Seven-Membered Heterodimetallic Ring Systems from (Conjugated Diene) Group 4 Metallocene Complexes and Organoaluminium Reagents

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Received October 20, 1993

Key Words: Bent metallocene complexes / Heterodimetallic zirconium-aluminium compounds / Hydrocarbyl-bridging ligands / "π-Agostic" interaction

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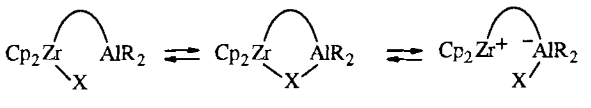
The (*s-trans*/*s-cis*-η^4-butadiene)zirconocene reagent adds dimethylaluminium chloride to yield the heterodimetallacyclic main group/transition-metal system **2b**, containing a seven-membered metallacyclic framework that exhibits a "π-agostic" σ-allyl zirconium interaction. Similar compounds (**2c–f**, **5a**, **6**) are obtained upon reaction of (butadiene)zirconocene with Et_2AlI and (butadiene)hafnocene with Me_2AlCl or Et_2AlI. Addition of Me_2AlCl or Et_2AlI to (isoprene)zirconocene proceeds regioselectively to yield the corresponding heterodimetallacycles bearing the methyl substituent at C-3 (i.e. near to the attached aluminium center). The iodide-bridged heterodimetallacycles exhibit dynamic NMR spectra that indicate a rapid enantiomerization process on the NMR time scale ($\Delta G^{\ddagger}_{ent} \approx 11-12$ kcal mol^{-1}). It is assumed that this automerization reaction proceeds by rate-limiting aluminium-halogen bond cleavage leading to an acyclic mixed metal heterodimetallic intermediate. This process is markedly inhibited by the presence of excess diethylaluminium iodide.

Many group 4 metallocene complexes react with organoaluminium compounds to give highly active Ziegler-type catalyst systems for olefin coupling reactions[1]. Homogeneous systems of this type probably contain metallocene cations (e.g. Cp_2M-R^+; R = H or alkyl) as the catalytically active species[2], and the added aluminium component is likely to be converted to a sufficiently non-nucleophilic counteranion during the activation process. It is tempting to speculate that a cationic metallocene center might alternatively become available from suitably designed systems in an intramolecular equilibrium situation starting from a neutral ligand-bridged dinuclear transition-metal/aluminium system. Containing the correct substitution pattern a doubly bridged dimetallic species such as the Zr/Al system **2** could probably form easily (e.g. from **1**) and may have the potential of undergoing subsequent Zr–X bond cleavage to generate reversibly a betain system (**3**, X = H, alkyl, halogen) that contains the cationic zirconium center.



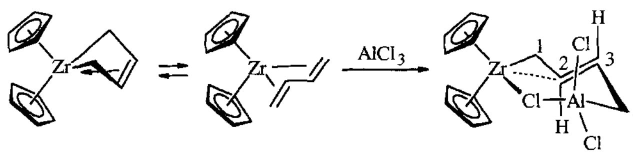
1 **2** **3**

There have been a few attempts to develop synthetic entries to such dinuclear main group metal/transition metal systems, mostly exhibiting bridging ligands that contain electronegative heteroatoms[3]. We have now found a very simple new reaction that makes zirconium- *and* aluminium-containing heterodimetallic complexes of the general type **2** very easily available. In all those complexes a butadiene-derived ligand system is used to make a strong connection between the metal centers. Usually, a halogen atom or hydride serves as the additional bridging ligand (X). In this paper we report on the preparation and characterization of a variety of examples of this interesting class of heterodimetallic organometallic systems, including a description of the dynamic behavior of some of these compounds.

Results and Discussion

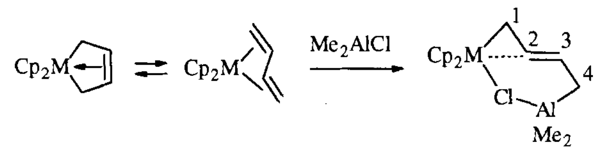
We have recently reported that (butadiene)zirconocene readily adds one molar equivalent of aluminium trichloride to give the metallacyclic coupling product **2a** in good yield (67% isolated)[4]. Complex **2a** exhibits NMR data typical of a metallacyclic allylzirconocene system (see Table 1). Its structure was determined by an X-ray crystal structure analysis. It reveals a unique arrangement of the substituted allylmetallocene structural subunit characterized by a strong, short Zr–C(1) bond [2.348(2) Å], a longer Zr–C(2) linkage [2.525(3) Å], and a Zr–C(3) separation (3.04 Å) being just outside of a typical zirconium-to-carbon bonding range. This structural type seems to mark a limiting situation for severely distorted *syn*-allyl bonding in a rather small and rigid metallacyclic ring system[5]. We have suggested that the term "π-agostic"[6] might be suited to characterize this unusual allyl coordination mode[7] which is probably originating from a very special interplay of steric and electronic features of this organometallic *trans*-cycloheptene-like molecule.

We have now treated (butadiene)zirconocene and -hafnocene (**4a, b**)[8] with a variety of alkylaluminium halides (and a corresponding hydride) and obtained a variety of similarly composed heterodimetallacyclic main group/transition metal systems.



