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Bis(enamino-Cp) Group 4 metal complex chemistry: developing a Mannich-type carbon–carbon coupling reaction at the bent metallocene famework

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Abstract

Treatment of 6-methyl-6-dimethylaminofulvene (**2a**) with methyl lithium in ether results in a deprotonation reaction to yield the enamino-substituted lithium cyclopentadienide reagent **3a**. Its reaction with zirconium tetrachloride (0.5 molar equivalents) results in the formation of the [1-dimethylaminobutadien-1,3-diyl-bis(cyclopentadienyl)]zirconium dichloride product **4a**. The unsaturated *ansa*-metallocene is probably formed via a Lewis acid-catalyzed Mannich-type carbon–carbon coupling reaction of an in situ generated bis[(dimethylaminoethenyl)cyclopentadienyl]$ZrCl_2$ intermediate. A number of related examples of this condensation reaction at the intact Group 4 bent metallocene framework is described, using different amino-substituents and Ti, Zr and Hf systems. Three examples of the unsaturated *ansa*-metallocene systems were characterized by X-ray diffraction. In a few cases it was possible to isolate the open (enamino-Cp)$_2ZrCl_2$ complexes. In the case of, e.g., (piperidinoethenylcyclopentadienyl)$_2ZrCl_2$ (**13c**) treatment with a catalytic quantity of the Lewis acid $ZrCl_4$ or the Brønsted acid $[PhNMe_2H^+][BPh_4^-]$ resulted in a clean conversion to the respective Mannich condensation product, here the *ansa*-metallocene complex **4c**. The strongly electrophilic borane $HB(C_6F_5)_2$ did not catalyze the CC-coupling reaction under the applied reaction conditions but added cleanly to the enamino-C=C double bond of, e.g., **13c** to yield a cyclic nitrogen donor-stabilized hydroboration product (**19**).

Keywords: Zirconocene; *ansa*-Metallocene; Mannich reaction; Carbon–carbon coupling; Hydroboration; Enamines

1. Introduction

Organic functional group chemistry at substituted η^5-cyclopentadienyl ligands is very well developed in the case of many late transition metal complexes. Ferrocene chemistry is a prominent example where equivalents of arene substitution chemistry has very well been worked out, and typical functional group conversions have been described for many examples [1]. This is very different for Group 4 metallocene chemistry. Functional group interconversion at Cp-substituents has very rarely been described. The introduction of functional groups is usually not carried out at the metallocene stage (although an increasing number of specific examples seems to appear in the recent literature) [2] – organic functional groups are mostly introduced at the ligand stage and then carried along with the Cp-anion systems in the course of the actual bent metallocene synthesis [3,4].

Conventional CC-coupling of functional groups is difficult to achieve at the sensitive Group 4 metallocene frameworks since the oxophilic metals titanium and especially zirconium and hafnium possess chemical features that are often not easily compatible with the typical reaction conditions usually applied when performing

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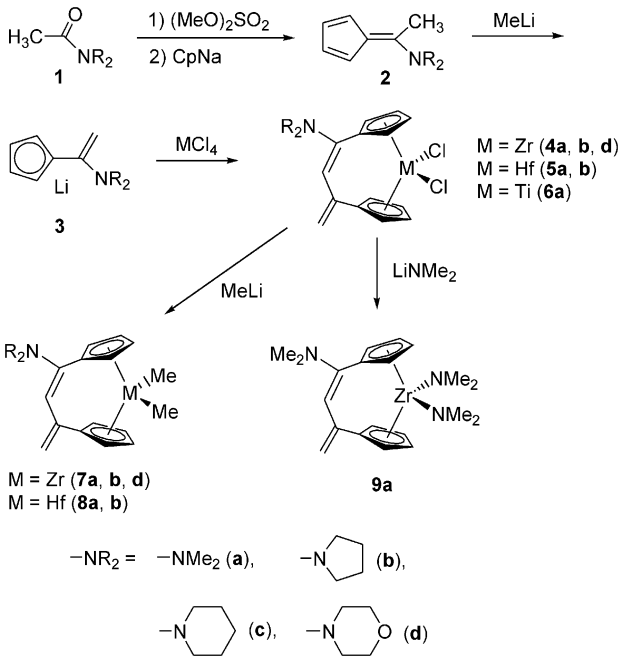
coupling reactions e.g. of the aldol condensation family. A short while ago we found that some such reactions can successfully being carried out at Group 4 bent metallocene frameworks when care is taken that the actual reaction conditions are adjusted to the specific features of these Group 4 metal compounds [5,6]. We here describe some details of carrying out carbon–carbon coupling reactions of the Mannich-type at suitably substituted zirconocene or hafnocene frameworks that are fully compatible with the typical properties of such sensitive organometallic educts and products.

In this way, interesting series of new *ansa*-metallocenes have become readily available. In addition, it has turned out that this methodology, originally developed to cope with the specific requirements of the sensitive Group 4 bent metallocenes has even been found to be a very useful addition to the synthetic methodology applied at the organic functional group chemistry of the ferrocenes [7].



Scheme 1.

2. Results and discussion

For this study we have chosen enamines as the functional groups at the Cp-ring systems. The enamino functionalities were in all cases introduced by means of a fulvene route. Following a general procedure described by Hafner et al. [8] a series of 6-amino-6-methyl fulvenes were prepared starting from the corresponding acetamide precursors. O-methylation was achieved by treatment with dimethylsulfate [9]. Subsequent treatment with cyclopentadienide then gave the respective amino-fulvenes **2a**–**d** (see Scheme 1). The amino-fulvenes are C–H acidic [10]. Deprotonation at the 6-methyl group was carried out by treatment with a suitable base (methyl lithium or LDA) to cleanly yield the enamino-substituted cyclopentadienides **3a**–**d**.

The reagents **3** were then reacted with zirconium tetrachloride in the following way: A suspension of **3a** in ether was cooled to −78 °C and then solid $ZrCl_4$ was added. After warming, the mixture was stirred for 12 h at room temperature. Workup including recrystallization from diethyl ether then gave an orange crystalline solid (56% isolated) which was not the bis(enamino-Cp)$ZrCl_2$ product, that might have been expected, but the condensation product **4a** [5]. Similarly, the reaction of the enamino-Cp anion equivalents **3b** and **d** with $ZrCl_4$ gave the unsaturated *ansa*-zirconocene dichlorides **4b** and **d** (69% and 22% isolated). Analogous treatment of **3a** or **3b** with $HfCl_4$ gave the *ansa*-hafnocene dichlorides **5a** and **5b**, respectively, and the *ansa*-titanocene dichloride **6a** was obtained from the reaction of the (1-dimethylamino-ethenyl)cyclopentadienide **3a** with $TiCl_4$ under similar conditions.

The unsaturated *ansa*-metallocenes undergo salt metathesis reactions at the central $[M]Cl_2$ unit without affecting the backbone. This treatment of the *ansa*-zirconocene- or -hafnocene dichlorides (**4**, **5**) with methyl lithium gave the corresponding $[Zr]Me_2$ and $[Hf]Me_2$ complexes (**7**, **8**, see Scheme 1). Treatment of complex **4a** (M = Zr, $NR_2 = NMe_2$) with two molar equivalents of $LiNMe_2$ cleanly gave the bis(dimethylamido) *ansa*-zirconocene complex **9a** (see Scheme 1).

The *ansa*-metallocene complexes show very characteristic NMR spectra. A typical example is the zirconium complex **7a**. It exhibits four ^{13}C NMR signals of the four pairs of C_5H_4 methine (*C*H) carbon centers at δ 116.2, 116.1, 109.8 and 107.5 (corresponding *ipso*-carbon resonances at δ 140.1 and δ 118.6). The carbon NMR signals of the 1-(dimethylamino)-1,4-butadien-1,3-diyl bridge occur at δ 148.0 (*C*NMe_2), 103.7 (CH), 128.3 (C) and 107.7 (=CH_2). The corresponding ^1H NMR signals of the *ansa*-bridge of complex **7a** were located at δ 5.32 (=C*H*–) and δ 4.85/4.65 (=CH_2), respectively. Complex **7a** features only a single NMe_2 ^1H NMR resonance at δ 2.58 [6H] (^{13}C: δ 41.4) and also only a single $ZrMe_2$ signal (δ −0.37, s, 6H) [^{13}C: δ 29.1]. Thus, in solution complex **7a** behaves as if it were C_s-symmetric (as do the other complexes in this series). However, this is probably due to a rapid conformational equilibration of a non-mirror symmetric structure in a degenerate double-minimum situation.

Evidence for this interpretation originates from the results of the X-ray crystal structure analysis of three representative examples of this class of unsaturated C_3-bridged *ansa*-Group 4 metallocenes. Single crystals suitable for the X-diffraction study were obtained from

the complexes **4a** (M = Zr), **5a** (M = Hf) and **9a** (M = Zr).

The structure of compound **9a** shall be discussed as a typical example. The dienamino-bridge of **9a** is planar. It shows the typical bond alternation that is expected for such a system [C6–C7: 1.333(3) Å, C6–C8: 1.464(3) Å, C8–C9: 1.345(3) Å, C9–N10: 1.411(3) Å]. The enamino-nitrogen center is trigonal planar [angles C9–N10–C12: 116.0(2)°, C9–N10–C11: 114.9(2)°, C11–N10–C12: 111.6(2)°]. The sum of the bonding angles at N10 amounts to 342.5°.

Both the bent metallocene frame and the aminodiendiyl bridge are not strained. The Zr–C(Cp) bond lengths are within a narrow range (2.514(2)–2.637(2) Å), and the bond angles at the bridge are in the normal range [C5–C6–C8: 119.2(2)°, C6–C8–C9: 125.4(2)°, C8–C9–C13: 123.5(2)°]. This situation is achieved by an internal rotation of the *ansa*-metallocene framework from C_s-symmetrical to a chiral "twist" conformation (see Fig. 1). This conformation may be characterized by the angle between the C7–C6–C8–C9–N10 plane and the "σ-ligand plane at zirconium" (i.e., the N18–Zr–N21 plane) which amounts to 45.7°.

The complexes **4a** (Zr) and **5a** (Hf) (NR_2 = NMe_2) are both very similar (see Fig. 2). The structures of these complexes seem to be determined more by the rigid framework of the ligand system than by the metal. As expected, the hafnium complex (**5a**) features slightly shorter M–C(Cp) bond lengths [11] (see Fig. 2 and Table 1).

We introduced a stereochemical component into the system by using the 3-methyl- or 3-*tert*-butylenamino-Cp lithium reagents **10a** and **10b**, respectively, for our synthesis. Treatment of **10a** with $ZrCl_4$ analogously as described for the previous cases (see above) resulted in Mannich-CC-coupling and the formation of the *ansa*-metallocene dichloride complex **11a**. This system was obtained as a mixture of two diastereoisomers, *meso*-**11a** and *rac*-**11a** in a close to 1:1 mixture (total yield isolated: 44%). The reaction of the *tert*-butyl-substituted reagent **10b** with $ZrCl_4$ gave a 1:1 mixture of the closely related *meso*-**11b** and *rac*-**11b** isomers (48% isolated, see Scheme 2). The analogous reactions of **10a** and **10b** were also carried out with $HfCl_4$ to yield similar mixtures of the corresponding *ansa*-hafnocenes *meso*-**12**(**a**,**b**) and *rac*-**12**(**a**,**b**).

