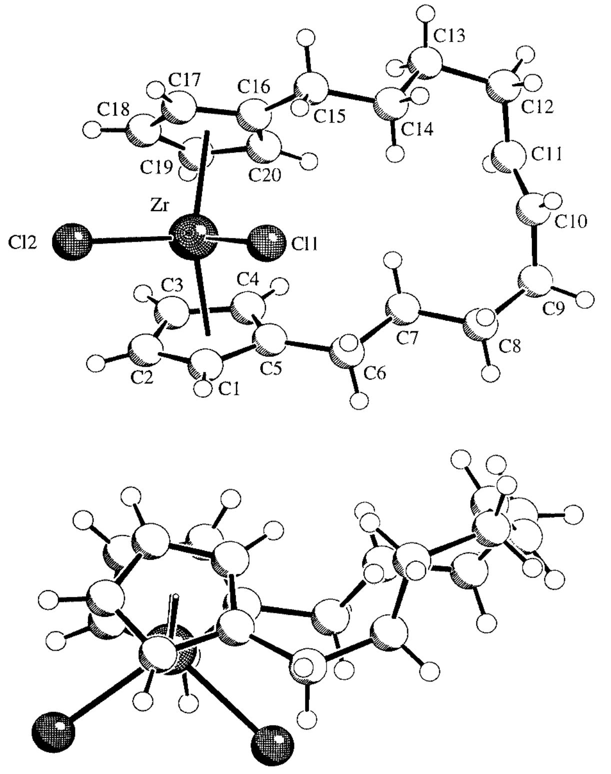
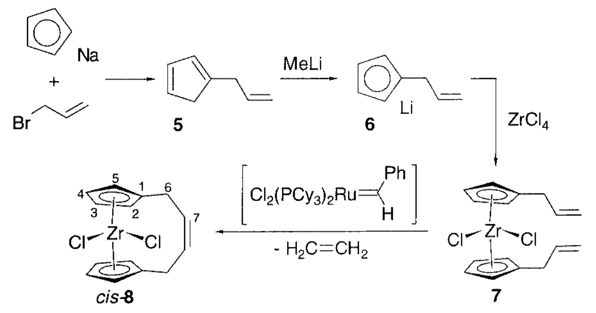


Figure 1. Two views of the organometallic olefin metathesis product **4**; selected bond lengths [Å] and angles [°]: Zr−Cl1 2.437(3), Zr−Cl2 2.430(3), C5−C6 1.526(14), C6−C7 1.489(14), C7−C8 1.516(14), C8−C9 1.500(17), C9−C10 1.472(19), C10−C11 1.291(18), C11−C12 1.455(23), C12−C13 1.538(22), C13−C14 1.505(20), C14−C15 1.528(19), C15−C16 1.510(16); Cl1−Zr−Cl2 98.2(1), C5−C6−C7 113.6(9), C6−C7−C8 113.8(9), C7−C8−C9 112.3(9), C8−C9−C10 111.7(11), C9−C10−C11 128.0(15), C10−C11−C12 126.7(16), C11−C12−C13 114.0(13), C12−C13−C14 112.0(12), C13−C14−C15 116.3(13), C14−C15−C16 118.0(11); C5−C6−C7−C8 −175.4(10), C6−C7−C8−C9 179.2(11), C7−C8−C9−C10 71.2(14), C8−C9−C10−C11 -107.6(15), C9−C10−C11−C12 176.2(14), C10−C11−C12−C13 -108.4(16), C11−C12−C13−C14 65.1(19), C12−C13−C14−C15 -175.6(13), C13−C14−C15−C16 74.4(18)

The X-ray crystal structure analysis of **8** (single crystals were obtained from [D$_6$]benzene at room temperature) again shows the presence of an unconstrained *ansa*-metallo-



Scheme 2

cene framework. The metal−C(Cp) bond lengths are in a rather narrow range between 2.486(2) Å (Zr−C13) and 2.536(2) Å (Zr−C11). The Cp(centroid)−Zr−Cp(centroid) angle amounts to an ideal bent metallocene value of 130.0°.[42] The Cl1−Zr−Cl2 angle in **8** [95.95(2)°] is only marginally smaller than that in the parent compound Cp_2ZrCl_2.[43] Zr−Cl1 [2.437(1) Å] and Zr−Cl2 [2.455(1) Å] are very similar in lengths.

The *ansa*-metallocene complex **8** features an endocyclic *cis*-carbon−carbon double bond [C16−C26 1.319(3) Å]. This value is in the range typical for an uncoordinated C=C bond.[44] Close inspection reveals that there is no immediate coordinative interaction between the *cis*-C=C double bond inside the *ansa* bridge and its adjacent, slightly electron-deficient Group 4 metal centre. The observed Zr···C16/C26 distances of ca. 4 Å rule out any significant direct interaction. Consequently, an eclipsed metallocene conformation is attained in complex *cis*-**8**, with the C10−C15 and C20−C25 vectors oriented to the same lateral sector of the bent metallocene wedge and the $-CH_2-CH=CH-CH_2-$ unit bent back towards the back side of the metallocene framework (as illustrated by the top view projection of *cis*-**8** in Figure 2).

In solution one finds a single set of NMR signals, indicating that there is only one isomer present. This shows a ^{13}C NMR signal of the allylic C-6 $CH_2-CH=$ carbon centre (see Scheme 1) at δ = 24.8 ppm, consistent with the *cis*-**8** structure (*trans*-**4** shows the analogous $-CH_2-CH=$ signal at δ = 31.9 ppm, see above). In addition, there are the olefinic $-CH=$ resonance at δ = 129.7 ppm and three Cp signals at δ = 119.3, 115.3 (both *C*H) and δ = 121.2 ppm (*C*). The pairwise identical C-2/C-5 and C-3/C-4 resonances indicate rapid conformational equilibration of *cis*-**8** on the NMR timescale. Probably both the Cp−Zr rotation *and* the inversion of the metallacycle that includes the *ansa* bridge atoms are fast.[45] Consequently, only two C_5H_4 resonances are observed in the ^1H NMR spectrum of *cis*-**8** at "high" temperatures. In a $CDFCl_2/CDF_2Cl$ mixture[46] at 253 K this pair of ^1H NMR Cp signals is observed at δ = 6.32 and 6.66 ppm. On lowering the temperature these signals each decoalesce to a new pair of Cp signals that at 128 K have become separated by 517 and 128 Hz, respectively (see Figure 7). From these temperature-dependent ^1H NMR spectra an averaged activation barrier has been calculated as $\Delta G^{\ddagger}_{\mathrm{inv}}$ (128 K) = 5.1 ± 0.3 kcal mol^{-1}.[47] We assume that this Gibbs activation energy primarily characterises the inversion barrier of the *ansa*-metallacycle, but it is in principle possible that this has coincided with "freezing" of the Cp−M rotation on the NMR timescale at this very temperature.[48−50]