2a

(Butadiene)zirconocene reacts rapidly with dimethylaluminium chloride at 0°C in toluene solution to yield the similarly structured 1:1 addition product **2b** (>90% isolated). It contains a *trans*-configurated C=C bond inside the heterodimetallic ring system [^{1}H/^{13}C NMR: δ = 3.93/95.5 ($^1J_{CH}$ = 147 Hz), C^2–H; 5.77/157.5 ($^1J_{CH}$ = 145 Hz), C^3–H; $^2J_{2\text{-H},3\text{-H}}$ = 14.5 Hz], which seems to be similarly coordinated to zirconium as was previously observed for complex **2a** (see Table 1). The Zr-bound butadiene-derived CH$_2$ group gives rise to ^{1}H/^{13}C-NMR signals at δ = 1.48, 1.83/43.1 ($^1J_{CH}$ = 146 Hz), whereas the corresponding resonances of the methylene group adjacent to aluminium appear at δ = 1.70, 1.75/32.8 ($^1J_{CH}$ = 122 Hz). Complex **2b** is chiral. It exhibits diastereotopic pairs of Cp ligands at zirconium (^{1}H/^{13}C NMR: δ = 5.35, 5.22/108.3, 107.4) and methyl groups at aluminium (^{1}H/^{13}C NMR: δ = −0.01, −0.25/−3.1, −6.4). The IR allyl C=C stretch of **2b** is observed at $\tilde{\nu}$ = 1564 cm^{-1}.



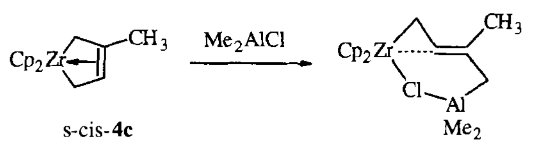
s-cis-**4** s-trans-**4**

M = Zr (**a**), Hf (**b**) **2** [M = Zr (**b**), Hf (**c**)]

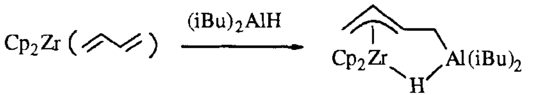
The adduct formation of dimethylaluminium chloride with (butadiene)hafnocene works equally well. Treatment of a 60:40 mixture of (*s-trans*/*s-cis*-η^4-C$_4$H$_6$)HfCp$_2$ (**4b**) with Me$_2$AlCl led to the formation of the Hf,Al-metallacycle **2c** in nearly 90% isolated yield. Complex **2c** shows spectroscopic data which are very similar to those of **2b** (Table 1).

(*s-cis*-η^4-Isoprene)zirconocene (**4c**) also adds the Me$_2$AlCl reagent. In this case one could principally expect the occurrence of two regioisomeric metallacyclic addition products. ^{1}H-NMR monitoring of the reaction has shown that only a single regioisomer is formed. It was isolated in ca. 40% yield. From the characteristic NMR data of the CH$_2$CHC(CH$_3$)CH$_2$ portion of the molecule (see Table 1) we assign to it the structure **5a**, bearing the methyl substituent at C-3, i.e. oriented close to the aluminium center.

Diisobutylaluminium hydride adds to the (butadiene)zirconocene equilibrium mixture (*s-cis*/*s-trans*-**4a**) at ambient temperature. After a 24 h reaction time the addition is complete, and the metallacyclic 1:1 addition product **6** is obtained as an orange-colored solid in >60% yield. The overall structural composition of **6** is similar to those of the above-mentioned complexes **2** and **5**. However, there are several pronounced differences of the chemical shifts that point to a slightly different attachment of the allyl moiety to the zirconium center within the organometallic seven-membered ring system. The ^{13}C-NMR resonance of C-3 is usually found in the range from ca. δ = 140 to 160 in the (butadiene)zirconocene-derived addition products **2**. In complex **6** the C-3 resonance is observed at ca. δ = 120. In **2** there is a marked difference between the chemical shifts of the 2-H and 3-H signals of the μ-C$_4$H$_6$ ligand (see Table 1), not so in complex **6** (δ = 4.28, 4.87). We assume, that the hydride-bridged product **6** is probably much closer to a conventional π-allyl structural type[7] than the complexes **2** and **5** which may be regarded as examples of the isomeric "π-agostic" variety[4] of the allyl transition metal complex family.



s-cis-**4c** **5a**



4a **6**

Diethylaluminium iodide reacts with (butadiene)zirconocene in toluene solution during 2 h at ambient temperature to yield the metallacyclic addition product **2d** (60% isolated). The complex exhibits the typical NMR signals of the CH$_2$CH=CHCH$_2$ moiety of the "π-agostic" structural type with pairs of diastereotopic methylene protons at δ = 1.84, 1.33 (1-H, 1-H′) and 2.18, ≈1.65 (4-H, 4-H′) in [D$_8$]toluene at 233 K. At this temperature there is also observed a diastereotopic pair of ethyl groups at aluminium [^{1}H-NMR: δ = 1.60, 1.50 (CH$_3$), 0.63, 0.30 (CH$_2$)] and a pair of diastereotopic cyclopentadienyl ligands at zirconium [^{1}H-NMR (233 K): δ = 5.17, 5.06; ^{13}C-NMR ([D$_6$]benzene, 300 K): δ = 107.5 and 106.5].