Several of the *ansa*-metallocene complexes were employed as components for the generation of active homogeneous Ziegler-Natta catalysts [12]. We had previously described some of their typical features in ethene polymerization as well as in copolymerization reactions. The systems *meso*-/*rac*-**11a**/MAO were also employed in propene polymerization [5]. Propene polymerization of the *meso*-/*rac*-**11a**/methylalumoxane catalyst in toluene at room temperature (2 bar propene) gave a mixture of polypropylene products that was separated by solvent extraction. The combined pentane to heptane soluble fractions (ca. 60% of the polymer) was close to atactic (ca. 30% mmmm) [13], but had a rather high molecular weight ($M_\eta \approx 420.000$), whereas the remaining heptane insoluble fraction showed a much higher isotacticity (ca. 70% mmmm) [14], but had a lower molecular weight ($M_\eta \approx 82.000$). The overall catalyst activity amounted to ca. 220 g of polypropylene/mmol[cat] · bar (propene) · h.

Since it was likely that the non-bridged bis(enamino-Cp)MCl_2 complexes (**13**) were the essential precursors for the metallocene Mannich coupling reaction we tried to prepare and isolate them. This was successful when we treated the morpholino-ethenyl-CpLi reagent **3d** with $ZrCl_4 \cdot 2$ THF in ether at 0 °C. Workup after 1 h reaction time at this temperature led us isolate the (morpholino-ethenyl-Cp)$_2ZrCl_2$ product (**13d**) as a solid in 44% yield. In a similar reaction the bis(piperidino-ethenyl-Cp)$ZrCl_2$ product (**13c**) was obtained and isolated as a yellow solid (50% yield).

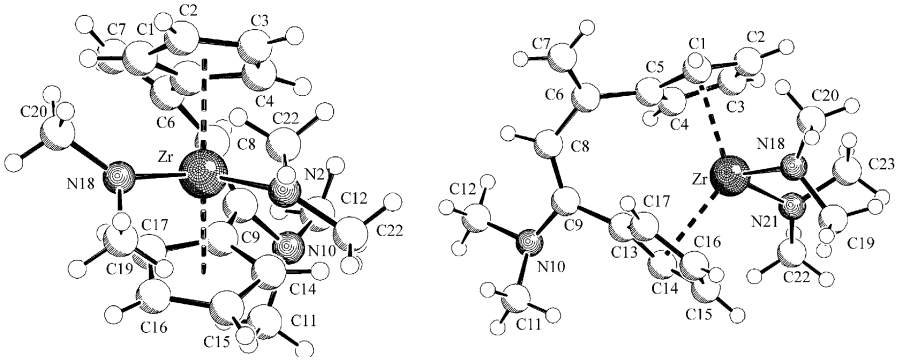


Fig. 1. Two projections of the molecular structure of complex **9a**. Selected bond lengths (Å) and angles (°): C5–C6 1.476(3), C6–C7 1.333(3), C6–C8 1.464(3), C8–C9 1.345(3), C9–C13 1.478(3), C9–N10 1.411(3), N10–C11 1.458(3), N10–C12 1.453(3), Zr–N18 2.087(2), Zr–N21 2.087(2), N18–C19 1.463(3), N18–C20 1.448(3), N21–C22 1.451(3), N21–C23 1.459(3); C5–C6–C8 119.2(2), C6–C8–C9 125.4(2), C8–C9–C13 123.5(2), C8–C9–N10 123.2(2), C9–N10–C11 114.9(2), C9–N10–C12 116.0(2), C11–N10–C12 111.6(2), N18–Zr–N21 94.4(1), Zr–N18–C19 115.7(1), Zr–N18–C20 136.4(2), C19–N18–C20 107.9(2), Zr–N21–C22 134.5(2), Zr–N21–C23 116.8(2), C22–N21–C23 108.3(2).

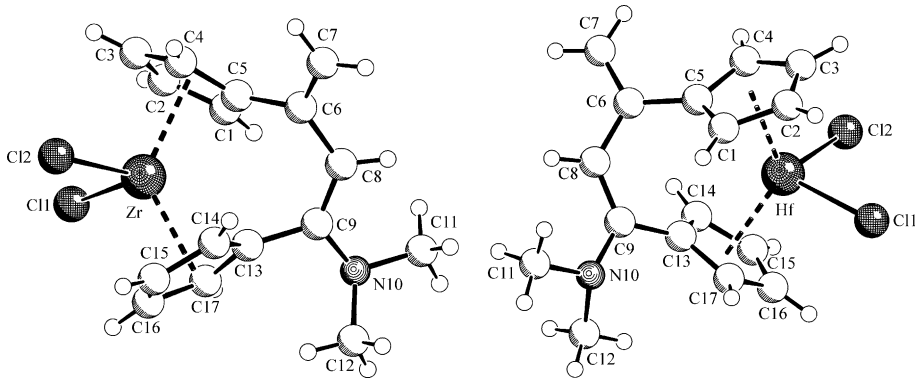
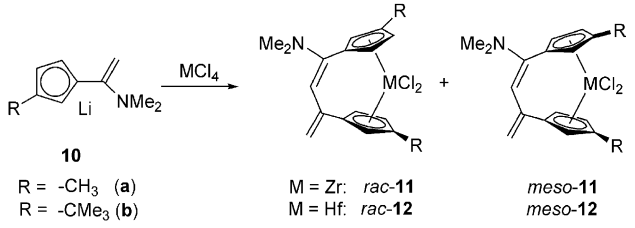


Fig. 2. Projections of the molecular structures of complexes **4a** (M = Zr, left) and **5a** (M = Hf, right). Selected bond lengths (Å) and angles (°) of **4a**: C5–C6 1.490(5), C6–C7 1.333(6), C6–C8 1.464(6), C8–C9 1.353(6), C9–C13 1.481(5), C9–N10 1.399(5), N10–C11 1.455(5), N10–C12 1.468(6), Zr–Cl1 2.432(1), Zr–Cl2 2.441(1); C5–C6–C8 117.5(4), C6–C8–C9 125.1(3), C8–C9–C13 123.1(3), C8–C9–N10 122.9(3), C9–N10–C11 117.2(4), C9–N10–C12 118.5 (3), C11–N10–C12 112.4(3), Cl1–Zr–Cl2 97.4(1); of **5a** C5–C6 1.482(7), C6–C7 1.337(7), C6–C8 1.457(7), C8–C9 1.360(7), C9–C13 1.484(6), C9–N10 1.391(6), N10–C11 1.457(6), N10–C12 1.461(7), Hf–Cl1 2.410(1), Hf–Cl2 2.415(1); C5–C6–C8 117.3(4), C6–C8–C9 125.2(4), C8–C9–C13 122.7(4), C8–C9–N10 122.7(4), C9–N10–C11 117.6(4), C9–N10–C12 118.7 (4), C11–N10–C12 112.3(4), Cl1–Hf–Cl2 96.3(1).

Table 1
A comparison of typical bonding parameters of the complexes **4a**, **5a** and **9a**

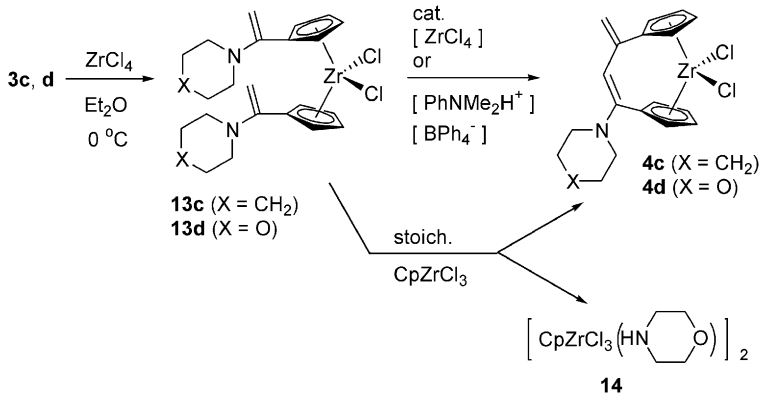
	C5–C6	C6–C7	C6–C8	C8–C9	C9–C13	C9–N10	D1–M	D2–M
4a	1.490(5)	1.333(6)	1.464(6)	1.353(6)	1.481(5)	1.399(5)	2.192	2.206
5a	1.482(7)	1.337(7)	1.457(7)	1.360(7)	1.484(6)	1.391(6)	2.176	2.183
9a	1.476(3)	1.333(3)	1.464(3)	1.345(3)	1.478(3)	1.411(3)	2.253	2.281
	C5–C6–C8	C6–C8–C9	C8–C9–C13	C8–C9–N10	D1–M–D2			
4a	117.5(4)	125.1(3)	123.1(3)	122.9(3)	128.1			
5a	117.3(4)	125.2(4)	122.7(4)	122.7(4)	128.4			
9a	119.2(2)	125.4(2)	123.5(2)	123.2(2)	123.9			



Scheme 2.

In solution, complex **13d** features the NMR spectra of a conformationally equilibrating non-bridged bent metallocene. It shows two ^{1}H NMR signals of the η^5-C_5H_4 moieties at δ 6.76 and δ 6.03 (in d_6-benzene, each multiplet representing 4H) and the $=CH_2$ hydrogen resonances at δ 4.81 and δ 4.15 [2H each, ^{13}C signals at δ 150.3 and 95.5 ($C{=}CH_2$), δ 122.2 (*ipso*-C), 118.8, 116.5 (C_5H_4)].

The (piperidino-ethenyl-Cp)$_2$ZrCl$_2$ system (**13c**) features similar NMR spectra [^{1}H: δ 4.85/4.24; ^{13}C: δ 151.5/95.2 ($C{=}CH_2$) in d_6-benzene]. This complex was treated with 3 mol% of $ZrCl_4$ in ether for 12 h at ambient temperature to cleanly yield the Mannich condensation product **4c** [84% isolated, ^{1}H NMR: δ 5.43 (1H, 8-H), δ 4.82/4.77 (2H, $=CH_2$)]. The morpholino-substituted system **13d** was employed in more systematic short series of investigations that revealed that the Mannich condensation reaction of this (enamino-Cp)$_2$ZrCl$_2$ complex was generally catalyzed by suitable Lewis acids or by Brønsted acids (see Scheme 3). Thus, treatment of **13d** with 30 mol% of $ZrCl_4$ in dichloromethane (introduced as the bis-THF adduct) completely converted this functionalized open bent metallocene at room temperature to the C_3-bridged unsaturated *ansa*-metallocene product **4d** within 24 h. Brønsted catalysis seems even more effective: when **13d** was mixed with 30 mol% of $[PhNMe_2H]^+[BPh_4]^-$ in CD_2Cl_2 at ambient temperature, ca. 17% conversion to **4d** was found when the mixture was monitored by ^{1}H NMR. Control by ^{1}H NMR after 24 h also revealed complete conversion to **4d**. Under the same conditions a solution of **13d** in CD_2Cl_2 was found unchanged even after 7 d. The weak Lewis acid $CpZrCl_3$ [15] also catalyzes the **13d**–**4d** condensation reaction, albeit at much lower overall reaction rates. When we treated the starting material **13d** with one molar equivalent of $CpZrCl_3$ in dichloromethane at room temperature, only ca. 5% conversion was



Scheme 3.

observed after 24 h. It required 7 d at ambient temperature to eventually achieve a near to quantitative conversion to **4d**. According to the stoichiometry of the reaction cleavage of one equivalent of the amine must be assumed in all these cases. For the example of the **13d**–**4d** conversion mediated by a stoichiometric quantity of $CpZrCl_3$ we actually isolated a small quantity of the $[CpZrCl_3 \cdot (morpholine)]$ adduct as a chloride-bridged dimer (**14**) [16] that was identified by an X-ray crystal structure analysis (see Fig. 3).