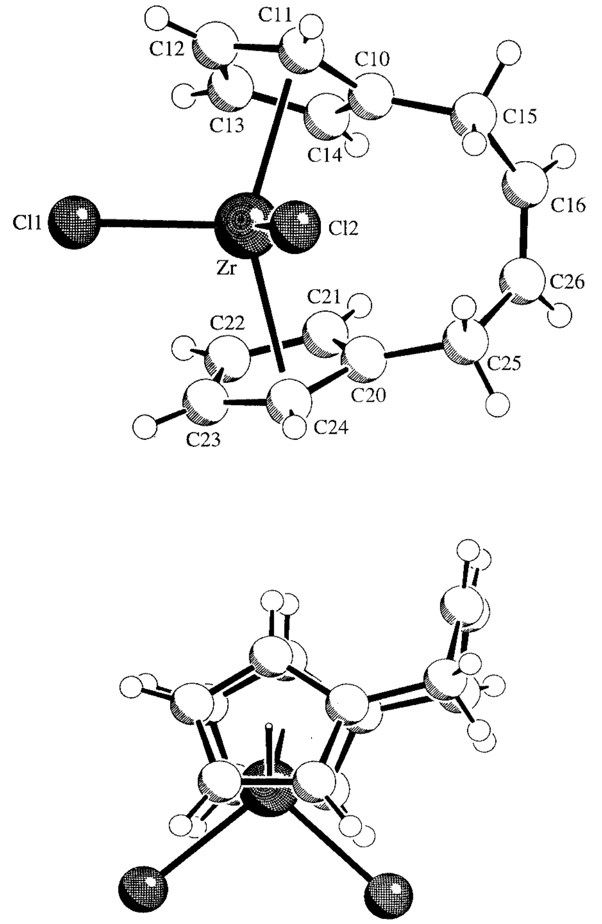
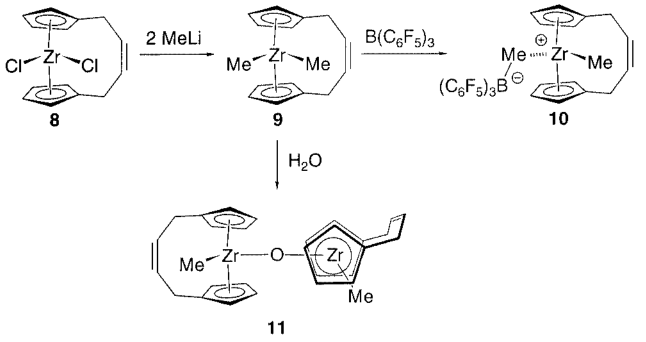


Figure 2. Top and side views of the molecular structure of complex *cis*-**8**; selected bond lengths [Å] and angles [°]: Zr−Cl1 2.437(1), Zr−Cl2 2.455(1), C10−C15 1.513(3), C15−C16 1.496(3), C16−C26 1.319(3), C26−C25 1.503(3), C25−C20 1.518(3); Cl1−Zr−Cl2 95.95(2), C10−C15−C16 114.7(2), C15−C16−C26 126.2(2), C16−C26−C25 126.1(2), C26−C25−C20 112.5(2); C10−C15−C16−C26 −83.5(3), C15−C16−C26−C25 0.9(3), C16−C26−C25−C20 86.0(3)

Reactions of the *ansa*-Metallocenes

Treatment of the *ansa*-zirconocene dichloride **8** with methyllithium (2 equiv.) gave the corresponding dimethylmetallocene complex **9** {$^1H/^{13}C$ NMR of $[Zr](CH_3)_2$: δ = −0.05/31.0 ppm ($^1J_{CH}$ = 117 Hz) in [D$_6$]benzene}. Treatment of **9** with $B(C_6F_5)_3$ in [D$_8$]toluene with NMR monitoring generated the ion-pair **10** {^1H NMR of $[Zr]CH_3/[B]CH_3$: δ = 1.34/0.94}. Compound **10** separated from the solution as a red oil after some time. An attempt to crystallise **10** from [D$_6$]benzene resulted in partial hydrolysis of the moisture-sensitive complex, and we isolated single crystals of the corresponding dinuclear μ-oxobis(*ansa*-metallocene) compound **11** suitable for an X-ray crystal structure determination (see Scheme 3 and Figure 3).



Scheme 3

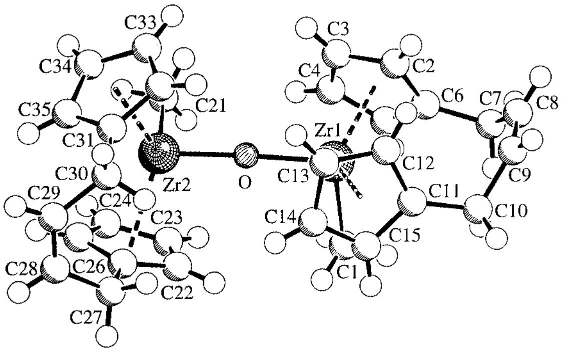
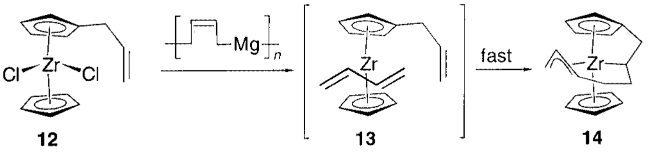


Figure 3. A projection of the molecular structure of the μ-oxobis(*ansa*-metallocene) complex **11**; selected bond lengths [Å] and angles [°]: Zr1−O 1.951(2), Zr1−C1 2.294(3), Zr2−O1 1.954(2), Zr2−C21 2.291(3), C6−C7 1.509(4), C7−C8 1.499(4), C8−C9 1.312(4), C9−C10 1.503(4), C10−C11 1.502(4), C26−C27 1.514(4), C27−C28 1.483(4), C28−C29 1.317(4), C29−C30 1.489(4), C30−C31 1.503(4); Zr1−O−Zr2 170.53(9), C1−Zr1−O 97.55(9), C21−Zr2−O 97.97(9), C6−C7−C8 113.7(2), C7−C8−C9 124.4(3), C8−C9−C10 123.8(2), C9−C10−C11 112.8(2), C26−C27−C28 114.7(3), C27−C28−C29 124.0(3), C28−C29−C30 124.0(3), C29−C30−C31 113.6(2); C6−C7−C8−C9 84.3(3), C7−C8−C9−C10 −0.9(5), C8−C9−C10−C11 −88.9(3), C26−C27−C28−C29 −81.7(4), C27−C28−C29−C30 0.2(5), C28−C29−C30−C31 88.8(4)

The X-ray crystal structure analysis of **11** shows the presence of two C_4-*ansa*-metallocene subunits, bridged by a close to linear μ-oxobridge [angle Zr1−O−Zr2: 170.53(9)°]. Both the zirconium−oxygen bonds are rather short, at 1.951(2) Å (Zr1−O) and 1.954(2) Å (Zr2−O), respectively. This indicates considerable μ-oxygen ligand-to-metal π-backbonding,[51] making use of the available acceptor orbital at the (formally) 16-electron metal centre.[52] Consequently, the overall structural arrangement of the two metallocene subunits of **11** along the metal-oxygen-metal vector is close to perpendicular (dihedral angle C1−Zr1···Zr2−C21 −85.8°). The conformational arrangement of the strongly bent *ansa*-bridge is noteworthy, as it is different in the two metallocene subunits. On both sides the $-CH_2-CH=CH-CH_2-$ bridge is oriented toward a lateral sector of the bent metallocene wedge, and this is toward the oxygen side in both cases, but the *ansa* bridge at Zr1 is bent in the direction toward the front side of the bent metallocene, whereas at Zr2 this hydrocarbyl bridge is bent away from the μ-oxygen atom and prefers to point toward the narrow back side of the bent metallocene wedge.