In contrast to the chloride- and hydride-bridged complexes **2a–c**, **5a**, and **6** the iodide-bridged heterodinuclear complex **2d** shows dynamic NMR spectra. An increase of the temperature at which the ^{1}H-NMR spectrum of **2d** is monitored rapidly leads to broadening of the pair of Cp resonances and coalescence to a single signal at δ = 5.31 (at 362 K). The AlEt$_2$-derived set of signals shows an analogous behavior and, in addition, the pairs of hydrogens at C-1 and C-4 loose their diastereotopic differentiation. At 362 K a very simple ^{1}H-NMR spectrum of **2d** is observed (see Figure 1) showing only a single Cp resonance, one set of Al(C$_2$H$_5$) signals, and the simplified set of resonances originating from the Zr,Al-bridging C$_4$H$_6$ ligand. Thus, **2d** undergoes a thermally induced automerization process which results in a concealment of the chirality information of the asymmetric seven-membered metallacyclic ring system due to rapid enantiomerization.

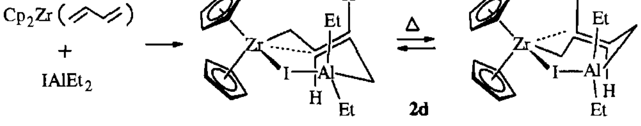
This dynamic enantiomerization process, which can readily be followed on the ^{1}H-NMR time scale, exhibits a few uncommon features that seem noteworthy. When we attempted to derive its activation barrier we noticed that the

Table 1. Selected NMR data of the heterodimetallic complexes **2**, **5**, and **6**[a]

compd.	metallocene	diene	Al-component	C1	C2	C3	C4	H1/1'	H2	H3	H4/4'	^2J(2-H,3-H)
2a	Cp_2Zr	[b]	$AlCl_3$	42.8 (147)	102.6 (149)	140.5 (149)	25.4	1.72/1.46	3.92	4.99	1.92/1.42	15.4
2b	Cp_2Zr	[b]	Me_2AlCl	43.1 (146)	95.5 (147)	157.5 (145)	32.8 (122)	1.83/1.48	3.93	5.77	1.75/1.70	14.5
2c	Cp_2Hf	[b]	Me_2AlCl	43.4	93.5	158.2	32.3	~1.7/1.36	3.84	5.79	1.80-1.60	14.8
2d	Cp_2Zr	[b]	Et_2AlI	41.5 (146)	92.6 (147)	162.5 (145)	32.7 (122)	1.84/1.33	3.36	5.58	2.18/~1.65	14.6
2e	Cp_2Hf	[b]	Et_2AlI	42.5 (142)	90.2 (142)	163.5 (145)	32.5 (124)	1.71/1.22	3.23	5.60	2.12/~1.55	14.7
2f	$(MeCp)_2Zr$	[b]	Et_2AlI	44.6 (145)	94.7 (145)	161.1 (145)	31.7 (121)	1.79/1.29	3.47	5.64	2.21/1.60	14.7
6	Cp_2Zr	[b]	iBu_2AlH	38.2 (147)	102.0 (147)	119.9 (142)	18.2 (124)	~1.7/~1.3	4.28	4.87	1.87-1.65	15.9
5a	Cp_2Zr	[c]	Me_2AlCl	39.5	85.6	180.0	42.9	1.86-1.75	3.61	-	2.01/1.8	-
5b	Cp_2Zr	[c]	Et_2AlI	38.1 (145)	84.3 (142)	182.2 (-)	42.1 (123)	2.1-1.7	3.28	-	2.1-1.7	-

[a] Chemical shifts rel. to TMS, δ scale, coupling constants in Hz, $^1J_{CH}$ given in parentheses; for solvents see Experimental. – [b] 1,3-Butadiene. – [c] Isoprene.

coalescence temperature and thus the Gibbs activation energy obtained varied markedly when different samples were used for carrying out the dynamic NMR experiment. Series of control experiments rapidly revealed that this unexpected behavior was probably not due to a concentration effect nor was it dependent on the amount of the Cp_2ZrI_2 byproduct, small amounts of which were present in most of our **2d** samples. However, a substantial retardation in the rearrangement rate could be achieved by the deliberate addition of diethylaluminium iodide. It turned out that even very small amounts of $IAlEt_2$ (for details see Experimental) reproducibly led to a substantial increase of the apparent activation barrier of the automerization process of **2d**. This effect of a "negative catalysis" by a fractional concentration of the aluminium alkyl reagent could be eliminated easily by adding a slight excess of (butadiene)$ZrCp_2$ as a scavenger. Excess $(C_4H_6)ZrCp_2$ does not interfere with the dynamic NMR process observed of **2d**, but its presence assured that small amounts of the aluminium component, which might have been formed by some decomposition of **2d** and thus be present in different concentrations in solutions of the heterodimetallacycle, are trapped and thus are no longer interfering with the kinetics of the thermally induced automerization process of **2d**. In the presence of excess (butadiene)zirconocene the Gibbs activation barrier of the thermally induced enantiomerization was reproducibly determined as $\Delta G^{\neq}$ (230 K) = 11.5 ± 0.5 kcal mol^{-1}[9].



(Butadiene)hafnocene reacts analogously with diethylaluminium iodide to give **2e**. The Hf,Al-containing heterodimetallacycle also exhibits dynamic NMR behavior. The Gibbs activation barrier of the enantiomerization process for the limiting situation in the presence of a sufficient quantity of the (butadiene)metallocene was determined as $\Delta G^{\neq}$ (244 K) = 12.3 ± 0.5 kcal mol^{-1}.