Our observations indicate that we here have a Mannich-type carbon–carbon coupling reaction [17] take place under these conditions at the Group 4 bent metallocene framework. A schematic reaction course is depicted in Scheme 4. The reaction sequence is probably

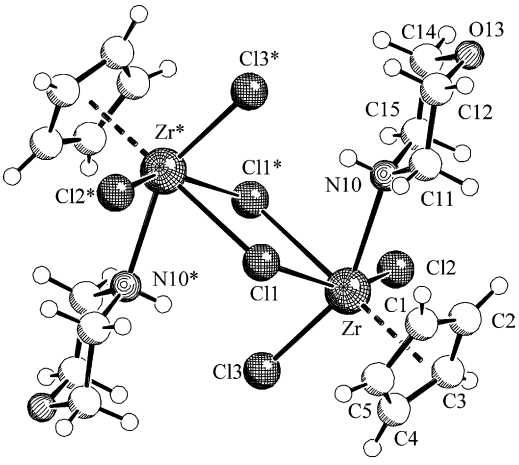
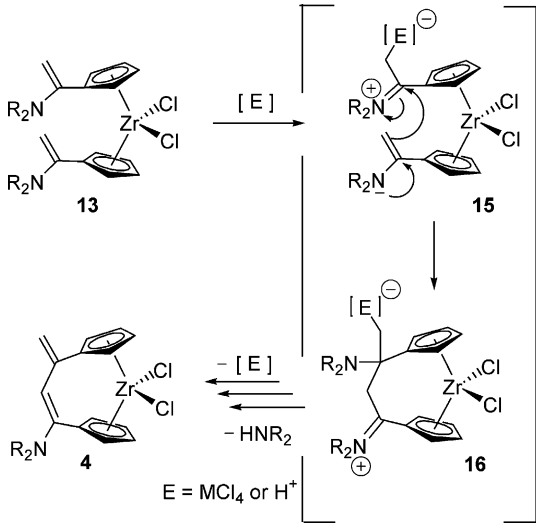


Fig. 3. A view of the molecular structure of the $[CpZrCl_3(morpholine)]$ dimer **14**. Selected bond lengths (Å) and angles (°): Zr–N10 2.446(2), N10–C11 1.490(4), N10–C15 1.488(3), C11–C12 1.515(4), C12–O13 1.419(4), O13–C14 1.428(4), C14–C15 1.507(4), Zr–Cl1 2.579(1), Zr–Cl1* 2.824(1), Zr–Cl2 2.449(1), Zr–Cl3 2.474(1); Zr–N10–C11 119.9(2), Zr–N10–C15 117.28(2), C15–N10–C11 108.0(2), N10–C11–C12 113.2(2), C11–C12–O13 111.7(3), C12–O13–C14 108.3(2), O13–C14–C15 111.2(3), C14–C15–N10 112.0(3), Cl1–Zr–Cl1* 72.19(2), Cl1–Zr–Cl2 150.34(3), Cl1*–Zr–Cl2 78.66(2), Cl1–Zr–Cl3 88.20(2), Cl1*–Cl3 78.12(2), Cl2–Zr–Cl3 91.15(3), Cl1–Zr–N10 79.76(6), Cl1*–Zr–N10 73.35(6), Cl2–Zr–N10 86.89(6), Cl3–Zr–N10 151.24(6).



Scheme 4.

initiated by addition of the Lewis acid catalyst to the nucleophilic β-carbon atom of an enamino substituent to generate a dipolar iminium-type intermediate (**15a**). Alternatively, protonation of the enamine would directly give an iminium-ion intermediate (**15b**). The activated iminium carbon center of **15** is then intramolecularly attacked by the adjacent enamine nucleophile, that is attached at the other Cp-ring, to form a new carbon–carbon linkage (**16**). Subsequent amine elimination and cleavage of the metal Lewis acid (or deprotonation, respectively) then would directly lead to the observed *ansa*-metallocene products (e.g., **4**) and close the catalytic cycle (see Scheme 4). The transformations described in this article probably represent the first examples of efficiently catalyzed aldol-type carbon–carbon coupling reactions that were carried out in the coordination sphere of a series of sensitive Group 4 metallocene complexes to yield the respective unsaturated functionalized C_3-bridged *ansa*-metallocene dihalide products in a simple and straightforward way.

We wanted to learn more about the structural and chemical features of the bis(enamino-Cp)zirconocenes as a class of compounds. For that purpose we synthesized the substituted (enamino-Cp)zirconium complexes **13e** and **13f** and investigated their structures in the solid state. Both the ligand systems were prepared by means of the above mentioned fulvene route. Treatment of the [*Z*-(2-phenylethenyl)Cp]lithium reagent **3e** with zirconium tetrachloride in ether gave *Z*-**13e** (52% isolated). It is characterized by a pair of ^{1}H NMR C_5H_4 signals at δ 6.66 and 6.10 [in d_6-benzene, ^{13}C NMR signals at δ 119.0, 117.0 and 124.3 (*ipso*-C)] as well as a single ^{1}H NMR resonance of the alkenyl substituent hydrogen (7-H) at δ 6.10 [^{13}C: δ 113.8 (C7), δ 142.9 (C6)]. Photolysis of *Z*-**13e** (3 h, HPK 125, Pyrex filter) in d_6-benzene resulted in a complete ($\geqslant$99%) conversion to the *E*-**13e** isomer under photostationary conditions [18]. Complex *E*-**13e** shows typically different ^{1}H and ^{13}C NMR spectra [^{1}H: δ 6.12, 5.87 (^{13}C: δ 115.9, 115.1, 128.2, C_5H_4), δ 6.01 (^{13}C: 116.2, C7), and δ 116.1 (C6)].

Single crystals were obtained from complex *Z*-**13e** that were suited for an X-ray crystal structure analysis.

The X-ray crystal structure analysis of *Z*-**13e** shows a pseudotetrahedral coordination geometry of the zirconium center with typical parameter Zr–Cl = 2.435(1) Å, Cp(centroid)–Zr = 2.207 Å and angles Cp(centroid)–Zr–Cp(centroid) = 127.9°, Cl–Zr–Cp(centroid) = 107.5°. The complex is C_2-symmetric. The enamino substituents are arranged close to coplanar with their adjacent Cp rings (dihedral angles C1–C5–C6–C7 = −24.7(3)° and C1–C5–C6–N = 160.2(2)°). The C5–C6 bond is rather long at 1.487(3) Å. The C6–N bond is short (1.398(3) Å) and the length of the C6–C7 double bond was found at typical 1.343(3) Å. The phenyl substituent at the terminal enamino carbon atom C7 is rotated markedly from the enamino plane (C6–C7–C10–C11: −38.3(4)°).

The overall conformation of the substituted bent metallocene complex [19] *Z*-**13e** is such that the bulky –C(NMe$_2$)=CH–Ph substituents are both oriented toward the hind lateral sector of the bent metallocene wedge (“4-o’clock and 8-o’clock positions”) with the phenyl rings protruding to opposite metallocene sides. Both the –NMe$_2$ groups point C_2-symmetrically toward the narrow metallocene backside (see Fig. 4).

Complex **13f** was prepared analogously (see Scheme 5). The X-ray crystal structure analysis (single crystals from dichloromethane) again shows a C_2-symmetric structure of this di-substituted Group 4 metallocene in the solid state. However, complex **13f** features a metallocene conformation that is distinctly different from that of *Z*-**13e**. In **13f** both bulky 1-aminoethenyl groups are oriented toward the open front side of the bent metallocene wedge. The torsional angle between the C5–C6 and C5*–C6* vectors amount to ca. 20° (compared to ca. 250° for *Z*-**13e**). The enamino substituent planes in **13f** are again close to coplanar with their

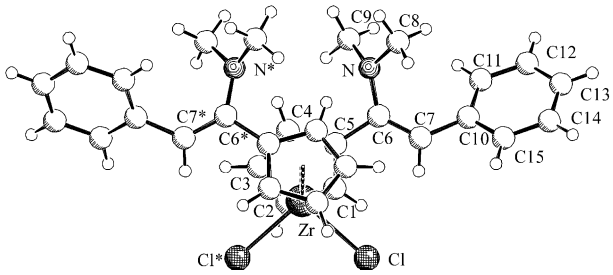
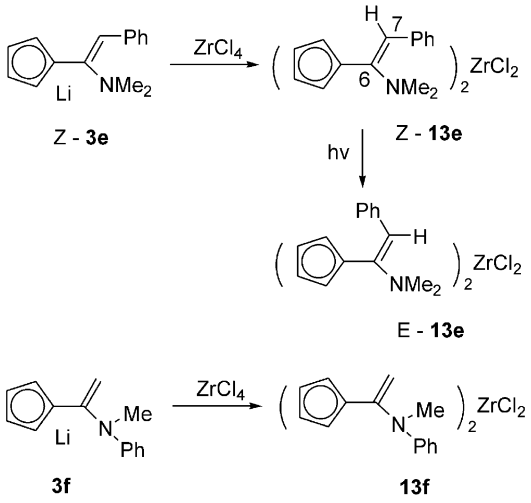


Fig. 4. A projection of the molecular structure of complex *Z*-**13e**, showing the conformational arrangement of the pair of enamino substituents at the bent metallocene wedge. Selected bond lengths (Å) and angles (°): C5–C6 1.487(3), C6–C7 1.343(3), C7–C10 1.473(3), C6–N 1.398(3), N–C8 1.450(3), N–C9 1.449(3), Zr–Cl 2.435(1); C5–C6–C7 119.8(2), C5–C6–N 114.0(2), C6–C7–C10 129.1(2), C6–N–C8 120.4(2), C6–N–C9 119.3(2), C8–N–C9 114.5(2), Cl–Zr–Cl* 97.2(1).



Scheme 5.

adjacent Cp rings (θC1–C5–C6–C7: 158.2(5), C1–C5–C6–N: −19.1(7)°). The C6–C7 bond length amounts to 1.325(8) Å, the C6–N distance is 1.416(6) Å (see Fig. 5).

Very electrophilic boranes have found extensive use in organometallic chemistry and catalysis. Especially, the C_6F_5-substituted examples have been of great value in that sense [20,21]. In the course of this study we have

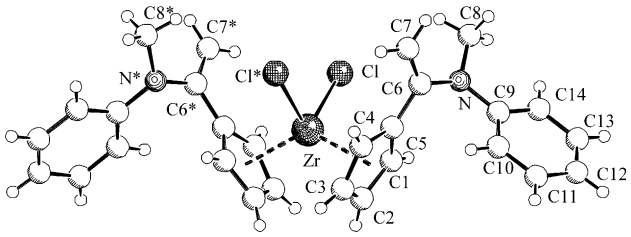


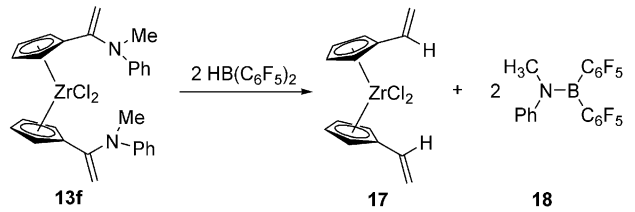
Fig. 5. A view of the molecular structure of complex **13f**. Selected bond lengths (Å) and angles (°): C5–C6 1.465(7), C6–C7 1.325(8), C6–N 1.416(6), N–C8 1.443(7), N–C9 1.411(6), Zr–Cl 2.457(1); C5–C6–C7 121.9(5), C5–C6–N 115.9(4), C7–C6–N 122.1(5), C6–N–C8 116.9(5), C6–N–C9 119.2(4), C8–N–C9 118.0(4), Cl–Zr–Cl* 98.8(1).

briefly investigated whether the strongly electrophilic borane $HB(C_6F_5)_2$ [22] was reacting with the enamino-substituted bent metallocene systems **13** primarily as a Lewis acid to induce the intramolecular Mannich coupling reaction or predominantly exhibit its H[B]-functionality. Complex **13f** was treated with a stoichiometric quantity of $HB(C_6F_5)_2$ in toluene for 12 h at room temperature. This reaction cleanly resulted in a desamination reaction to yield the known organometallic product $(vinyl\text{-}C_5H_4)_2ZrCl_2$ (**17**) [23] [^{1}H NMR: δ 6.32 (1H), 6.02/5.80 (2H, –CH=CH_2)] and the corresponding aminoborane **18** (see Scheme 6).