Both the complexes **8** and **9** were used as starting materials for the generation of active homogeneous Ziegler−Natta catalysts. In the case of the dimethylzirconium complex, activation was achieved by treatment with B(C_6F_5)$_3$ in a close to equimolar ratio (the active species probably being **10**, see Scheme 3).[53] The *ansa*-metallocene dichloride **8** was activated by treatment with a large excess of methylalumoxane in toluene solution (Al/Zr > 1000).[1,54] Both systems turned out to be excellent ethylene polymerization catalysts (see Table 1). They also polymerized propene at room temperature, although not with high activities (a = 38). The obtained polypropylene was atactic.

We had previously shown that Cp-bound alkenyl groups can undergo a C−C coupling reaction with metal-coordinated butadiene ligands at the Group 4 metallocene frameworks.[22] The formation of **14** from **12** via **13** is a typical example.

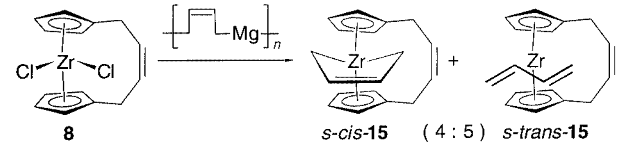


We were curious to see whether there would be any interaction between the endocyclic *cis*-C=C double bond in the *ansa*-metallocene framework and a butadiene ligand attached at, for example, the framework of complex **8**. We therefore treated complex **8** directly with 1 mol-equiv. of the (butadiene)Mg·(THF)$_n$ reagent[55] in [D$_8$]toluene at room temperature. Formation of the (butadiene)metallocenes took place. NMR analysis revealed the presence of the (*s-cis*- and *s-trans*-η^4-butadiene)[Zr] complex isomers (*s-cis*-**15**;

Table 1. Ethylene polymerization with homogeneous Ziegler−Natta catalysts derived from the complexes **8** and **9**

Cat. precursor[a]	Activator	Al(B)/Zr ratio	T [°C]	Reaction time [min]	PE [g]	M.p. [°C]	Act.[b]
9	B(C_6F_5)$_3$	1.1	25	4	12.8	128	2600
8	MAO	1000	25	10	43.6	128	3660
9	B(C_6F_5)$_3$	1.1	60	10	25.0	129	2150
8	MAO	1250	60	10	37.1	126	3750

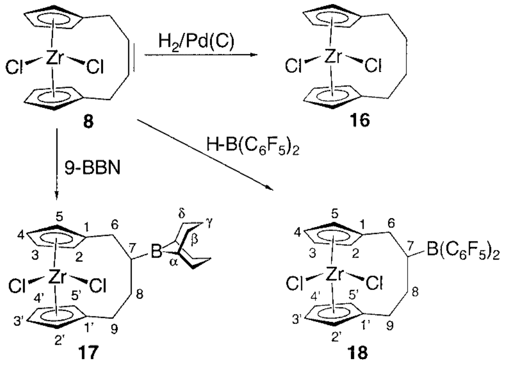
[a] In toluene solution at 2 bar ethene pressure. [b] Catalyst activity in kg(polymer)/mol[Zr]·h·bar(ethene).



Scheme 4

s-trans-**15**, see Scheme 4) in a 4:5 ratio. The *s-cis* isomer is easily identified by its dynamic NMR behaviour, due to a rapid inversion of its five-membered σ^2,π-metallacyclopentene core on the NMR timescale at room temperature, becoming frozen at low temperature.[56] This results in the observation of a 1:1 pair of ^{1}H NMR singlets at 298 K (δ = 5.09, 4.88 ppm) that decoalesces to a set of four Cp signals of equal intensity at 213 K in the [D$_8$]toluene solvent (δ = 5.55, 4.91, 4.78, 4.53 ppm). In contrast, the chiral (averaged C_2-symmetric) *s-trans*-**15** isomer exhibits temperature-invariant NMR spectra showing four separate ^{1}H NMR Cp resonances (213 K: δ = 4.87, 4.85, 4.53, 4.35 ppm) throughout this temperature range. The ^{1}H/^{13}C NMR shifts of the (*s-cis*-η^4-butadiene)[Zr] complex [213 K: δ = 4.76, 3.42, −0.59 (H_{meso}, H_{syn}, H_{anti})/112.1, 49.7 (C-2/3, C-1/4) ppm] and its *s-trans*-**15** isomer [213 K: δ = 3.04, 3.14, 1.38 ppm (^{1}H)/96.7, 59.1 ppm (^{13}C)] are characteristically different.[56] The *s-cis*- and *s-trans*-**15** complexes are stable as such in the examined temperature range. We have so far found no evidence of the occurrence of a C−C coupling reaction with the disubstituted C=C double bond of the adjacent *ansa* bridge.

The C=C double bond in *cis*-**8** undergoes reactions typical of olefins, however. Catalytic hydrogenation (H_2, Pd/C) cleanly yields the saturated tetramethylene-bridged *ansa*-zirconocene dichloride complex **16** (see Scheme 5). Hydroboration takes place equally facilely and also leaves the metallocene nucleus untouched. We have used two sterically and electronically quite different boranes for this purpose. 9-BBN[57,58] adds to the endocyclic double bond in *cis*-**8** to yield the product **17**. The borylated complex **18** was formed by treatment of *cis*-**8** with the electrophilic borane $H-B(C_6F_5)_2$.[59,60] As expected, each of these products now shows eight ^{1}H NMR signals of the pair of monosubstituted Cp ligands [**17**: δ = 6.53, 6.45 (2 H), 6.42, 6.40, 6.35, 6.33, 6.25 ppm]. It is interesting to note that complex **18** has an electrophilic $-B(C_6F_5)_2$ unit covalently bonded to its *ansa*-metallocene framework. Future studies should show if this can be utilized as an internal activator component for the generation of an active single-component metallocene Ziegler−Natta catalyst system.[61,62]



Scheme 5

L_nM^+ cations can sometimes be generated by treatment of the respective metal halide complexes (e.g., L_nM-Cl) with alkali metal cations in combination with anions of low nucleophilicity.[63] An interesting alternative reaction, namely Li^+ addition, was observed in one case starting from **8**. When we treated the *ansa*-metallocene complex *cis*-**8** with $Li^+[B(C_6F_5)_4{}^-]$ in [D$_8$]toluene at room temperature, the crystalline adduct **19** was obtained. Its rather interesting structure was determined by X-ray diffraction (see Figures 4 and 5).