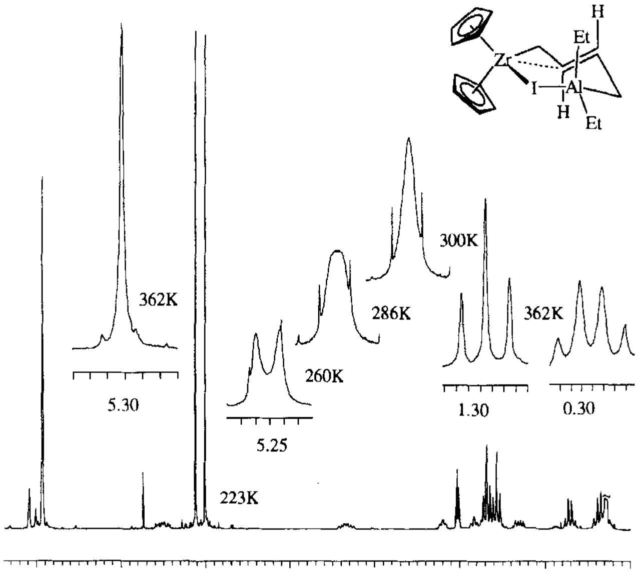
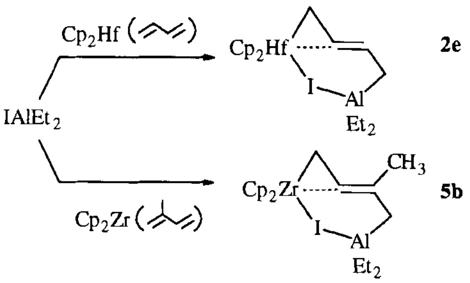
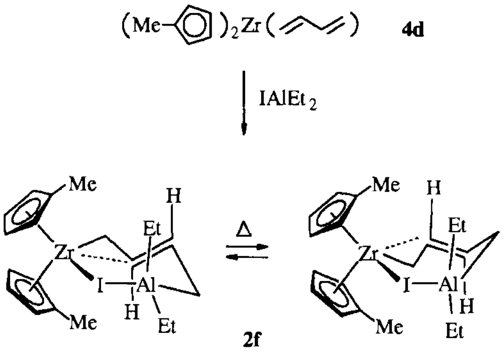


Figure 1. Dynamic ^1H-NMR spectra of **2d** in the absence of excess (butadiene)zirconocene

(Isoprene)zirconocene adds one equivalent of $IAlEt_2$ to give a single regioisomeric heterodimetallic complex (**5b**). From its NMR spectra we conclude that the methyl substituent in **5b** is located at the C-3 ring position analogously as in **5a**. Complex **5b** also features the thermally induced intramolecular enantiomerization reaction. In the presence of free (butadiene)$ZrCp_2$ the activation barrier of the automerization of **5b** was determined as $\Delta G^{\neq}$ (237 K) = 11.9 ± 0.5 kcal mol^{-1}.

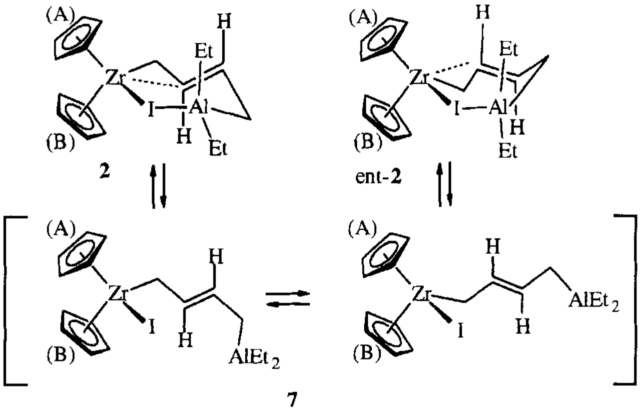


(η^4-Butadiene)bis(methylcyclopentadienyl)zirconocene (**4d**) adds diethylaluminium iodide to yield the "π-agostic" seven-membered heterodimetallacycle **2f**. It shows the expected dynamic NMR behavior. Below the coalescence temperature, complex **2f** exhibits the NMR signals of two diastereomeric methylcyclopentadienyl ligands featuring a total of eight methine resonances at δ = 5.55, 5.32, 5.22, 4.95, 4.85, 4.79, 4.71, and 4.55 in addition to the methyl singlets at δ = 1.56 and 1.44 (195 K, [D$_8$]toluene solvent). The signals coalesce to a single set of $C_5H_4CH_3$ resonances at high temperature. The fact that a total of four methine resonances is observed above the coalescence point indicates that the "left"/"right" differentiation caused by the presence of a pair of non-identical σ ligands at the zirconium center is retained throughout the rearrangement process. During this thermally induced reorganization symmetry equivalence of pairs of groups above and below the σ ligand plane is achieved but the characteristic differentiation of the structural subunits in the σ plane is apparently retained.



There are two general mechanistic types that may be discussed to explain the dynamic behavior of the chiral seven-membered metallacycles **2d–f** and **5b** containing iodide bridges between the group 4 metal and aluminium, differing in whether the metallacyclic frame is retained or not. If the metallacycle remained intact the dynamics of these chiral organometallic complexes would be considered analogous to the topomerization behavior of the *trans*-cycloalkenes[10]. Probably, the ring perimeter of e.g. **2d** is somewhere in size between *trans*-cycloheptene and *trans*-cyclooctene. Therefore, enantiomerization of **2d** without breaking a peripheral bond in this mechanistic model would require opening of the π bond between the metal and C-2 followed either by *trans*-dimetallaiodocycloheptene topomerization or consecutive *trans* ⇌ *cis* ⇌ *trans*-C=C isomerization with concurrent *cis*-dimetallaiodocycloheptene conformational equilibration. From a comparison with the energetics of the related processes as they occur in the *trans*-cycloalkene series[10] it can be deduced that the observed activation parameters of the **2d–f** and **5b** enantiomerization processes are probably far too low for any of these processes involving intact metallacyclic ring systems to take part in the rearrangement.