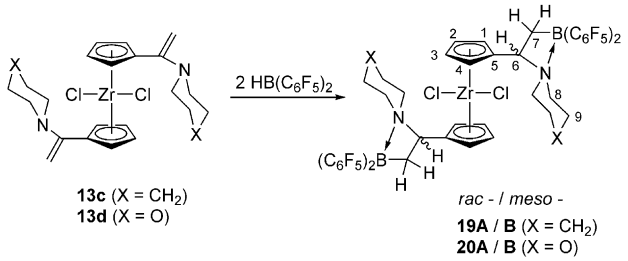
Desamination reactions of organic enamines is commonly observed upon treatment with boranes. Such reactions had been shown to proceed by means of regioselective hydroboration to yield a β-amino alkylborane, which is often stable in unpolar solvent but is rapidly cleaved to the products upon addition of e.g. methanol [24].

We were able to show for two examples, that a similar reaction course was followed in the case of the organometallic enamines **13**. Treatment of the bis(piperidinoethenyl-Cp)zirconium dichloride complex **13c** with two molar equivalents of $HB(C_6F_5)_2$ in toluene at room temperature (48 h) gave the addition product **19** (81% isolated). The borane was regioselectively added to the C=C double bond of the enamino substitutents. This created a pair of chiral centers (at the α-carbon atoms of the substituents), and consequently a mixture of two diastereoisomers, *meso*-**19** and *rac*-**19**, was formed. From the spectra we could not positively identify which of the components of the 2:3 mixture was *meso*-**19** and which was *rac*-**19**.

There is indication that the nucleophilic amino-nitrogen atoms in the complexes **19** were coordinated to their electrophilic borane neighbors, to form a "azaboretidine" moiety. Such C_2BN-four membered ring structures had previously been characterized by X-ray diffraction in remotely related functionalized zirconocene systems [25]. The internal adduct formation in the systems **19** is strongly indicated by their typical ^{11}B NMR resonance (δ 2.76) and the occurrence of diastereomeric C_6F_5 pairs of substituents (^{19}F NMR: δ −162.4/−162.3 (*m*-), −156.2/−154.7 (*p*-), −128.3/−127.3 (*o*-F); the ^{11}B and ^{19}F NMR resonances were not differentiated for the *rac*- and *meso*-**19** isomers). The small separation



Scheme 6.



Scheme 7.

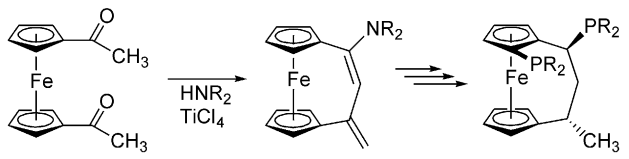
of the *m*-F and *p*-F resonances is an additional indication of the presence of four-coordinated boron in the complexes **19** (see Scheme 7).

The azaboretidine structure in **19** makes the α- and β-carbon atoms of the piperidine ring diastereotopic. This is observed for each of the isomers [**19A**: δ 56.9 (C8), 47.7 (C12); **19B**: δ 56.9 (C8), 47.4 (C12), δ 22.1 (C9), 21.7 (C11), δ 21.2 (C10)]. The reaction of the morpholino-ethenyl-substituted metallocene **13d** with $HB(C_6F_5)_2$ takes a similar course. A *rac*-/*meso*-mixture of the addition products **20** (**20A**/**20B** = 3:4) is formed (isolated in a combined yield of 65%). The complexes **20** again exhibit the typical spectroscopic features of the internal four-membered amine/borane adducts [^{11}B NMR: δ 2.52; ^{19}F NMR: δ −162.1/−160.5, δ −154.7/−151.3; δ −127.7/−122.9]. Again, typical diastereotopic splitting of the α- and β-carbon (and hydrogen) NMR resonances of the six-membered heterocycle is observed [^{13}C NMR, **20A**: δ 68.2 (C9)/62.1 (C10), δ 55.6 (C8)/48.9 (C11); **20B**: δ 67.7 (C9)/61.8 (C10), δ 55.6 (C8)/50.3 (C11)]. The complexes **19** and **20** are stable in toluene solution, but they are rapidly cleaved when dissolved in, e.g., chloroform to yield **17** and the respective aminoborane products.

3. Some conclusions

Our study shows that a well defined and selective functional group chemistry can be devised and carried out even at the frameworks of sensitive Group 4 bent metallocene complexes when the overall reaction conditions are adjusted to take account of the specific features of such organometallic systems. We have shown that even reactions out of the greater family of the aldol-type condensation reactions – here the Mannich reaction – can be carried out successfully at the titanocene, zirconocene, and hafnocene frameworks under easily adjustable conditions. This has opened up a useful entry to the synthesis of a variety of novel *ansa*-metallocene systems.

Moreover, this type of an intramolecular Mannich-type coupling is so easy to perform that is has even been found very useful in preparative ferrocene chemistry, a synthetic area where a great variety of functional group



Scheme 8.

interconversion has been established. However, our metallocene Mannich coupling protocol has been found to be a very useful entry to the synthesis of a number of [3] ferrocenophane systems that were converted to optically active chelate ligands for asymmetric catalysis (see Scheme 8) [7,26].

4. Experimental

Reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information including a compilation of instruments used for physical and spectroscopic characterization, see Hüerländer et al. [2a] and [2c]. Most fulvenes used in this study were prepared analogously to literature procedures. [27] The borane $HB(C_6F_5)_2$ was prepared as described by Piers and co-workers [22]. Polymerization reactions and polymer characterization was carried out analogously as previously described [5,14e]. A preliminary communication about some of this work was published a while ago [5]. Most NMR assignments made in the course of this study were secured by series of 2D NMR measurements, and in some cases also by NOE NMR experiments [28].

Data sets were collected with Enraf-Nonius CAD4, Nonius MACH3, and KappaCCD diffractometers, the later one equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MOLEN (K. Fair, Enraf-Nonius B.V., 1990) and DENZO-SMN (Z. Otwinowski, W. Minor, Meth. Enzymol. 276 (1997) 307), absorption correction for CCD data SORTAV (R.H. Blessing, Acta Crystallogr. A51 (1995) 33; R.H. Blessing, J. Appl. Crystallogr. 30 (1997) 421), structure solution SHELXS-97 (G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

4.1. Synthesis of 6-methyl-6-N-piperidino-fulvene (2c)

At 50 °C freshly distilled dimethylsulfate (15.8 ml, 21.0 g, 167 mmol) was added dropwise with stirring to N-acetylpiperidine (**1c**, 21.2 g, 167 mmol). The mixture was then stirred for 2 h at 70 °C. This solution was added at −20 °C to a THF solution of 12.0 g (167 mmol) of lithium cyclopentadienide at such a rate that the internal temperature of the reaction mixture did not rise above −5 °C. After 12 h stirring the mixture was evaporated in vacuo to dryness and the residue taken up in 200 ml of ether. The formed lithium methylsulfate was removed by filtration and the solvent removed from the filtrate in vacuo to yield 9.23 g (32%) of **2c** of single crystal quality, m.p. 83 °C. HRMS, calcd. for $C_{12}H_{17}N$: 175.13609, found 175.13666. ^{1}H NMR (benzene-d_6, 200.13 MHz): δ = 6.87–6.83 (m, 1H, Cp–H), 6.81–6.77 (m, 1H, Cp–H), 6.75–6.72 (m, 1H, Cp–H), 6.67–6.64 (m, 1H, Cp–H), 3.15–3.10 (m, 4H, 8-H), 1.89 (s, 3H, 7-H), 1.13–1.05 (m, 6H, 9-H/10-H) ppm. ^{13}C NMR (benzene-d_6, 50.32 MHz): δ = 156.1 (C-6), 123.4, 121.6, 120.6, 119.7, 116.9 (C-1/C-2/C-3/C-4 and C-5), 51.33 (C-8), 26.3 (C-9), 24.3 (C-10), 20.5 (C-7) ppm. IR (KBr): $\tilde{\nu}$ = 3082 (m), 3057 (m), 2935 (s), 2921 (s), 1550 (vs), 1441 (s), 1371 (s), 1351(vs), 1265 (s), 1049 (s), 1022 (s), 975 (s), 895 (s), 734 (s), 646 (s) cm^{-1}.

4.2. X-ray crystal structure analysis of the fulvene 2c

Formula $C_{12}H_{17}N$, M = 175.27, yellow crystal 0.45 × 0.25 × 0.25 mm, a = 7.854(1) Å, b = 10.032(2) Å, c = 13.245(3) Å, β = 99.76(2)°, V = 1028.5(3) Å^3, ρ_{calc} = 1.132 g cm^{-3}, μ = 4.91 cm^{-1}, empirical absorption correction via ψ scan data ($0.809 \leqslant T \leqslant 0.887$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 1936 reflections collected ($+h$, $-k$, l), $[(\sin\theta)/\lambda]$ = 0.62 Å^{-1}, 1800 independent (R_{int} = 0.019) and 1365 observed reflections [$I \geqslant 2\sigma(I)$], 120 refined parameters, R = 0.037, wR^2 = 0.100, maximum residual electron density 0.14 (−0.10) e Å^{-3}, hydrogens calculated and refined as riding atoms (see Fig. 6).

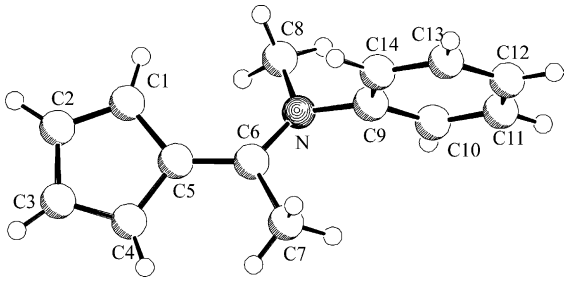


Fig. 6. Molecular structure of the fulvene **2c**. Selected bond lengths (Å) and angles (°): C5–C6 1.396(2), C6–C7 1.506(2), C6–N 1.341(2), N–C8 1.467(2), N–C12 1.465(2); C5–C6–C7 119.3(1), C5–C6–N 124.5(1), C7–C6–N 116.2(1), C6–N–C8 124.7(1), C6–N–C12 123.9(1), C8–N–C12 111.3(1).

4.3. X-ray crystal structure analysis of 6-methyl-6-N-methylanilino-fulvene **2f**

The fulvene **2f** was prepared as described in the literature. Single crystals were obtained from dichloromethane.