The X-ray crystal structure analysis revealed that the Li^+ cations of two independent molecules are (electrostatically) coordinated to the pair of chloride ligands[64,65] at the zirconium center in a chelate fashion. The coordination sphere around the lithium ion is complemented by two additional

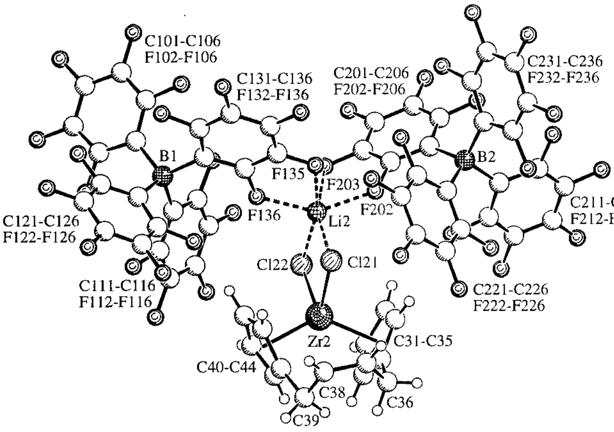


Figure 4. A view of the *cis*-**8**·$Li^+[B(C_6F_5)_4{}^-]$ adduct structure (**19**); selected bond lengths [Å] and angles [°]: Zr1−Cl11 2.479(1), Zr1−Cl21 2.487(1), Zr2−Cl21 2.454(1), Zr2−Cl22 2.477(1), C11−C16 1.518(5), C31−C36 1.504(6), C16−C17 1.480(6), C36−C37 1.517(10), C17−C18 1.327(5), C37−C38 1.436(12), C18−C19 1.467(5), C38−C39 1.445(12), C19−C20 1.516(4), C39−C40 1.480(8); Cl11−Zr1−Cl12 87.53(2), Cl21−Zr2−Cl22 89.50(3), C11−C16−C17 112.5(3), C31−C36−C37 115.3(4), C16−C17−C18 126.0(4), C36−C37−C38 117.8(5), C17−C18−C19 125.5(4), C37−C38−C39 116.9(6), C18−C19−C20 112.4(3), C38−C39−C40 105.0(8); C11−C16−C17−C18 −85.4(5), C31−C36−C37−C38 80.7(8), C16−C17−C18−C19 0.4(6), C36−C37−C38−C39 −0.8(7), C17−C18−C19−C20 87.5(5), C37−C38−C39−C40 −102.7(6); Li1−Cl11 2.376(5), Li1−Cl12 2.385(5), Li2−Cl21 2.379(6), Li2−Cl22 2.420(6), Li1−F115 2.812(6), Li1−F116 1.985(5), Li2−F203 2.567(6), Li2−F202 2.045(5), Li1−F235 2.235(5), Li1−F236 2.087(5), Li2−F135 2.223(6), Li2−F136 2.052(5); Cl11−Li1−Cl12 92.4(2), Cl21−Li2−Cl22 92.7(2), Cl11−Li1−F115 159.1(2), Cl21−Li2−F203 160.8(2), Cl11−Li1−F116 101.9(2), Cl21−Li2−F202 96.9(2), Cl11−Li1−F235 91.6(2), Cl21−Li2−F135 86.1(2), Cl11−Li1−F236 115.8(2), Cl21−Li2−F136 105.2(2), Cl12−Li1−F115 78.9(2), Cl22−Li2−F203 83.4(2), Cl12−Li1−F116 105.0(2), Cl22−Li2−F202 110.0(2), Cl12−Li1−F235 168.5(2), Cl22−Li2−F135 165.9(3), Cl12−Li1−F236 96.1(2), Cl22−Li2−F136 93.3(2), F115−Li1−F116 63.1(2), F203−Li2−F202 67.2(2), F115−Li1−F235 100.7(2), F203−Li2−F135 102.1(2), F115−Li1−F236 84.2(2), F203−Li2−F136 93.8(2), F116−Li1−F235 84.8(2), F202−Li2−F135 84.1(2), F116−Li1−F236 135.9(3), F202−Li2−F136 147.0(3), F235−Li1−F236 72.5(2), F135−Li2−F136 73.5(2)

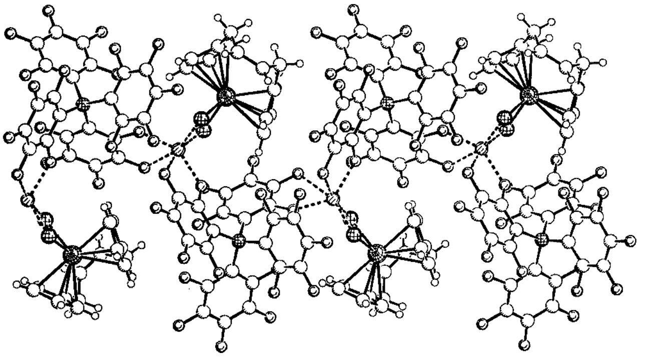


Figure 5. A projection of the chain structure of the adduct **19** in the crystal

chelate interactions, each with a pair of *ortho*- and *meta*-fluorine atoms of one C_6F_5 substituent from two different adjacent $[B(C_6F_5)_4^-]$ anions. This complements a distorted octahedral coordination sphere around the alkali metal cation (see Figure 4). The octahedral geometry is, however, markedly distorted. Of the (idealised) three 180° bonding angles around the central (alkali) metal ion, only two are close to linear [F135−Li2−Cl22: 165.9(3)° and Cl21−Li2−F203: 160.8(2)°; only the data of one of the crystallographically independent units (here around Li2) are given, those around Li1 are similar], whereas the third is markedly smaller at 147.0(3)° (F202−Li2−F136). Most of the remaining twelve bonding angles at the origin of the distorted octahedron are reasonably close to the expected 90° [F202−Li2−F135: 84.1(2)°, F202−Li2−Cl21: 96.9(2)°, F135−Li2−Cl21: 86.1(2)°, F136−Li2−Cl22: 93.3(2)°, Cl21−Li2−Cl22: 92.7(2)°, F136−Li2−F203: 93.8(2)°, Cl22−Li2−F203: 83.4(2)°], with the exception of the two narrow internal *o*-/*m*-F chelate angles [F136−Li2−F135: 73.5(2)° and F202−Li2−F203: 67.2(2)°] and some secondary deviation, caused by this chelate effect [F136−Li2−Cl21: 105.2(2)°, F202−Li2−Cl22: 110.0(2)°, F135−Li2−F203: 102.1(2)°].

The lithium chloride contact lengths in the adduct **19** amount to 2.379(6) Å (Li2−Cl21) and 2.420(6) Å (Li2−Cl22). The Li−F distances cover a wider range [Li2−F202: 2.045(5) Å, Li2−F136: 2.052(5) Å, Li2−F135: 2.223(6) Å, and Li2−F203: 2.567(6) Å]. Each $[B(C_6F_5)_4^-]$ anion in the adduct **19** contains two C_6F_5 units that exhibit chelate contacts to two different Li^+ cations, whereas the remaining C_6F_5 pair of substituents is oriented away from the alkali metal centres. This results in a chain-type suprastructure of **19**, depicted in Figure 5.

The electrostatic Li^+ coordination has changed the $[Zr]Cl_2$ geometry slightly. In comparison with the starting material **8**, the Zr−Cl bond lengths in the adduct **19** are slightly longer [Zr1−Cl11: 2.479(1) Å, Zr1−Cl12: 2.487(1) Å, Zr2−Cl21: 2.454(1) Å, Zr2−Cl22: 2.477(1) Å; see for comparison: *cis*-**8** Zr−Cl1: 2.437(1) Å, Zr−Cl2: 2.455(1) Å]. Consequently, the Cl11−Zr1−Cl12 angle in **19** is markedly smaller [87.53(2)°; Cl21−Zr2−Cl22: 89.50(3)] than in *cis*-**8** [Cl1−Zr2−Cl2: 95.95(2)°].

It is also noteworthy that the conformational arrangement of the $-CH_2-CH=CH-CH_2-$ *ansa* bridge in *cis*-**8** and in the adduct **19** are quite different. In the former, the C=C double bond in the strongly bent structural subunit is oriented toward the back side (Zr···C=C separation ca. 4 Å), whereas in the latter it is found in the inverted position (see Figure 6), which brings the C=C π-system closer to the electron-deficient d^0-configurated Group 4 metal centre (in **19** the Zr···C=C separation is only ca. 3.5 Å).