Therefore, we think that it is very likely that a metal-to-halogen linkage is opened to allow the enantiomerization reaction to take place and be observed on the NMR time scale. Complete reversal of ring formation with liberation of (butadiene)MCp$_2$ can be ruled out as there is neither C1/C4 and C2/C3 exchange nor equilibration between **2(d–f)** and added (butadiene)metallocene reagent observed during the rapid enantiomerization process. Of the remaining alternatives – ring opening by breaking a single M–I bond – the mechanistic pathway seems to be favored during which the Al–I rather than the Zr–I interaction is temporarily lost. This would be in accord with the observation that the "left/right" differentiation of the methylcyclopentadienyl symmetry probe is retained during the rearrangement of **2f**. We thus propose that the observed fast enantiomerization process of **2d–f** and **5b** takes place via an acyclic heterodimetallic σ-allyl intermediate (e.g. such as **7**).



Explaining the strong inhibition of the enantiomerization reaction by small amounts of added dialkylaluminium halide is much more difficult. One might try to attribute this "negative catalysis" to a different response of global and local minimum structures towards a changing solvent polarity[11] or alternatively consider the possibility of reversible interception of a reactive intermediate (e.g. **7**), which is responsible for rapid symmetrization, by added $XAlR_2$. Unfortunately, at present the experimental material does not allow a clear mechanistic description of this interesting effect.

This study has shown that hydrocarbyl-bridged zirconium- and aluminium-containing mixed metal complexes are readily available by treating the respective conjugated (diene)metallocenes with dialkylaluminium halides and related reagents. It appears, that these heterodimetallacycles of the structural type **2** (as depicted in the introductory paragraph) may indeed open to produce the acyclic isomers **1**. Whether the interesting betain isomers **3** can also be generated from the stable starting materials **2** under suitable reaction conditions must await further studies.

Financial support from the *Fonds der Chemischen Industrie*, the *Volkswagen-Stiftung*, and the *Alfried Krupp von Bohlen und Halbach-Stiftung* is gratefully acknowledged.

Experimental

All reactions were carried out in an argon atmosphere by using Schlenk-type glassware or a glove box. Solvents were dried and distilled prior to use. – NMR: Bruker AC 200 P (^{1}H: 200 MHz, ^{13}C: 50.3 MHz) and Bruker ARX 300 (^{13}C: 75.0 MHz). – IR: Nicolet 5 DXC FT. – Melting points: Du Pont 910 DSC and gallenkamp melting point apparatus. – Elemental analyses: Voss-Heraeus CHNO-rapid. Elemental analyses of the heterodimetallic complexes were corrected for the small amounts of Cp_2ZrX_2 admixtures that they always contained. – (Conjugated diene)metallocene complexes were prepared as described in the literature[8]. The complexes **2b–f**, **5**, and **6** are rather sensitive. The diethylaluminium iodide adducts cannot be kept without decomposition for prolonged periods of time. For investigation they are best prepared freshly from their readily available organometallic precursors.

Preparation of **2b**: (Butadiene)zirconocene (1.10 g, 3.99 mmol) was dissolved in 60 ml of toluene and dimethylaluminium chloride (480 mg, 5.19 mmol in 5 ml of toluene) was added at 0°C. The solution was stirred for 1 h. The solvent was then removed at 0°C and the residue washed with 30 ml of pentane. The pale yellow powder (1.33 g, 91%) was isolated and dried in vacuo to give complex **2b** which was contaminated with ca. 5% of zirconocene dichloride; m.p. (DSC) 143°C. – IR (KBr): $\tilde{\nu}$ = 3113, 1438, 1014, 815 (Cp), 2962, 2923, 2882, 1564, 1182, 1109, 994, 736, 699 cm^{-1}. – ^{1}H NMR ([D$_6$]benzene): δ = 5.77 (m, 1H, 3-H), 5.35, 5.22 (s, each 5H, Cp), 3.93 (m, 1H, 2-H), 1.83 (m, 1H, 1-H), 1.75 (m, 1H, 4-H), 1.70 (m, 1H, 4-H'), 1.48 (m, 1H, 1-H'), −0.01, −0.25 (s, each 3H, CH_3); coupling constants (Hz), from homodecoupling and PANIC iteration: ^2J = 7.2 (1-H, 1-H'), 7.8 (4-H, 4-H'), ^3J = 14.5 (2-H, 3-H), 7.2 (1-H, 2-H), 12.8 (1-H', 2-H), 5.8 (3-H, 4-H), 12.9 (3-H, 4-H'). – ^{13}C NMR ([D$_6$]benzene): δ = 157.5 ($^1J_{CH}$ = 145 Hz, C-3), 108.3 (173, Cp), 107.4 (175, Cp), 95.5 (147, C-2), 43.1 (146, C-1), 32.8 (122, C-4), −3.1, −6.4 [$Al(CH_3)_2$]. – $C_{16}H_{22}AlClZr$ (368.0): calcd. (corrected for Cp_2ZrCl_2 contamination) C 51.19, H 5.82; found C 50.16, H 5.93.