Formula $C_{14}H_{15}N$, $M = 197.27$, yellow crystal $0.30 \times 0.20 \times 0.10$ mm, $a = 8.740(1)$ Å, $b = 18.268(2)$ Å, $c = 7.256(3)$ Å, $\beta = 103.14(2)$ Å, $V = 1128.2(4)$ Å^3, $\rho_{calc} = 1.161$ g cm^{-3}, $\mu = 0.67$ cm^{-1}, no absorption correction ($0.980 \leqslant T \leqslant 0.993$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 2070 reflections collected (h, $+k$, $+l$), [$(\sin\theta)/\lambda$] = 0.62Å^{-1}, 1910 independent ($R_{int} = 0.055$) and 846 observed reflections [$I \geqslant 2\sigma(I)$], 138 refined parameters, $R = 0.049$, $wR^2 = 0.101$, maximum residual electron density 0.17 (−0.20) e Å^{-3}, hydrogens calculated and refined as riding atoms (see Fig. 7).

4.4. Preparation of the lithium(dialkylaminoethenyl)cyclopentadienide reagents **3**. General procedure

A suspension of ca. 40 mmol of the respective 6-dialkylamino-6-alkylfulvene (**2**) in 80 ml of THF was cooled to −78 °C. A solution of ca. 40 mmol of methyl lithium in ether was added dropwise with stirring. Methane was evolved. The mixture was slowly warmed to room temperature and stirred for a total of 12 h. Solvent was removed from the clear solution in vacuo. The residue was solidified by treatment with pentane for 2 h. The solid was allowed to precipitate and the pentane phase decanted off. The remaining solid was dried in vacuo to yield the respective substituted lithium cyclopentadienide reagent **3** as an amorphous solid in good yield.

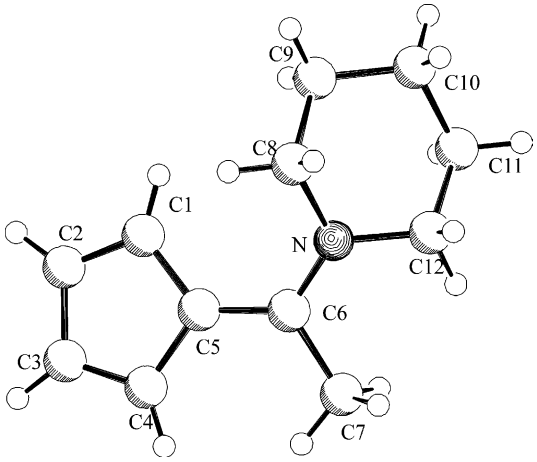


Fig. 7. Molecular structure of the fulvene **2f**. Selected bond lengths (Å) and angles (°): C5–C6 1.393(4), C6–C7 1.513(4), C6–N 1.342(4), N–C8 1.458(3), N–C9 1.444(4); C5–C6–C7 119.6(3), C5–C6–N 125.2(3), C7–C6–N 115.1(3), C6–N–C8 123.9(3), C6–N–C9 120.6(3), C8–N–C9 115.2(2).

4.4.1. Lithium(dimethylaminoethenyl)cyclopentadienide (**3a**)

Reaction of 6.0 g (44 mmol) of the fulvene **2a** with 27.7 ml (44 mmol) of a 1.6 M ethereal MeLi solution gave 5.6 g (89%) of **3a**. ^{1}H NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 200.13 MHz): $\delta = 6.28$–6.25 (m, 2H, Cp–H), 6.07–6.04 (m, 2H, Cp–H), 4.33 (d, 1H, 7-H, $^2J_{7'\text{-H}} = 1$ Hz), 3.91 (d, 1H, 7′-H, $^2J_{7\text{-H}} = 1$ Hz), 2.77 (s, 6H, 8-H) ppm. ^{13}C NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 50.32 MHz): $\delta = 157.6$ (C-6), 119.1 (C-5), 104.6 (C-2/C-3), 103.7 (C-1/C-4), 81.6 (C-7), 42.2 (C-8) ppm.

4.4.2. Lithium (N-pyrrolidinoethenyl)cyclopentadienide (**3b**)

The reaction of 5.0 g (31 mmol) of 6-methyl-6-pyrrolidinylfulvene (**2b**) with 19.5 ml (31 mmol) of a 1.6 M methyl lithium solution in ether gave 5.1 g (98%) of **3b**. ^{1}H NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 200.13 MHz): $\delta = 6.23$–6.20 (m, 2H, Cp–H), 6.02–5.99 (m, 2H, Cp–H), 4.04 (d, 1H, 7-H, $^2J_{7'\text{-H}} = 1$ Hz), 3.73 (d, 1H, 7′-H, $^2J_{7\text{-H}} = 1$ Hz), 3.53–3.47 (m, 4H, 8-H), 1.68–1.58 (m, 4H, 9-H) ppm. ^{13}C NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 50.32 MHz): $\delta = 154.3$ (C-6), 119.6 (C-5), 104.6, 103.3 (C–Cp), 77.8 (C-7), 49.9 (C-8), 25.3 (C-9) ppm.

4.4.3. Lithium(N-piperidinoethenyl)cyclopentadienide (**3c**)

The reaction of 6.0 g (34 mmol) of the fulvene **2c** with 21.3 ml (34 mmol) of a 1.6 M ethereal methyl lithium solution gave 6.0 g (97%) of **3c**. ^{1}H NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 200.13 MHz): $\delta = 6.26$–6.23 (m, 2H, Cp–H), 6.04–5.93 (m, 2H, Cp–H), 4.36 (s, 1H, 7-H), 3.93 (s, 1H, 7′-H), 3.08 (m, 4H, 8-H), 1.62–1.52 (m, 4H, 9-H), 1.47–1.41 (m, 2H, 10-H) ppm. ^{13}C NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 50.32 MHz): $\delta = 158.4$ (C-6), 119.5 (C-5), 104.2 (C-2/C-3), 103.9 (C-1/C-4), 81.8 (C-7), 51.9 (C-8), 27.1 (C-9), 25.6 (C-10) ppm.

4.4.4. Lithium(N-morpholinoethenyl)cyclopentadienide (**3d**)

The reaction of 6.9 g (42 mmol) of the aminofulvene **2d** with 24.0 ml (42 mmol) of a 1.75 M methyl lithium solution in diethyl ether yielded 7.1 g (92%) of **3d**. ^{1}H NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 200.13 MHz): $\delta = 6.14$–6.12 (m, 2H, Cp–H), 5.96–5.92 (m, 2H, Cp–H), 4.23 (d, $^2J_{7'\text{-H}} = 1$ Hz, 1H, 7-H), 3.79 (d, $^2J_{7\text{-H}} = 1$ Hz, 1H, 7′-H), 3.64–3.60 (m, 4H, 9-H), 3.0–2.96 (m, 4H, 8-H) ppm. ^{13}C NMR (benzene-d$_6$:tetrahydrofuran-d$_8$ 8:1, 50.32 MHz): $\delta = 153.9$ (C-6), 121.2

(C-5), 104.3, 104.0 (C–Cp), 81.4 (C-7), 67.6 (C-9), 51.5 (C-8) ppm.

4.4.5. Lithium(Z-1-dimethylamino-2-phenylethenyl)cyclopentadienide (3e)

The reaction of 3.0 g (14 mmol) of 6-benzyl-6-dimethylaminofulvene (**2e**) with 8.9 ml (14 mmol) of a 1.6 M methyl lithium solution in diethyl ether yielded 2.6 g (84%) of **3e** (*Z*:*E*-ratio, 10:1). ^{1}H NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 200.13 MHz) (*Z*): δ = 7.18–7.12 (m, 5H, 9-H/10-H/11-H), 6.25–6.22 (m, 2H, Cp–H), 6.05–6.03 (m, 2H, Cp–H), 5.64 (s, 1H, 7-H), 2.79 (s, 6H, 12-H) ppm. ^{1}H NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 200.13 MHz) (*E*): δ = 6.91–6.88 (m, 5H, 9-H/10-H/11-H), 6.04–6.02 (m, 2H, Cp–H), 6.00–5.98 (m, 2H, Cp–H), 5.46 (s, 1H, 7-H), 2.69 (s, 6H, 12-H) ppm. ^{13}C NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 200.13 MHz) (*Z*): δ = 152.5 (C-6), 142.7 (C-8), 127.9, 127.8, 122.1 (C-9/C-10/C-11), 120.0 (C-5), 106.7, 104.8 (C-1/C-2/C-3/C-4), 100.4 (C-7), 43.3 (C-12) ppm.

4.4.6. Lithium(N-methylanilinoethenyl)cyclopentadienide (3f)

The reaction of 7.0 g (36 mmol) of the fulvene **2f** with 22.2 ml (36 mmol) of a 1.6 M ethereal methyl lithium solution gave 7.1 g (98%) of **3f**. ^{1}H NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 200.13 MHz): δ = 7.05–6.87 (m, 3H, 10-H/11-H), 6.58–6.51 (m, 2H, 9-H), 6.01–5.98 (m, 2H, Cp–H), 5.88–5.81 (m 2H, Cp–H), 5.03 (ps, 1H, 7-H), 4.48 (ps, 1H, 7′-H), 3.14 (s, 3H, 8-H) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 50.32 MHz): δ = 154.1 (C-6), 151.4 (C-9), 128.82 (C–Ph), 117.5 (C-5), 116.6 (C–Ph), 115.5 (C–Ph), 104.9, 104.7 (C–Cp), 95.3 (C-7), 40.2 (C-8) ppm.

4.4.7. Lithium[1-(dimethylaminoethenyl)-3-methyl]cyclopentadienide (10a)

The reaction of 8.0 g (54 mmol) of 2-methyl-6-methyl-6-dimethylaminofulvene with 33.5 ml (54 mmol) of a 1.6 M methyl lithium solution in ether gave 7.9 g (95%) of **10a**. ^{1}H NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 200.13 MHz): δ = 6.15–6.10 (m, 1H, Cp–H), 6.08–6.06 (m, 1H, Cp–H), 5.95–5.84 (m, 1H, Cp–H), 4.25 (s, 1H, 7-H), 3.82 (ps, 1H, 7′-H), 2.77 (s, 6H, 8-H), 2.37 (s, 3H, 9-H) ppm. ^{13}C NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 50.32 MHz): δ = 158.2 (C-6), 117.8 (C-2), 114.2 (C-5), 104.9, 104.0, 103.5 (C-1/C-3/C-4), 80.6 (C-7), 42.2 (C-8), 15.6 (C-9) ppm.

4.4.8. Lithium[1-(dimethylaminoethenyl)-3-tert-butyl]-cyclopentadienide (10b)

The reaction of 5.0 g (26 mmol) of 2-*tert*-butyl-6-methyl-6-dimethylaminofulvene with 16.4 ml (26 mmol) of a 1.6 M ethereal methyl lithium solution yielded 5.2 g (99%) of **10b**. ^{1}H NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 200.13 MHz): δ = 6.12–6.09 (m, 2H, Cp–H), 5.90–5.87 (m, 1H, Cp–H), 4.37 (s, 1H, 7-H), 3.97 (ps, 1H, 7′-H), 2.77 (s, 6H, 8-H), 1.47 (s, 9H, 10-H) ppm. ^{13}C NMR (benzene-d_6:tetrahydrofuran-d_8 8:1, 50.32 MHz): δ = 158.7 (C-6), 131.4 (C-2), 116.8 (C-5), 102.7, 101.0, 100.6 (C-1/C-3/C-4), 80.3 (C-7), 42.4 (C-8), 33.8 (C-10), 31.7 (C-9) ppm.