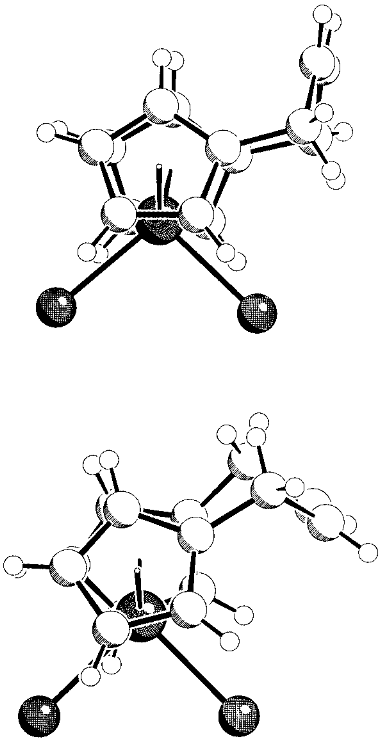


Figure 6. A comparison of the *ansa*-metallocene core conformation as found in *cis*-**8** (top) and the adduct **19** (bottom)

We conclude that olefin metathesis at the Cp−alkenyl unit of Group 4 metallocenes can easily be carried out intramolecularly, cleanly yielding the respective unsaturated *ansa*-metallocenes with loss of ethene. The C=C bond inside the *ansa*-metallocene bridge undergoes a variety of typical reactions without affecting the Group 4 metallocene backbone. Such combinations of reactions may potentially open up new synthetic pathways to functionalized bent metallocene complexes that may turn out to be useful for the development of improved catalysts for rapid and selective C−C coupling reactions and/or for use as reagents in organic synthesis. Studies aimed at finding out about such properties are being carried out in our laboratory.

Experimental Section

General: All reactions were carried out under dry argon in Schlenk-type glassware or in a glove-box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. For additional general conditions, including a list of instruments used for physical characterization of the compounds, see ref.[41b] or ref.[66] NMR assignments were usually secured by carrying out a variety of 2D NMR experiments.[67] The starting materials **3** and **7** were prepared according to literature procedures.[8,22]

Preparation of [Dec-5-ene-1,10-diylbis(η^5-cyclopentadienyl)]zirconium Dichloride (*trans*-4): A solution containing $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (45.3 mg, 0.06 mmol, 10 mol %) in 400 mL of dichloromethane was brought to reflux temperature in a three-necked flask, equipped with stirrer, reflux condenser and a septum. Over 6 h a solution of bis[η^5-(5-hexen-1-yl)cyclopentadienyl]$ZrCl_2$ (**3**, 250 mg, 0.55 mmol) in 100 mL of dichloromethane was added by syringe pump. The mixture was heated under reflux for an additional 3 h, and then cooled to room temperature and filtered. Solvent was removed in vacuo, and the residue was washed with pentane (2 × 20 mL). Fractional crystallization from toluene (10 mL) gave 58.9 mg (25%) of *trans*-**4** as a white solid, m.p. 162 °C. IR (KBr): $\tilde{\nu}$ = 3103 w, 2929 m, 2856 w, 2387 w, 1497 w, 1263 m, 1102 s, 1035 s, 969 w, 841 w, 828 s, 825 vs cm^{-1}. ^1H NMR ([D_6]benzene, 599.9 MHz, 298 K): δ = 5.97 (m, 4 H, 3,4-H), 5.73 (m, 4 H, 2,5-H), 5.25 (m, 2 H, 10-H), 2.52 (m, 4 H, 6-H), 2.01 (m, 4 H, 9-H), 1.30 (m, 4 H, 8-H), 1.22 (m, 4 H, 7-H) ppm. $^{13}C\{^1H\}$ NMR ([D_6]benzene, 150.8 MHz, 298 K): δ = 139.3 (C, C-1), 131.5 (CH, C-10), 115.1 (CH, C-3,4), 111.0 (CH, C-2,5), 31.9 (CH_2, C-9), 29.3 (CH_2, C-6), 28.5 (CH_2, C-8), 26.4 (CH_2, C-7) ppm. $C_{20}H_{26}Cl_2Zr$ (428.5): calcd. C 56.05, H 6.12; found C 56.35, H 6.63.

X-ray Crystal Structure Analysis of *trans*-4: Single crystals were obtained from [D_6]benzene at ambient temperature. $C_{20}H_{26}Cl_2Zr$, M = 428.53, yellow crystal, 0.30 × 0.04 × 0.03 mm, a = 6.581(1), b = 20.480(1), c = 14.451(1) Å, β = 97.47(1)°, V = 1931.2(3) Å^3, $\rho_{calcd.}$ = 1.474 g cm^{-3}, μ = 8.43 cm^{-1}, empirical absorption correction by SORTAV ($0.786 \le T \le 0.975$), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 5920 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.59 Å^{-1}, 3401 independent (R_{int} = 0.066) and 2048 observed reflections [$I \ge 2\,\sigma(I)$], 209 refined parameters, R = 0.094, wR^2 = 0.165, max. (min.) residual electron density 1.46 (−1.19) e Å^{-3}, weakly diffracting crystal due to its shape; therefore the accuracy of the resulting data is poor, hydrogen atoms calculated and refined as riding atoms.

Synthesis of [But-2-ene-1,4-diylbis(η^5-cyclopentadienyl)]zirconium Dichloride (*cis*-8): Analogously to the procedure described above, bis[η^5-(2-propen-1-yl)cyclopentadienyl]$ZrCl_2$ (**7**, 1.60 g, 4.30 mmol) was metathesized by treatment with $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (248 mg, 0.30 mmol, 7 mol %) in a total of 500 mL of dichloromethane under high-dilution conditions. The mixture was heated under reflux for an additional 6 h, cooled to room temperature and filtered. The volume of the resulting solution was reduced to 20 mL in vacuo. Crystallization at −30 °C overnight gave a crystalline precipitate that was washed with pentane (15 mL) and dried in vacuo to give 740 mg (50%) of *cis*-**8** as a microcrystalline solid, m.p. 182 °C. IR (KBr): $\tilde{\nu}$ = 3117 w, 2968 w, 2922 w, 2848 w, 2373 w, 1487 w, 1447 m, 1430 w, 1269 m, 1098 w, 1046 s, 960 w, 903 m, 829 s, 817 vs, 795 s cm^{-1}. ^1H NMR ([D_6]benzene, 599.9 MHz, 298 K): δ = 6.02 (m, 4 H, 2,5-H), 6.00 (m, 4 H, 3,4-H), 5.61 (m, 2 H, 7-H), 2.74 (m, 4 H, 6-H) ppm. ^1H NMR ($CDFCl_2/CDF_2Cl$, 599.9 MHz): δ (253 K) = 6.66, 6.32 (each m, each 4 H, 2,5-H, 3,4-H), 6.31 (m, 2 H, 7-H), 3.35 (m, 4 H, 6-H); δ (128 K) = 6.83/6.61, 6.74/5.87 (each br., each 2 H, 2,5-H, 3,4-H), 6.33 (br., 2 H, 7-H), 3.29, 3.25 (each br., each 2 H, 6-H) ppm. $^{13}C\{^1H\}$ NMR ([D_6]benzene, 150.8 MHz, 298 K): δ = 129.7 (CH, $^1J_{CH}$ = 145 Hz, C-7), 121.2 (C, C-1), 119.3 (CH, $^1J_{CH}$ = 176 Hz, C-2,5), 115.3 (CH, $^1J_{CH}$ = 175 Hz, C-3,4), 24.8 (CH_2, $^1J_{CH}$ = 129 Hz, C-6) ppm. $C_{14}H_{14}Cl_2Zr$ (344.4): calcd. C 48.83, H 4.10; found C 48.70, H 4.84. The dynamic behaviour of *cis*-**8** was monitored by ^1H NMR over a temperature range of 253 to 128 K (Figure 7). The AA′BB′ spin system of the Cp protons at high temperature changed to an ABCD spin system at low temperature. The activation energies were estimated as $\Delta G^{\neq}_{inv}$ [T_c: 153 K; $\Delta\nu$ (128 K): 517 Hz] = 5.22 kcal·mol^{-1} for one group of protons and $\Delta G^{\neq}_{inv}$ [T_c: 138 K; $\Delta\nu$ (128 K) = 128 Hz] = 5.07 kcal·mol^{-1} for the other. The average activation energy was calculated as $\Delta G^{\neq}_{inv}$ = 5.1 ± 0.3 kcal·mol^{-1}.