Preparation of **2c**: (Butadiene)hafnocene (667 mg, 1.84 mmol) was dissolved in 50 ml of toluene. At 0°C a solution of dimethylaluminium chloride (320 mg, 3.45 mmol in 5 ml of toluene) was added. After stirring of the reaction mixture at this temp. for 90 min the solvent was removed in vacuo. The product was washed with pentane and dried in vacuo to yield 680 mg (81%) of **2c**. The crude product was recrystallized from toluene/pentane; m.p. (DSC) 131°C. – IR (KBr): $\tilde{\nu}$ = 3107, 2963, 2922, 2882, 1632, 1567, 1439, 1262, 1176, 1100, 1070, 1015, 995, 911, 817, 698 cm^{-1}. – ^{1}H NMR ([D$_6$]benzene): δ = 5.79 (m, 1H, 3-H), 5.29, 5.17 (s, each 5H, Cp), 3.84 (m, 1H, 2-H), 1.80–1.60 (m, 3H, 1-H, 4-H, 4-H'), 1.36 (dd, 1H, 1-H'), −0.03, −0.28 (s, each 3H, CH_3); coupling constants (Hz): ^2J = 8.2 (1-H, 1-H'), ^3J = 14.8 (2-H, 3-H), 12.6 (1-H', 2-H). – ^{13}C NMR ([D$_6$]benzene): δ = 158.2 (C-3), 107.6, 106.3 (Cp), 93.5 (C-2), 43.4 (C-1), 32.3 (C-4), −2.1, −6.4 (CH_3). – $C_{16}H_{22}AlClHf$ (455.3): calcd. C 41.56, H 4.74; found C 40.75, H 4.63.

Preparation of **2d**: (Butadiene)zirconocene (448 mg, 1.63 mmol) was dissolved in 20 ml of toluene and treated with diethylaluminium iodide (345 mg, 1.63 mmol in 3 ml of toluene). After stirring for 2 h the reaction mixture was filtered and the solvent removed from the filtrate. The product was washed with 15 ml of pentane and dried in vacuo. 480 mg (60%) of **2d** was isolated as a dark-yellow powder, which was contaminated with ca. 4% of zirconocene diiodide; m.p. (DSC) 104°C. – IR (KBr): $\tilde{\nu}$ = 3101, 1438, 1014, 810 (Cp); 2962, 2930, 2897, 2855, 1559, 1263, 733 cm^{-1}. – ^{1}H NMR (233 K, [D$_8$]toluene): δ = 5.58 (m, 1H, 3-H), 5.17, 5.06 (s, each 5H, Cp), 3.36 (m, 1H, 2-H), 2.18 (m, 1H, 4-H), 1.84 (m, 1H, 1-H), 1.60, 1.50 (m, each 3H, CH_3), ≈1.65 (m, 1H, 4-H'), 1.33 (dd, 1H, 1-H'), 0.63, 0.30 (m, each 2H, CH_2); coupling constants (Hz), from homodecoupling and PANIC iteration: ^2J = 7 (1-H, 1-H'), 7 (4-H, 4-H'), ^3J = 14.6 (2-H, 3-H), 6.5 (1-H, 2-H), 12.7 (1-H', 2-H), 7.0 (3-H, 4-H). – Several experiments were carried out to learn about the influence of various added reagents on the temperature-dependent NMR spectra. A freshly prepared sample of complex **2d** in [D$_8$]toluene exhibited a coalescence temperature T_c = 254 K and a Gibbs activation barrier $\Delta G^{\ddagger}_{ent}$ = 12.7 ± 0.5 kcal mol^{-1}. This value did not change by adding first 5 mg and then 25 mg of Cp_2ZrI_2. An analogous sample of **2d** in [D$_8$]toluene showed gradually rising coalescence temperatures T_c upon addition of increasing amounts of Et_2AlI: a) (20 mg of **2d**, no Et_2AlI added): T_c = 254 K, $\Delta G^{\ddagger}_{ent}$ = 12.7 (± 0.5) kcal mol^{-1}; b) +0.1 mg of Et_2AlI: 257 K, 12.9 kcal mol^{-1}; c) +0.8 mg of Et_2AlI: 315 K, 16.1 kcal mol^{-1}; d) +3 mg of Et_2AlI: 340 K, 17.7 kcal mol^{-1}; e) +12 mg of Et_2AlI: 334 K, 17.2 kcal mol^{-1}; f) +75 mg of Et_2AlI: 322 K, 16.8 kcal mol^{-1}. The inhibition caused by Et_2AlI could be fully reversed by adding an excess of the (butadiene)zirconocene scavenger. Typical example: A mixture containing ca. 20 mg of **2d** and some Et_2AlI exhibited a coalescence temperature of T_c = 286 K and an apparent $\Delta G^{\ddagger}_{ent}$ = 14.4 kcal mol^{-1}. These values changed upon (butadiene)zirconocene addition as follows: a) +1 mg of $(C_4H_6)ZrCp_2$ (**4a**): T_c = 253 K, $\Delta G^{\ddagger}_{ent}$ = 12.7 kcal mol^{-1}; b) +3 mg of **4a**: 238 K, 11.9 kcal mol^{-1}; c) +6 mg of **4a**: 235 K, 11.8 kcal mol^{-1}; d) +12 mg of **4a**: 232 K, 11.5 kcal mol^{-1}; e) +24 mg of **4a**: 230 K, 11.5 kcal mol^{-1}. All $\Delta G^{\ddagger}_{ent}$ values given in this article were obtained analogously. – ^{13}C NMR ([D$_6$]benzene): δ = 162.5 ($^1J_{CH}$ = 145 Hz, C-3), 107.5, 106.5 (each: 175, Cp), 92.6 (147, C-2), 41.5 (146, C-1), 32.7 (122, C-4), 10.4 (124, CH_3), 6.5, 3.0 (each: $Al-CH_2-$). – $C_{18}H_{26}AlIZr$ (487.5): calcd. (corrected for Cp_2ZrI_2 contamination) C 43.59, H 5.25; found C 43.91, H 5.45.