4.5. Preparation of the bis[(1-dialkylaminoethenyl)cyclopentadienyl]zirconium dichloride complexes. General procedure

Solid zirconium tetrachloride (ca. 4 mmol) was added to a suspension of the respective lithium(1-dialkylaminoethenyl)cyclopentadienide (ca. 8 mmol) in ca. 100 ml of ether at 0 °C. The mixture was stirred for 1 h at 0 °C. The precipitate was removed by filtration through Cellite and washed with dichloromethane (2 × 15 ml). Solvent was removed from the combined filtrates and the residue washed with 30 ml of pentane. The metallocene complexes were usually obtained as orange colored solids.

4.5.1. Bis[(1-pyrrolidinoethenyl)cyclopentadienyl]zirconium dichloride (13b)

The reaction of 1.32 g (7.92 mmol) of **3b** with 923 mg $ZrCl_4$ (3.96 mmol) in 100 ml of ether at 0 °C yielded 1.07 g (56%) of complex **13b**. This product turned out to be so unstable that it was only characterized spectroscopically. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.68–6.66 (m, 2H, Cp–H), 6.19–6.16 (m, 2H, Cp–H), 4.29 (s, 1H, 7-H), 4.07 (s, 1H, 7-H′), 3.14–3.07 (m, 4H, 8-H), 2.03–1.88 (m, 4H, 9-H) ppm. IR (KBr): $\tilde{\nu}$ = 3072 (w), 2963 (m), 2868 (m), 1551 (vs), 1393 (s), 1380 (s), 1335 (vs), 1058 (m), 807 (m), 731 (s) cm^{-1}.

4.5.2. Bis[(1-piperidinoethenyl)cyclopentadienyl]zirconium dichloride (13c)

The reaction of 1.50 g (8.28 mmol) of **3c** with 841 mg $ZrCl_4$ (4.14 mmol) in 80 ml of ether at 0 °C gave 1.06 g (50%) of complex **13c**, m.p. 120 °C. Anal. Calc. for $C_{24}H_{32}N_2ZrCl_2$ (*M* = 510.65): C, 56.45; H, 6.52; N, 5.49. Found: C, 56.42; H, 6.68; N, 5.38%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.72 (m, 2H, Cp–H), 6.14 (m, 2H, Cp–H), 4.59 (s, 1H, 7-H), 4.33 (s, 1H, 7-H′), 2.88–2.83 (m, 4H, 8-H), 1.72 (m, 6H, 9-H/10-H) ppm. ^{13}C NMR (benzene-d_6, 50.32 MHz): δ = 151.3 (C-6), 120.9, 118.7, 116.6 (C-1/C-2/C-3/C-4/C-5), 95.2 (C-7), 51.3 (C-8), 26.5 (C-9), 24.6 (C-10) ppm. IR (KBr): $\tilde{\nu}$ = 3098 (w), 2937 (vs), 2846 (s), 2801 (s), 1594 (vs), 1550 (s), 1377 (s), 1273 (s), 1113(s), 1032 (s), 975 (s), 820 (vs), 807 (vs) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 232 nm (ε = 40,465), 350 nm (ε = 27,226).

*4.5.3. Bis[(1-morpholinoethenyl)cyclopentadienyl]zirconium dichloride (**13d**)*

The reaction of 3.54 g (13.80 mmol) of **3d** with 2.61 g (6.90 mmol) of $ZrCl_4 \cdot 2$ THF in 80 ml of ether at 0 °C gave 1.56 g (44%) of complex **13d**, m.p. 93 °C. Anal. Calc. for $C_{22}H_{28}N_2O_2ZrCl_2$ (M = 514.60): C, 51.35; H, 5.48; N, 5.44. Found: C, 51.93; H, 6.54; N, 3.51%. ^{1}H NMR (benzene-d_6, 200.13 MHz): δ = 6.76 (m, 2H, Cp–H), 6.03 (m, 2H, Cp–H), 4.81 (ps, 1H, 7-H), 4.15 (ps, 1H, 7-H′), 3.54 (bm, 4H, 9-H), 2.44 (bm, 4H, 8-H) ppm. ^{13}C NMR (benzene-d_6, 50.32 MHz): δ = 150.3 (C-6), 122.2 (C-5), 118.8, 116.5 (C–Cp), 95.5 (C-7), 67.0 (C-9), 50.6 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3094 (m), 2963 (s), 2845 (s), 2829 (s), 1600 (s), 1553 (s), 1263 (vs), 1120 (vs), 986 (s), 865 (s), 820 (vs) cm^{-1}.

*4.5.3.1. Bis[Z-(1-dimethylamino-2-phenylethenyl)cyclopentadienyl]zirconium dichloride (Z-**13e**).* The reaction of 900 mg (4.14 mmol) of **3e** with 483 mg (2.07 mmol) of $ZrCl_4$ in 80 ml of ether at 0 °C gave 753 mg (62%) of the product *Z*-**13e**, m.p. 70 °C (decomp.). Anal. Calc. for $C_{30}H_{32}N_2ZrCl_2$ (M = 582.7): C, 61.84; H, 5.54; N, 4.81. Found: C, 62.42; H, 5.84; N, 4.51%. ^{1}H NMR (benzene-d_6, 200.13 MHz) (*Z*): δ = 7.13–6.95 (m, 10H, 9-H/10-H/11-H), 6.46 (m, 2H, Cp–H), 6.32 (s, 1H, 7-H), 6.08 (m, 2H, Cp–H), 2.31 (s, 6H, 12-H) ppm. ^{13}C NMR (benzene-d_6, 200.13 MHz) (*Z*): δ = 142.9 (C-6), 138.2 (C-8), 127.5, 126.6, 126.2 (C-9/C-10/C-11), 124.3 (C-5), 119.0, 117.0 (C-1/C-2/C-3/C-4), 113.8 (C-7), 42.3 (C-12) ppm. IR (KBr): $\tilde{\nu}$ = 3107 (w), 3070 (w), 3029 (w), 2920 (m), 2901 (m), 2797 (w), 1607 (s), 1562 (vs), 1510 (s), 1451 (s), 1373 (vs), 1152 (m), 1094 (s), 1036 (s), 964 (m), 905 (m), 814 (s), 723 (s) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 254 nm (ε = 42,808), 327 nm (ε = 47,279).

*4.5.3.2. X-ray crystal structure analysis of complex Z-**13e**.* Single crystals were obtained from dichloromethane. Formula $C_{30}H_{32}Cl_2N_2Zr$, M = 582.70, yellow crystal $0.70 \times 0.50 \times 0.30$ mm, a = 14.950(1) Å, b = 9.954(1) Å, c = 19.100(1) Å, β = 94.90(1)°, V = 2831.9(5) Å^3, ρ_{calc} = 1.367 g cm^{-3}, μ = 5.97 cm^{-1}, empirical absorption correction via ψ scan data ($0.680 \leqslant T \leqslant 0.841$), Z = 4, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 5727 reflections collected (h, $-k$, $+l$), [$(\sin\theta)/\lambda$] = 0.62Å^{-1}, 2861 independent (R_{int} = 0.105) and 2322 observed reflections [$I \geqslant 2\sigma(I)$], 161 refined parameters, R = 0.043, wR^2 = 0.094, maximum residual electron density 0.88 (−1.19) e Å^{-3}, hydrogens calculated and refined as riding atoms.

*4.5.4. Photolysis of complex Z-**13e**. Formation of E-**13e***

A solution of 35 mg (60 μmol) of complex *Z*-**13e** in benzene-d_6 was irradiated for 3 h with a HPK 125 lamp (Pyrex filter). After this time the complex was quantitatively isomerized to *E*-**13e**. ^{1}H NMR (benzene-d_6, 200.13 MHz) (*E*): δ = 7.08–6.75 (m, 5H, 9-H/10-H/11-H), 6.12 (m, 2H, Cp–H), 6.01 (s, 1H, 7-H), 5.87 (m, 2H, Cp–H), 2.44 (s, 6H, 12-H) ppm. ^{13}C NMR (benzene-d_6, 200.13 MHz) (*E*): δ = 145.6 (C-6), 138.7 (C-8), 129.8, 128.6, 126.6 (C-9/C-10/C-11), 128.2 (C-5), 116.2 (C-7), 115.9, 115.1 (C-1/C-2/C-3/C-4), 44.0 (C-12) ppm.

*4.5.4.1. Bis[(N-methylanilinoethenyl)cyclopentadienyl]zirconium dichloride **13f**.* The reaction of 2.60 g (12.79 mmol) of **3f** with 1.30 g (6.39 mmol) of $ZrCl_4$ in 100 ml of ether at 0 °C yielded 1.85 g (52%) of complex **13f**, m.p. 112 °C. Anal. Calc. for $C_{28}H_{28}N_2ZrCl_2$ (M = 554.67): C, 60.63; H, 5.09; N, 5.05. Found: C, 60.73; H, 5.47; N, 4.43%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 7.22–7.19 (m, 3H, 11-H/12-H), 7.15 (m, 2H, 10-H), 6.42 (m, 2H, Cp–H), 6.08 (m, 2H, Cp–H), 5.08 (s, 1H, 7-H), 4.75 (s, 1H, 7-H′), 3.22 (s, 3H, 8-H) ppm. ^{13}C NMR (chloroform-d_1, 50.32 MHz): δ = 148.6 (C-6), 146.1 (C-9), 128.9, 121.8, 121.1 (C-10/C-11/C-12), 124.0 (C-5), 118.4, 114.9 (C-1/C-2/ C-3/C-4), 101.1 (C-7), 41.8 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3083 (m), 3095 (m), 3965 (m), 2941 (m), 2880 (m), 1615 (m), 1596 (vs), 1553 (s), 1496 (vs), 1376 (s), 1363 (s), 1349 (s), 1292 (s), 1132 (s), 1119 (m), 1096 (m), 1032(m), 880 (m), 845 (s), 752 (s) cm^{-1}.

*4.5.4.2. X-ray crystal structure analysis of complex **13f**.* Single crystals were obtained from dichloromethane. Formula $C_{28}H_{28}Cl_2N_2Zr$, M = 554.64, yellow-red crystal $0.40 \times 0.30 \times 0.10$ mm, a = 29.231(4) Å, b = 6.988(1) Å, c = 12.599(1) Å, β = 103.70(1)°, V = 2500.3(5) Å^3, ρ_{calc} = 1.473 g cm^{-3}, μ = 6.73 cm^{-1}, empirical absorption correction via ψ scan data ($0.775 \leqslant T \leqslant 0.936$), Z = 4, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 2667 reflections collected (h, $+k$, $-l$), [$(\sin\theta)/\lambda$] = 0.62 Å^{-1}, 2541 independent (R_{int} = 0.020) and 1961 observed reflections [$I \geqslant 2\sigma(I)$], 151 refined parameters, R = 0.031, wR^2 = 0.082, maximum residual electron density 0.96 (−1.29) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.6. Preparation of the [dialkylaminobutadien-1,3-diyl-bis(cyclopentadienyl)] Group 4 metal dichloride complexes. General procedure of the Mannich-type condensation reaction

The respective lithium(dialkylaminoethenyl)cyclopentadienide (**3**, ca. 40 mmol) was suspended in ca. 60 ml of ether at −78 °C. The pure Group 4 metal tetrachloride (ca. 20 mmol) was added with vigorous stirring. The mixture was slowly allowed to warm to room temperature and stirred for a total of 12 h. The precipitate was removed by filtration and washed with ether, then with dichloromethane. Solvent was removed from the

combined filtrates in vacuo to yield the respective *ansa*-metallocene complex.