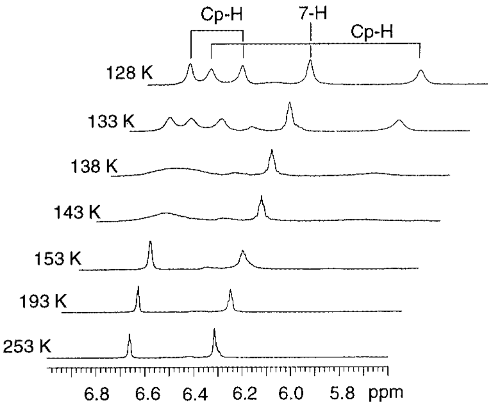


Figure 7. Dynamic ^1H NMR spectrum of *cis*-**8** (in $CDFCl_2/CDF_2Cl$)

X-ray Crystal Structure Analysis of *cis*-8: Single crystals of the *ansa*-metallocene were obtained from [D_6]benzene at room temperature. $C_{14}H_{14}Cl_2Zr$, M = 344.37, light yellow crystal, 0.40 × 0.20 × 0.10 mm, a = 7.798(1), b = 12.887(1), c = 13.044(1) Å, V = 1310.8(2) Å^3, $\rho_{calcd.}$ = 1.745 g cm^{-3}, μ = 12.19 cm^{-1}, empirical absorption correction by SORTAV ($0.641 \le T \le 0.888$), Z = 4, orthorhombic, space group $P2_12_12_1$ (no. 19), λ = 0.71073 Å, T = 198 K, ω and φ scans, 10,955 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 3159 independent (R_{int} = 0.037) and 3025 observed reflections [$I \ge 2\,\sigma(I)$], 156 refined parameters, R = 0.020, wR^2 = 0.043, max. (min.) residual electron density 0.29 (−0.40) e Å^{-3}, refined as racemic twin, Flack parameter 0.17(3), hydrogen atoms calculated and refined as riding atoms.

[But-2-ene-1,4-diylbis(η^5-cyclopentadienyl)]dimethylzirconium (9): [But-2-ene-1,4-diylbis(η^5-cyclopentadienyl)]zirconium dichloride (**8**, 50 mg, 0.15 mmol) and methyllithium (6.4 mg, 0.3 mmol) were suspended in 2 mL of toluene, precooled to −78 °C. The suspension was allowed to warm up to room temperature and stirred overnight. The reaction mixture was filtered through Celite. After removal of the solvent in vacuo, product **9** was isolated as a brown solid (yield: 32 mg, 72%), m.p. 48 °C. IR (KBr): $\tilde{\nu}$ = 3115 w, 2961 m, 2926 w, 2869 w, 1458 w, 1412 w, 1269 vs, 1097 s, 1028 s, 965 w, 867 w, 793 vs, 729 m cm^{-1}. ^1H NMR ([D_6]benzene, 599.9 MHz, 298 K): δ = 6.01, 5.62 (each m, each 4 H, Cp-H), 5.58 (m, 2 H, 7-H), 2.66 (m, 4 H, 6-H), −0.05 (s, 6 H, CH_3) ppm. ^{13}C\{GATED\} NMR ([D_6]benzene, 150.8 MHz, 298 K): δ = 129.6 (dm, $^1J_{CH}$ = 158 Hz, C-7), 120.8 (s, C-1), 111.9 (d, $^1J_{CH}$ = 172 Hz, Cp), 110.2 (d, $^1J_{CH}$ = 171 Hz, Cp), 31.0 (q, $^1J_{CH}$ = 117 Hz, CH_3), 24.4 (t, $^1J_{CH}$ = 128 Hz, C-6) ppm. $C_{16}H_{20}Zr$ (303.56): calcd. C 63.31, H 6.64; found C 61.64, H 6.72. Single crystals of the partial hydrolysis product **11**, suitable for X-ray diffraction, were obtained from a concentrated [D_6]benzene solution of **9**.

X-ray Crystal Structure Analysis of 11: $C_{30}H_{34}OZr_2$, M = 593.01, colourless crystal 0.60 × 0.20 × 0.08 mm, a = 8.218(1), b =

10.985(1), $c = 27.805(1)$ Å, $\beta = 94.07(1)°$, $V = 2503.8(4)$ Å^3, $\rho_{calcd.} = 1.573$ g cm^{-3}, $\mu = 8.53$ cm^{-1}, empirical absorption correction by SORTAV ($0.629 \leq T \leq 0.935$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 17976 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-1}, 5886 independent ($R_{int} = 0.048$) and 4599 observed reflections [$I \geq 2\sigma(I)$], 300 refined parameters, $R = 0.035$, $wR^2 = 0.061$, max. (min.) residual electron density 0.39 (−0.52) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Ethene Polymerization Reactions: These were carried out in a 1-L Büchi glass autoclave, charged with 300 mL of toluene. In the cases in which the *ansa*-metallocene dichloride *cis*-**8** was used as a precursor, methylalumoxane (MAO) in toluene (10.5%, 20 mL, 9.05 mmol) was added. In the case of the dimethylmetallocene/$B(C_6F_5)_3$ catalysts, triisobutylaluminium (0.5 mL) was added instead as a water scavenger. The autoclave was brought to the desired temperature and the solution was then saturated with ethene at a 2 bar pressure with stirring (800 rpm) for ca. 40 min. Either *cis*-**8** or the **9**/$B(C_6F_5)_3$ mixture (see Table 1 for details) was injected. To end the polymerization reaction, the ethene addition was terminated, excess monomer was allowed to vent, and the mixture was quenched by injection of 40 mL of a solution of dilute aqueous HCl/methanol (1:1). After 20 min of stirring, 100 mL of H_2O was added. The precipitated polyethylene was collected by filtration, and washed with 50 mL of 2 N aqueous HCl and then with water. The polymer was dried in vacuo for 24 h. The observed ethene polymerization activities of the homogeneous Ziegler−Natta catalyst derived from **8** or **9** (Table 1) are in a range similar to those obtained with related unbridged systems under similar conditions (e.g., **7**/MAO: $a \approx 2400$ kg PE/mol [Zr]·h·bar at 25 °C). Propene polymerization reactions were carried out analogously (2 bar propene pressure). The **9**/$B(C_6F_5)_3$ system gave atactic polypropylene (stereochemical analysis by ^{13}C NMR spectroscopy) with a catalyst activity of $a = 38$ kg PP/mol [Zr]·h·bar at 25 °C. The **8**/MAO catalyst system produced atactic polypropylene at 25 °C with $a = 38$ (Al/Zr = 800) at 60 °C with $a = 40$ (Al/Zr = 1050).