Preparation of **2e**: A solution of diethylaluminium iodide (357 mg, 1.68 mmol) in 2 ml of toluene was added to a solution of 510 mg (1.41 mmol) of (butadiene)hafnocene. Then, the yellow solution was stirred for 2 h. The solvent was removed and the resulting yellow oil solidified by treating it with 30 ml of pentane. The precipitate was collected by filtration and dried in vacuo to give 490 mg (60%) of **2e** containing ca. 10% of Cp_2HfI_2, m.p. 106°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3103, 1439, 1015, 815 (Cp), 2962, 2931, 2899, 2860, 1633, 1563, 1262, 1101, 638 cm^{-1}. – ^{1}H NMR ([D$_8$]toluene, 227 K): δ = 5.60 (m, 1H, 3-H), 5.09, 5.00 (s, each 5H, Cp), 3.23 (m, 1H, 2-H), 2.12 (t, 1H, 4-H), 1.71 (t, 1H, 1-H), 1.63, 1.52 (t, each 3H, CH_3), ≈1.55 (4-H'), 1.22 (dd, 1H, 1-H'), 0.65, 0.32 (q, each 2H, $AlCH_2$), coupling constants (Hz): ^2J = 8.1 (1-H, 1-H'), ^3J = 14.7 (2-H, 3-H), ≈7 (1-H, 2-H), 12.7 (1-H', 2-H), ≈7 (3-H, 4-H). – ^{13}C NMR ([D$_6$]benzene): δ = 163.5 ($^1J_{CH}$ = 145 Hz, C-3), 106.2 (173, broad, Cp), 90.2 (142, C-2), 42.5 (142, C-1), 32.5 (124, C-4), 10.2 (124, CH_3), signals of the exocyclic methylene groups at aluminium were not observed. – $C_{18}H_{26}AlHfI$ (574.8): calcd. (corrected for Cp_2HfI_2 contamination) C 35.98, H 4.28; found: C 35.16, H 4.23.

Preparation of **2f**: (Butadiene)$Zr(MeCp)_2$ (370 mg, 1.22 mmol) was dissolved in 30 ml of toluene and treated with diethylaluminium iodide (260 mg, 1.23 mmol in 5 ml of toluene). After stirring for 1 h the solvent was removed in vacuo. The oily residue was extracted with 15 ml of pentane. The solvent was removed from the extract in vacuo, and 320 mg (51%) of **2f** was isolated. The brown semisolid product contained ca. 10% of $(MeCp)_2ZrI_2$. – IR (KBr): $\tilde{\nu}$ = 3099, 2963, 2922, 2897, 2888, 2852, 1559, 1492, 1452, 1405, 1377, 1262, 1106, 1041, 807 cm^{-1}. – ^{1}H NMR ([D_8]toluene, 222 K): δ = 5.64 (m, 1H, 3-H), 5.54 (1H), 5.24 (2H), 4.96 (3H), 4.85 (1H), 4.72 (1H, each: m, C_5H_4), 3.47 (m, 1H, 2-H), 2.21 (dd, 1H, 4-H), 1.79 (dd, 1H, 1-H), 1.57, 1.50 (s, each $Cp{-}C\mathit{H}_3$), 1.61, 1.52 (m, each 3H, CH_3), ≈1.60 (m, 1H, 4-H′), 1.29 (dd, 1H, 1-H′), 0.68, 0.36 (m, each 2H, CH_2), coupling constants (Hz) (from homodecoupling and PANIC iteration): ^{2}J = 7 (1-H, 1-H′), 7 (4-H, 4-H′), ^{3}J = 14.7 (2-H, 3-H), 7 (1-H, 2-H), 12.5 (1-H′, 2-H), ≈ 7 (3-H, 4-H). – ^{13}C NMR ([D_8]toluene, 222 K): δ = 161.1 ($^{1}J_{CH}$ = 145 Hz, C-3), 115.7, 114.3 (*ipso*-C, MeCp), 114.7, 111.7, 109.8, 108.9, 108.5, 107.1, 102.5, 101.3 (C_5H_4Me), 94.7 (145, C-2), 44.6 (145, C-1), 31.7 (121, C-4), 14.7, 14.4 (each 128, $Cp{-}\mathit{C}H_3$), 10.6, 10.5 (each 123, CH_3), 6.0, 2.4 (CH_2). – $C_{20}H_{30}AlIZr$ (515.6): calcd. [corrected for $(MeCp)_2ZrI_2$ contamination] C 44.80, H 5.56; found C 44.98, H 5.91.