4.6.1. [1-Dimethylaminobutadien-1,3-diyl-bis(cyclopentadienyl)]zirconium dichloride (**4a**)

The reaction of 2.12 g (15.0 mmol) of lithium(dimethylaminoethenyl)cyclopentadienide (**3a**) with 1.75 g (7.5 mmol) of zirconium tetrachloride gave 1.62 g (56%) of **4a**. Subsequent recrystallization of a different sample, that was obtained from the reaction of 5.29 g (37.5 mmol) of **3a** with 4.37 g (18.7 mmol) of $ZrCl_4$, from ether yielded 2.32 g (32%) of the pure crystalline complex **4a**, m.p. 195.1 °C (decomp.). Anal. Calc. for $C_{16}H_{17}NZrCl_2$ (M = 385.44): C, 49.86; H, 4.45; N, 3.63. Found: C, 49.62; H, 4.84; N, 3.52%. ^{1}H NMR (dichloromethane-d_2, 599.87 MHz, 268 K): δ = 6.71 (m, 2H, 15-H/16-H), 6.69 (m, 2H, 1-H/4-H), 6.15 (m, 2H, 14-H/17-H), 6.09 (m, 2H, 2-H/3-H), 5.64 (ps, 1H, 8-H), 5.01 (ps, 1H, 7-H), 4.93 (ps, 1H, 7-H′), 2.59 (s, 6H, 11-H) ppm. ^{13}C NMR (dichloromethane-d_2, 150.84 MHz): δ = 147.5 (C-9), 139.0 (C-5), 137.1 (C-6), 125.8 (C-13), 123.8 (C-1/C-4), 123.2 (C-15/C-16), 114.0 (C-14/C-17), 110.9 (C-2/C-3), 110.2 (C-7), 104.6 (C-8), 41.4 (C-11) ppm. IR (KBr): $\tilde{\nu}$ = 3095 (w), 3062 (w), 2939 (w), 2926 (w), 2872 (w), 1602 (s), 1559 (m), 1348 (m), 1105 (m), 1038 (m), 865 (m), 830 (s), 817 (s) cm^{-1}.

4.6.2. X-ray crystal structure analysis of complex **4a**

Single crystals were obtained from a dichloromethane solution by very slow solvent evaporation at ambient conditions. Formula $C_{16}H_{17}Cl_2NZr$, M = 385.43, yellow crystal 0.50 × 0.40 × 0.15 mm, a = 10.774(1) Å, b = 10.501(1) Å, c = 13.930(1) Å, β = 101.52(1)°, V = 1544.3(2) Å^3, ρ_{calc} = 1.658 g cm^{-3}, μ = 10.47 cm^{-1}, empirical absorption correction via ψ scan data ($0.623 \leqslant T \leqslant 0.859$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 3261 reflections collected (h, $-k$, $-l$), [(sin θ)/λ] = 0.62 Å^{-1}, 3132 independent (R_{int} = 0.013) and 2744 observed reflections [$I \geqslant 2\sigma(I)$], 183 refined parameters, R = 0.045, wR^2 = 0.165, maximum residual electron density 0.76 (−0.97) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.6.3. [Pyrrolidinobutadien-1,3-diyl-bis(cyclopentadienel)]zirconium dichloride (**4b**)

The reaction of 3.00 g (18.0 mmol) of **3b** with 2.10 g (9.00 mmol) $ZrCl_4$ gave 2.55 g (69%) of complex **4b**, m.p. 100 °C (decomp.). Anal. Calc. for $C_{18}H_{19}NZrCl_2$ (M = 411.48): C, 52.54; H, 4.65; N, 3.40. Found: C, 51.42; H, 5.77; N, 3.29%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.72 (m, 2H, 1-H/4-H), 6.67 (m, 2H, 15-H/16-H), 6.17 (m, 2H, 14-H/17-H), 6.07 (m, 2H, 2-H/3-H), 5.44 (ps 1H, 8-H), 4.92 (ps, 1H, 7-H), 4.84 (ps, 1H, 7-H′), 3.00 (m, 4H, 11-H), 1.88 (m, 4H, 12-H) ppm. ^{13}C NMR (chloroform-d_1, 50.32 MHz): δ = 144.2 (C-9), 138.9 (C-5), 135.1 (C-6), 120.7 (C-13), 123.2 (C-1/C-4), 123.0 (C-15/C-16), 112.9 (C-14/C-17), 111.4 (C-2/C-3), 109.3 (C-7), 99.5 (C-8), 49.4 (C-11), 25.1 (C-12) ppm. IR (KBr): $\tilde{\nu}$ = 3086 (m), 2960 (s), 2933 (s), 2870 (m), 1605 (vs), 1550 (vs), 1396 (s), 1359(s), 1338(s), 1289 (s), 1038 (s), 841 (m), 820 (vs), 816 (vs) cm^{-1}.

4.6.4. [Piperidinobutadien-1,3-diyl-bis(cyclopentadienyl)]zirconium dichloride (**4c**)

This *ansa*-metallocene complex was prepared in a different way. Bis[(piperidinoethenyl)cyclopentadienyl]zirconium dichloride (**13c**, 800 mg, 1.57 mmol) was suspended in 60 ml of diethyl ether. Solid zirconium tetrachloride (10 mg, 0.043 mmol) was added and the mixture stirred for 12 h at room temperature. Solvent was then removed in vacuo and the residue taken up in 40 ml of dichloromethane. The mixture was filtered and the filtrate concentrated in vacuo to a volume of 10 ml. The *ansa*-metallocene product **4c** precipitated at −20 °C. It was collected by filtration and dried in vacuo to yield 554 mg (84%) of complex **4e** as a beige-yellow solid, m.p. 144 °C. Anal. Calc. for $C_{19}H_{21}NZrCl_2$ (M = 425.51): C, 53.63; H, 4.97; N, 3.29. Found: C, 52.78; H, 5.83; N, 5.13%. ^{1}H NMR (benzene-d_6, 200.13 MHz): δ = 6.52 (m, 4H, 1-H/4-H/15-H/16-H), 5.90 (m, 2H, 14-H/17-H), 5.71 (m, 2H, 2-H/3-H), 5.43 (s, 1H, 8-H), 4.82 (s, 1H, 7-H), 4.77 (s, 1H, 7-H′), 3.03 (m, 4H, 11-H), 1.20 (m, 6H, 12-H/18-H) ppm. ^{13}C NMR (benzene-d_6, 50.32 MHz): δ = 148.2 (C-9), 139.4 (C-5), 136.8 (C-6), 125.7 (C-13), 124.1 (C-1/C-4), 123.2 (C-15/C-16), 113.3 (C-14/C-17), 110.2 (C-2/C-3), 110.3 (C-7), 105.9 (C-8), 50.8 (C-11), 26.0 (C-12), 24.5 (C-18) ppm. IR (KBr): $\tilde{\nu}$ = 3082 (m), 2937 (vs), 2918 (vs), 1593 (s), 1441 (s), 1259 (s), 110 (s), 1033 (s), 821 (vs), 809 (vs), 797 (s) cm^{-1}.

4.6.5. [Morpholinobutadien-1,3-diyl-bis(cyclopentadienyl)]zirconium dichloride (**4d**)

According to the general procedure described above **3d** (3.48 g, 19.0 mmol) was reacted with 2.23 g (9.5 mmol) of $ZrCl_4$ to yield 897 mg (22%) of complex **4d**, m.p. 184 °C. Anal. Calc. for $C_{18}H_{19}NOZrCl_2$ (M = 427.48): C, 50.57; H, 4.48; N, 3.28. Found: C, 50.07; H, 5.44; N, 3.33%. ^{1}H NMR (benzene-d_6, 599.87 MHz): δ = 6.55–6.48 (m, 4H, 1-H/4-H/15-H/16-H), 5.81 (m, 2H, 14-H/17-H), 5.71 (m, 2H, 2-H/3-H), 5.33 (ps, 1H, 8-H), 4.83 (m, 1H, 7-H), 4.76 (m, 1H, 7-H′), 3.33 (m, 4H, 12-H), 2.28 (m, 4H, 11-H) ppm. ^{13}C NMR (benzene-d_6, 150.84 MHz): δ = 147.7 (C-9), 138.9 (C-5), 136.4 (C-6), 124.5 (C-13), 124.0 (C-1/C-4), 123.3 (C-15/C-16), 113.3 (C-14/C-17), 111.1 (C-7), 110.2 (C-2/C-3), 106.3 (C-8), 66.5 (C-12), 50.2 (C-11) ppm. IR (KBr): $\tilde{\nu}$ = 3082 (w), 2953 (w), 2859 (w), 2818 (w), 1614 (m), 1583 (m), 1261 (s), 1230 (s), 1114 (s), 1021 (s), 887 (s), 824 (s), 807 (vs) cm^{-1}.

4.6.6. [Dimethylaminobutadien-1,3-diyl-bis(cyclopentadienyl)]hafnium dichloride (**5a**)

The reaction of the reagent **3a** (1.50 g, 10.6 mmol) with hafnium tetrachloride (1.70 g, 5.3 mmol) gave 1.48 g (59%) of complex **5a**, m.p. 174 °C (decomp.). Anal. Calc. for $C_{16}H_{17}NHfCl_2$ (M = 472.71): C, 40.65; H, 3.62; N, 2.96. Found: C, 40.56; H, 4.14; N, 3.34%. ^{1}H NMR (benzene-d_6, 200.13 MHz): δ = 6.44–6.38 (m, 4H, 1-H/4-H/15-H/16-H), 5.72 (m, 2H, 14-H/17-H), 5.63 (m, 2H, 2-H/3-H), 5.31 (ps, 1H, 8-H), 4.77 (m, 2H, 7-H/7-H′), 2.07 (m, 6H, 11-H) ppm. ^{13}C NMR (benzene-d_6, 50.32 MHz): δ = 147.6 (C-9), 138.8 (C-5), 134.7 (C-6), 124.6 (C-13), 122.4 (C-1/C-4), 121.6 (C-15/C-16), 111.7 (C-14/C-17), 108.5 (C-2/C-3), 110.5 (C-7), 104.3 (C-8), 41.9 (C-11) ppm. IR (KBr): $\tilde{\nu}$ = 3097 (w), 3065 (m), 2940 (m), 2873 (m), 1604 (vs), 1395 (s), 1348 (s), 1298 (s), 1105(vs), 1038 (vs), 875 (s), 866 (s), 832 (vs), 820 (vs) cm^{-1}.