Preparation of (Butadiene)metallocene Complexes *s-cis*-15 and *s-trans*-15: Samples of [but-2-ene-1,4-diylbis(η^5-cyclopentadienyl)]zirconium dichloride (**8**, 80 mg, 0.23 mmol) and 2-butene-1,4-diylbis(tetrahydrofuran)magnesium (95.1 mg, 0.23 mmol) were mixed as solids and then dissolved in 3 mL of toluene. The reaction mixture spontaneously changed colour to deep red, and a white precipitate was formed. Because of the rapid decomposition of the product upon filtration, all volatile components were removed in vacuo to obtain the product **15**·$MgCl_2(THF)_n$ (112 mg, 85%) as a red solid (in [D$_8$]toluene solution at 298 K both the *s-cis*-**15** and the *s-trans*-**15** isomers were detected in a 4:5 ratio). $(C_{18}H_{20}Zr)\cdot(THF)_2MgCl_2$ (327.58 + 239.42 = 567.00): calcd. C 55.08, H 6.40; found C 53.22, H 6.43. IR (KBr): $\tilde{\nu}$ = 2962 w, 2915 m, 2849 m, 1635 w, 1449 m, 1262 m, 1042 s, 797 s, 729 m cm^{-1}. *s-cis*-**15**: ^1H NMR ([D$_8$]toluene, 599.9 MHz, 298 K): δ (298 K) = 5.81 (m, 2 H, 7-H), 5.09 (br., 4 H, Cp-H), 4.88 (br. m, 4 H, Cp-H), 4.73 (m, 2 H, H_{meso}), 2.91 (m, 4 H, 6-H), 1.24 (br., 4 H, H_{syn}, H_{anti}) ppm; δ (213 K) = 5.89, 5.75 (each m, each 1 H, 7-H), 5.55, 4.91, 4.53 (each br., each 2 H, Cp-H), 4.78 (m, 2 H, Cp-H), 4.76 (m, 2 H, H_{meso}), 3.42 (m, 2 H, H_{syn}), 2.97 (m, 2 H, 6-H), 2.81 (m, 2 H, 6-H), −0.59 (m, 2 H, H_{anti}) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 150.8 MHz): δ (298 K) = 130.2 (CH, $^1J_{CH}$ = 157 Hz, C-7), 118.6 (C, C-1), 112.8 (CH, $^1J_{CH}$ = 157 Hz, butadiene-CH), 100.9 (CH, $^1J_{CH}$ = 173 Hz, Cp), 25.8 (CH_2, $^1J_{CH}$ = 121 Hz, C-6) ppm; δ (213 K) = 130.5, 129.4 (each CH, C-7), 121.5, 115.1 (each C, C-1), 112.1 (CH, butadiene-CH), 107.9, 101.1, 101.1(4) (each CH, Cp), 96.0 o. 97.6 (CH, Cp), 49.7 (butadiene-CH_2), 25.3, 25.0 (each CH_2, C-6) ppm. ***s-trans*-15:** ^1H NMR ([D$_8$]toluene, 599.9 MHz): δ (298 K) = 5.81 (m, 2 H, 7-H), 4.96, 4.93, 4.57, 4.39 (each m, each 2 H, Cp-H), 3.02 (m, 2 H, H_{syn}), 2.99 (m, 4 H, 6-H), 2.97 (m, 2 H, H_{meso}), 1.24 (m, 2 H, H_{anti}); δ (213 K) = 5.79 (m, 2 H, 7-H), 4.87, 4.85, 4.53, 4.35 (br) (each m, each 2 H, Cp-H), 3.14 (m, 2 H, H_{syn}), 3.04 (m, 2 H, H_{meso}), 2.97 (m, 4 H, 6-H), 1.38 (m, 2 H, H_{anti}) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 150.8 MHz, 298 K): δ = 130.2 (CH, $^1J_{CH}$ = 157 Hz, C-7), 112.1 (C, C-1), 104.4 (CH, $^1J_{CH}$ = 170 Hz, C-Cp), 101.7 (CH, $^1J_{CH}$ = 172 Hz, C-Cp), 98.0 (CH, $^1J_{CH}$ = 174 Hz, C-Cp), 96.1 (CH, $^1J_{CH}$ = 149 Hz, butadiene-CH), 95.9 (CH, $^1J_{CH}$ = 175 Hz, C-Cp), 59.5 (CH_2, $^1J_{CH}$ = 157, $^1J_{CH}$ = 146 Hz, butadiene-CH_2), 25.5 (CH_2, $^1J_{CH}$ = 125 Hz, C-6); δ (213) = 129.8 (CH, C-7), 111.1 (C, C-1), 104.0, 101.1(4) (CH, Cp), 97.6 o. 96.0 (CH, Cp), 95.7 (CH, butadiene-CH), 95.3 (CH, Cp), 59.1 (CH_2, butadiene-CH_2), 24.9 (CH_2, C-6) ppm.

Catalytic Hydrogenation of *cis*-8. Preparation of 16: Complex *cis*-**8** (77 mg, 0.22 mmol) was dissolved in dichloromethane (20 mL). Heterogeneous Pd(C) catalyst (10% palladium, 80 mg) was added. Hydrogen was passed through the solution through a frit at 1 bar with stirring for 2 h. The catalyst was removed by filtration and the solvent was evaporated in vacuo to yield 43 mg (56%) of the *ansa*-metallocene **16**. ^1H NMR ([D$_2$]dichloromethane, 599.9 MHz, 298 K): δ = 6.40 (m, 4 H, 2,5-H), 6.38 (m, 4 H, 3,4-H), 2.84 (br. m, 4 H, 6-H), 1.90 (m, 4 H, 7-H) ppm. $^{13}C\{^1H\}$ NMR ([D$_2$]dichloromethane, 150.8 MHz, 298 K): δ = 128.1 (C, C-1), 118.5 (CH, C-3,4), 117.6 (CH, C-2,5), 27.5 (CH_2, C-6), 26.1 (CH_2, C-7) ppm.