Preparation of **6**: (Butadiene)zirconocene (730 mg, 2.65 mmol) dissolved in 25 ml of toluene was treated in portions with 900 mg (6.33 mmol) of diisobutylaluminium hydride. The solvent was removed after 24 h and the residue extracted with 15 ml of pentane. The product **6** crystallized from the extract at −30°C as dark-orange colored crystals (700 mg, 63%), m.p. (DSC) 74°C. – IR (KBr): $\tilde{\nu}$ = 3105, 1439, 1014, 810 (Cp), 3039, 2947, 2859, 1629, 1550, 1461, 1359, 1157, 1005, 992, 693 cm^{-1}. – ^{1}H NMR ([D_6]benzene): δ = 5.29, 5.18 (s, each 5H, Cp), 4.87 (m, 1H, 3-H), 4.28 (m, 1H, 2-H), 2.30–2.02 (m, 2H, CH), 1.87–1.65 (m, 3H, 1-H, 4-H, 4-H′), 1.28, 1.23 (d, ^{3}J = 6.0, each 6H, CH_3), 1.00 (dd, 1H, 1-H′), 0.44–0.30 (m, 4H, $Al{-}C\mathit{H}_2CH$), −2.97 (broad, 1H, Zr−H−Al); coupling constants (Hz), from H,H-COSY, homodecoupling and PANIC simulation: ^{2}J = 5.8 (1-H, 1-H′), ^{3}J = 15.9 (2-H, 3-H), 7.3 (1-H, 2-H), 12.6 (1-H′, 2-H), 5.9 (3-H, 4-H), 12.4 (3-H, 4H′), ^{4}J = 1 (1-H′, 3-H), ^{5}J = 2 (1-H′, 4-H′). – ^{13}C NMR ([D_6]benzene): δ = 119.9 ($^{1}J_{CH}$ = 142 Hz, C-3), 104.1, 103.2 (each 173, Cp), 102.0 (147 ± 5, C-2), 38.2 (147, C-1), 28.8, 28.6 (each ≈123, CH_3), 27.7, 27.6 (each 124, −CH), 22.8, 22.5 [each ≈109, $Al(CH_2{-})$], 18.2 (124, C-4). – $C_{22}H_{35}AlZr$ (417.7): calcd. C 63.26, H 8.45; found C 61.65, H 8.93.

Preparation of **5a**: A solution of dimethylaluminium chloride (180 mg, 1.95 mmol) in 2 ml of toluene was added to a solution of 410 mg (1.42 mmol) of (isoprene)zirconocene in 50 ml of toluene. After stirring the reaction mixture for 1 h the solvent was removed. The oily product was washed with 30 ml of pentane and dried in vacuo to give 210 mg (39%) of **5a**, m.p. (DSC) 95°C. – IR (KBr): $\tilde{\nu}$ = 3113, 1440, 1015, 815 (Cp), 2969, 2930, 1549, 1234, 1182, 957, 734 cm^{-1}. – ^{1}H NMR ([D_6]benzene): δ = 5.35, 5.28 (s, each 5H, Cp), 3.61 (dd, 1H, 2-H), 2.01 (d, 1H, 4-H), 1.86–1.75 (m, 3H, 1-H, 1-H′, 4-H′), 1.65 (s, 3H, CH_3), 0.00, −0.25 (each 3H, $AlCH_3$); ^{2}J = 7.1 Hz (4-H, 4-H′). – ^{13}C NMR ([D_6]benzene): δ = 180.0 (C-3), 109.1, 108.2 (Cp), 85.6 (C-2), 42.9 (C-4, broad), 39.5 (C-1), 21.8 ($C{-}\mathit{C}H_3$), signals of the methyl groups at aluminium were not observed. – $C_{17}H_{24}AlClZr$ (382.0): calcd. (corrected for the Cp_2ZrI_2 contamination) C 53.08, H 6.24; found C 52.93, H 6.24.

Preparation of **5b**: A solution of diethylaluminium iodide (320 mg, 1.51 mmol) in 2 ml of toluene was added to a solution of (isoprene)zirconocene (410 mg, 1.42 mmol) in 50 ml of toluene. The color of the brown solution changed to orange. After 1 h the toluene was removed in vacuo and the remaining oil solidified by stirring it with 30 ml of pentane. The orange-colored product **5b** was isolated by filtration and dried in vacuo (550 mg, 77%) (7% Cp_2ZrI_2 could not be removed); m.p. 112–118°C. – IR (KBr): $\tilde{\nu}$ = 3109, 1438, 1014, 816 (Cp), 2964, 2931, 2896, 2853, 1539, 1375, 1233, 958, 681, 629 cm^{-1}. – ^{1}H NMR ([D_6]benzene): δ = 5.35, 5.29 (s, each 5H, Cp), 3.28 (dd, 1H, 2-H), 2.1–1.7 (m, 4H, 4-H, 1-H, 1-H′, 4-H′), 1.55, 1.47 (t, each 3H, $CH_2C\mathit{H}_3$), 1.44 (s, 3H, CH_3), 0.62, 0.37 (m, each 2H, $AlCH_2$). – ^{13}C NMR ([D_6]benzene): δ = 182.2 (C-3), 108.1, 107.4 (each $^{1}J_{CH}$ = 174 Hz, Cp), 84.3 (142, C-2), 42.1 (123, C-4), 38.1 (145, C-1), 22.3 (q, $=C{-}\mathit{C}H_3$), 10.4, 10.2 ($CH_2\mathit{C}H_3$), 6.7, 4.4 (each: t, $Al{-}\mathit{C}H_2CH_3$). – $C_{19}H_{28}AlIZr$ (501.5): calcd. (corrected for the Cp_2ZrI_2 contamination) C 44.08, H 5.38; found C 43.31, H 5.45.

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