Treatment of *cis*-8 with 9-BBN. Preparation of 17: A mixture of [but-2-ene-1,4-diylbis(η^5-cyclopentadienyl)]zirconium dichloride (**8**, 50 mg, 0.15 mmol) and 9-borabicyclo[3.3.1]nonane (17.7 mg, 0.15 mmol) was dissolved in 2 mL of dichloromethane at room temperature. The solution was stirred for 12 h and then concentrated to dryness in vacuo. The product (67.1 mg, 96%) was isolated as a white solid, m.p. 170 °C. IR (KBr): $\tilde{\nu}$ = 3094 w, 2911 m, 2837 m, 2362 w, 1492 w, 1452 m, 1355 w, 1309 w, 1195 w, 1012 m, 880 w, 817 vs cm^{-1}. ^1H NMR ([D$_2$]dichloromethane, 599.9 MHz, 298 K): δ = 6.53, 6.33 (each m, each 1 H, 2,5-H), 6.45, 6.25 (each m, each 1 H, 3,4-H), 6.45, 6.35 (each m, each 1 H, 2′,5′-H), 6.42, 6.40 (each m, each 1 H, 3′,4′-H), 3.03 (*A*BM, ^2J = 16.1, ^3J = 2.3 Hz, 1 H, 6-H), 2.99 (*A*BMN, ^2J = 16.2, ^3J = 3.0, ^3J = 7.1 Hz, 1 H, 9-H), 2.89 (A*B*MN, ^2J = 16.2, ^3J = 2.6, ^3J = 10.9 Hz, 1 H, 9-H′), 2.75 (A*B*M, ^2J = 16.1, ^3J = 9.0 Hz, 1 H, 6-H′), 2.09 (m, 1 H, 8-H), 1.88 (m, 1 H, 8-H′), 1.94, 1.72 (each m, each 4 H, β, δ-H), 1.93, 1.28 (each m, each 2 H, γ-H), 1.82 (m, 2 H, α-H), 1.71 (m, 1 H, 7-H) ppm. $^{13}C\{^1H\}$ NMR ([D$_2$]dichloromethane, 150.8 MHz, 298 K): δ = 129.4 (C, C-1), 128.1 (C, C-1′), 122.0, 115.1 (each CH, C-2,5), 120.5, 113.6 (each CH, C-2′,5′), 120.4, 117.4 (each CH, C-3,4), 118.4, 117.3 (each CH, C-3′,4′), 34.0, 33.9 (each CH_2, C-β, δ), 31.3 (br. CH, C-7), 30.7 (br. CH, C-α), 27.8 (CH_2, C-9), 27.4 (CH_2, C-6), 26.4 (CH_2, C-8), 23.5 (CH_2, C-γ) ppm. $^{11}B\{^1H\}$ NMR ([D$_6$]benzene, 64.2 MHz, 298 K): δ = 87 ($\nu_{1/2}$ = 329 Hz) ppm. $C_{22}H_{29}BCl_2Zr$ (466.41): calcd. C 56.65, H 6.27; found C 55.72, H 6.16.

Treatment of *cis*-8 with H-B(C_6F_5)$_2$. Preparation of 18: A mixture of [but-2-ene-1,4-diylbis(η^5-cyclopentadienyl)]zirconium dichloride (**8**, 50 mg, 0.15 mmol) and bis(pentafluorophenyl)borane (50.2 mg, 0.145 mmol) was dissolved in 2 mL of dichloromethane at room temperature. The solution was stirred for 1 h. Solvent was removed in vacuo to yield 90.3 mg (90%) of the product as a light brown solid, m.p. 238 °C. IR (KBr): $\tilde{\nu}$ = 3103 w, 2934 m, 2861 m, 1648 m, 1520 s, 1467 vs, 1386 m, 1316 m, 1288 w, 1094 m, 974 s, 813 s cm^{-1}. ^1H NMR ([D$_2$]dichloromethane, 599.9 MHz, 298 K): δ = 6.56, 6.43

(each m, each 1 H, 2,5-H), 6.49, 6.38 (each m, each 1 H, 3′,4′-H), 6.48, 6.47 (each m, each 1 H, 2′,5′-H), 6.40, 6.28 (each m, each 1 H, 3,4-H), 3.12 (*A*BMN, ^2J = 16.8, ^3J = 2.7, ^3J = 10.5 Hz, 1 H, 9-H), 3.05 (d, $^{2\text{ or }3}J$ = 15.9 Hz, 1 H, 6-H), 2.92 (A*B*MN, ^2J = 16.8, ^3J = 2.8, ^3J = 7.7 Hz, 1 H, 9-H′), 2.85 (m, 1 H, 6-H′), 2.56 (m, 1 H, 7-H), 2.16 (m, 1 H, 8-H), 1.96 (m, 1 H, 8-H′) ppm. $^{13}C\{^1H\}$ NMR ([D$_2$]dichloromethane, 150.8 MHz, 298 K): δ = 148.3 [dm, ^1J = 247.2 Hz, $B(C_6F_5)_2$], 139.4 [dm, ^1J = 253.0 Hz, $B(C_6F_5)_2$], 145.0 (dm, ^1J = 265.0 Hz, $B(C_6F_5)_2$], 128.4 (C, C-1), 128.3 (C, C-1′), 124.5, 117.9 (each CH, C-2,5), 121.5, 121.2 (CH, C-2′,5′), 120.4, 114.6 (each CH, C-3′,4′), 119.4, 118.6 (each CH, C-3,4), 115.0 [br., $B(C_6F_5)_2$], 30.2 (CH_2, C-9), 29.9 (CH_2, C-6), 27.5 (CH_2, C-8), (C-7 not observed) ppm. $^{11}B\{^1H\}$ NMR ([D$_6$]benzene, 64.2 MHz, 298 K): δ = 76 ($\nu_{1/2}$ = 340 Hz) ppm. ^{19}F NMR ([D$_6$]benzene, 563.6 MHz, 298 K): δ = −127.3 (br. m, 4 F, *o*-C_6F_5), −146.2 (br. m, 2 F, *p*-C_6F_5), −159,4 (br. m, 4 F, *m*-C_6F_5) ppm. $C_{26}H_{15}BCl_2F_{10}Zr$ (690.33): calcd. C 45.24, H 2.19; found C 45.02, H 2.42.

Adduct Formation between *cis*-8 and $Li^+[B(C_6F_5)_4^-]$. Generation of 19: In an NMR experiment, *cis*-**8** (23 mg, 0.07 mmol) was mixed with $Li^+[B(C_6F_5)_4^-]$ (46 mg, 0.07 mmol), and [D$_8$]toluene (1.0 mL) was then added. NMR spectra of the mixture were not distinguished from those of the single components, but the coordination product **19** crystallised from the mixture after ca. 1 d at ambient temperature to allow an X-ray crystal structure analysis.

X-ray Crystal Structure Determination of 19: $C_{14}H_{14}Cl_2Zr{\cdot}LiBC_{24}F_{20}$, M = 1030.36, colourless crystal, 0.50 × 0.40 × 0.15 mm, a = 13.8212(1), b = 14.7217(1), c = 18.2205(2) Å, α = 88.406(1), β = 77.278(1), γ = 89.484(1)°, V = 3614.92(5) Å^3, $\rho_{\text{calcd.}}$ = 1.893 g cm^{-3}, μ = 5.88 cm^{-1}, empirical absorption correction by SORTAV ($0.758 \leq T \leq 0.917$), Z = 4, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 26503 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.67 Å^{-1}, 17598 independent (R_{int} = 0.025) and 14617 observed reflections [$I \geq 2\sigma(I)$], 1135 refined parameters, R = 0.043, wR^2 = 0.105, max. (min.) residual electron density 1.24 (−1.44) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection COLLECT[68], data reduction Denzo-SMN[69], absorption correction SORTAV[70], structure solution SHELXS-97[71], structure refinement SHELXL-97[72], graphics SCHAKAL[73]. CCDC-180478 to -180481 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available: 2D NMR spectroscopic data of the complexes *trans*-**4**, *cis*-**8**, **9**, *s-cis-/s-trans*-**15**, **16**, **17** and **18** (see also the footnote on the first page of this article).

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