4.6.7. X-ray crystal structure analysis of complex **5a**

Single crystals were obtained from dichloromethane by slow evaporation of the solvent at ambient conditions. Formula $C_{16}H_{17}Cl_2HfN$, M = 472.70, yellow crystal 0.25 × 0.20 × 0.20 mm, a = 10.756(2) Å, b = 10.458(2) Å, c = 13.909(3) Å, β = 101.71(2)°, V = 1532.0(5) Å^3, ρ_{calc} = 2.049 g cm^{-3}, μ = 71.46 cm^{-1}, empirical absorption correction via ψ scan data ($0.268 \leqslant T \leqslant 0.329$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 3244 reflections collected (h, $-k$, $-l$), [(sin θ)/λ] = 0.62 Å^{-1}, 3116 independent (R_{int} = 0.052) and 2903 observed reflections [$I \geqslant 2\sigma(I)$], 184 refined parameters, R = 0.028, wR^2 = 0.087, maximum residual electron density 1.58 (−1.95) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.7. [Pyrrolidinobutadien-1,3-diyl-bis(cyclopentadienyl)]hafnium dichloride (**5b**)

The reaction of **3b** (1.50 g, 9.0 mmol) with 1.44 g (4.5 mmol) of hafnium tetrachloride carried out according to the general procedure described above gave 1.08 g (49%) of complex **5b**, m.p. 93 °C (decomp.). Anal. Calc. for $C_{18}H_{19}NHfCl_2$ (M = 498.75): C, 43.35; H, 3.84; N, 2.81. Found: C, 44.31; H, 4.94; N, 3.04%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.61 (m, 2H, 1-H/4-H), 6.56 (m, 2H, 15-H/16-H), 6.05 (m, 2H, 14-H/17-H), 5.99 (m, 2H, 2-H/3-H), 5.44 (ps, 1H, 8-H), 4.87–4.84 (m, 2H, 7-H/7-H′), 3.03–2.91 (m, 4H, 11-H), 1.89–1.83 (m, 4H, 12-H) ppm. ^{13}C NMR (chloroform-d_1, 50.32 MHz): δ = 148.7 (C-9), 133.5 (C-5), 124.2 (C-6), 122.7 (C-13) 121.6 (C-1/C-4), 121.5 (C-15/C-16), 111.1 (C-14/C-17), 109.5 (C-2/C-3), 109.7 (C-7), 99.4 (C-8), 49.4 (C-11), 25.0 (C-12) ppm. IR (KBr): $\tilde{\nu}$ = 3087 (w), 2956 (m), 2869 (m), 1604 (vs), 1540 (s), 1361 (s), 1336 (s), 1290 (s), 1038 (m), 842 (m), 821 (s) cm^{-1}.

4.7.1. [Dimethylamidobutadien-1,3-diyl-bis(cyclopentadienyl)]titanium dichloride (**6a**)

The reaction of 1.00 g (7.00 mmol) of **3a** with 673 mg (3.55 mmol) of titanium tetrachloride (added as a solution in 20 ml of ether) yielded 203 mg (17%) complex **6a** after recrystallization from diethyl ether, m.p. 129 °C (decomp.). Anal. Calc. for $C_{16}H_{17}TiCl_2$ (M = 342.12): C, 56.17; H, 5.01; N, 4.09. Found: C, 55.37; H, 5.67; N, 5.45%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.96–6.90 (m, 4H, 1-H/4-H/15-H/16-H), 6.11–6.05 (m, 4H, 2-H/3-H/14-H/17-H), 5.64 (ps, 1H, 8-H), 5.00 (ps, 1H, 7-H), 4.93 (ps, 1H, 7-H′), 2.63 (s, 6H, 11-H) ppm. ^{13}C NMR (chloroform-d_1, 50.32 MHz): δ = 147.4 (C-9), 139.2 (C-5), 134.7 (C-6), 126.8 (C-13), 129.7 (C-1/C-4), 128.8 (C15/C-16), 116.9 (C-14/C-17), 115.1 (C-2/C-3), 110.3 (C-7), 104.7 (C-8), 41.4 (C-11) ppm. IR (KBr): $\tilde{\nu}$ = 3101 (m), 3070 (m), 2943 (m), 2874 (m), 1605 (vs), 1569 (vs), 1363 (s), 1349 (s), 1110 (s), 1041 (s), 843 (s), 829 (vs) cm^{-1}.

4.7.2. [Dimethylaminobutadien-1,3-diyl-bis(3-methylcyclopentadienyl)]zirconium dichloride (**11a**)

The reaction of 2.00 g (12.9 mmol) of the reagent **10a** with 1.50 g (6.5 mmol) of $ZrCl_4$ was carried out as described in the general procedure to yield a 1:1 mixture of the *rac*- and *meso*-isomers of **11a** (isomer **A** and isomer **B**). Recrystallization from diethyl ether gave 1.17 g of the isomer mixture (44% yield), m.p. 92 °C (decomp.). Anal. Calc. for $C_{18}H_{21}NZrCl_2$ (413.50): C, 52.29; H, 5.12; N, 3.39. Found: C, 52.41; H, 6.57; N, 3.35%. ^{1}H NMR (dichloromethane-d_2, 599.87 MHz, 298 K, isomer **A**): δ = 6.43 (m, 1H, Cp–H), 6.38 (m, 1H, Cp–H), 6.33 (m, 1H, Cp–H), 6.05 (m, 1H, Cp–H), 5.85 (m, 1H, Cp–H), 5.72 (m, 1H, Cp–H), 5.60 (s, 1H, 8-H), 4.95 (m, 1H, 7-H), 4.85 (m, 1H, 7-H′), 2.63 (s, 6H, 11-H), 2.32 (s, 3H, 17-H), 2.30 (s, 3H, 18-H) ppm. ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, 298 K, isomer **A**): δ = 148.2 (C-9), 139.9 (C-6), 136.5 (C-5), 133.2 (C-3), 132.6 (C-15), 124.9 (C-12), 123.8, 123.5, 123.4, 114.8, 112.6, 110.6 (C-1/C-2/C-4/C-13/C-14/C-16), 109.1 (C-7), 104.4 (C-8), 41.7 (C-11), 15.7 (C-17/C-18) ppm. ^{1}H NMR (dichloromethane-d_2, 599.87 MHz, 298 K, isomer **B**): δ = 6.39 (m, 1H, Cp–H), 6.08 (m, 1H, Cp–H), 5.97 (m, 1H, Cp–H), 5.87 (m, 1H, Cp–H), 5.83 (m, 1H, Cp–H), 5.77 (m, 1H, Cp–H), 5.59 (ps, 1H, 8-H), 4.94 (m, 1H, 7-H), 4.84 (m, 1H, 7-H′), 2.62 (s, 6H, 11-H), 2.31 (s, 3H, 17-H), 2.29 (s, 3H, 18-H) ppm. ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, 298 K, isomer **B**): δ = 148.3 (C-9), 139.9 (C-6), 136.6 (C-5), 133.4 (C-2), 132.7 (C-15), 124.7 (C-12), 123.8, 115.6, 115.1, 113.6, 113.1, 112.5 (C-1/C-3/C-4/C-13/C-14/C-16), 109.0 (C-7), 104.4 (C-8), 41.6 (C-11), 15.6 (C-17/C-18) ppm. IR (KBr): $\tilde{\nu}$ = 3091 (w), 2960 (m),

2933 (m), 2871 (m), 2795 (m), 1630 (vs), 1563 (s), 1453 (s), 1356 (s), 1156 (m), 1081 (m), 1053 (m), 847 (s), 813 (s), 778 (s) cm^{-1}.

4.7.3. [Dimethylaminobutadien-1,3-diyl-bis(3-tert-butylcyclopentadienyl)]zirconium dichloride (**11b**)

The reaction of 1.70 g (8.6 mmol) of **10b** with 1.00 g (4.3 mmol) of zirconium tetrachloride gave a 1:1 mixture of the *rac*- and *meso*-isomers of the product **11b** (isomer **A** and isomer **B**), yield 1.03 g (48%) after recrystallization from ether, m.p. 65 °C (decomp.). Anal. Calc. for $C_{24}H_{33}NZrCl_2$ (M = 497.66): C, 57.92; H, 6.68; N, 2.81. Found: C, 57.42; H, 7.28; N, 3.65%. ^{1}H NMR (toluene-d_8, 599.87 MHz, 298 K, isomer **A**): δ = 6.47 (m, 1H, Cp–H), 6.44 (m, 1H, Cp–H), 6.14 (m, 1H, Cp–H), 5.90 (m, 1H, Cp–H), 5.80 (m, 1H, Cp–H), 5.75 (m, 1H, Cp–H), 5.36 (s, 1H, 8-H), 4.87 (m, 1H, 7-H), 4.73 (m, 1H, 7-H′), 2.19 (s, 6H, 11-H), 1.31 (s, 9H, 20-H), 1.29 (s, 9H, 18-H) ppm. ^{13}C NMR (toluene-d_8, 150.84 MHz, 298 K, isomer **A**): δ = 148.2 (C-9), 145.7 (C-15), 145.4 (C-3), 139.6 (C-6), 132.9 (C-5), 122.9 (C-12), 124.1, 122.7, 112.6, 112.0, 111.7, 109.1 (C-1/C-2/C-4/C-13/C-14/C-16), 108.7 (C-7), 103.8 (C-8), 41.0 (C-11), 31.2 (C-20), 31.1 (C-18), 29.9 (C-17/C-19) ppm. ^{1}H NMR (toluene-d_8, 599.87 MHz, 298 K, isomer **B**): δ = 6.35 (m, 1H, Cp–H), 6.24 (m, 1H, Cp–H), 6.22 (m, 1H, Cp–H), 6.02 (m, 1H, Cp–H), 5.87 (m, 1H, Cp–H), 5.73 (m, 1H, Cp–H), 5.38 (s, 1H, 8-H), 4.89 (m, 1H, 7-H), 4.75 (m, 1H, 7-H′), 2.18 (s, 6H, 11-H), 1.32 (s, 9H, 18-H), 1.30 (s, 9H, 20-H) ppm. ^{13}C NMR (toluene-d_8, 150.84 MHz, 298 K, isomer **B**): δ = 147.9 (C-9), 145.6 (C-2), 145.3 (C-15), 139.7 (C-6), 131.8 (C-5), 122.4 (C-12), 121.6, 119.4, 115.9, 113.7, 110.8, 110.3 (C-1/C-3/C-4/C-13/C-14/C-16), 109.2 (C-7), 104.1 (C-8), 40.9 (C-11), 31.1 (C-18), 31.1 (C-20), 29.8 (C-17/C-19) ppm. IR (KBr): $\tilde{\nu}$ = 3109 (w), 3089 (w), 2966 (vs), 2914 (s), 2868 (s), 2790 (m), 1620 (s), 1568(s), 1471 (s), 1367 (vs), 1243 (m), 1159 (s), 1055 (s), 1016 (s), 931 (m), 808 (s) cm^{-1}.

4.7.4. [Dimethylaminobutadien-1,3-diyl-bis(3-methylcyclopentadienyl)]hafnium dichloride (**12a**)

The reaction of 2.50 g (16.1 mmol) of the reagent **10a** with 2.58 g (8.1 mmol) of hafnium tetrachloride gave a 1:1 mixture of the *rac*- and *meso*-isomers of the product **12a**, yield after recrystallization from ether: 383 mg (9.5%), m.p. 83 °C (decomp.). Anal. Calc. for $C_{18}H_{21}NHfCl_2$ (M = 500.77): C, 43.17; H, 4.23; N, 2.80. Found: C, 44.58; H, 4.90; N, 3.07%. ^{1}H NMR (dichloromethane-d_2, 599.87 MHz, isomer **A**): δ = 6.26 (m, 1H, Cp–H), 6.21 (m, 1H, Cp–H), 5.98 (m, 1H, Cp–H), 5.93 (m, 1H, Cp–H), 5.67 (m, 1H, Cp–H), 5.60 (m, 1H, Cp–H), 5.57 (m, 1H, 8-H), 4.88 (m, 1H, 7-H), 4.84 (m, 1H, 7-H′), 2.62 (s, 6H, 11-H), 2.36 (s, 3H, 17-H), 2.34 (s, 3H, 18-H) ppm. ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, isomer **A**): δ = 148.1 (C-9), 139.7 (C-6), 134.4 (C-5), 131.5 (C-3), 130.8 (C-15), 124.6 (C-12), 122.4, 122.1, 121.6, 118.1, 112.0, 111.4 (C-1/C-2/C-4/C-13/C-14/C-16), 108.5 (C-7), 104.2 (C-8), 41.2 (C-11), 15.4 (C-17), 15.1 (C-18) ppm. ^{1}H NMR (dichloromethane-d_2, 599.87 MHz, isomer **B**): δ = 6.30 (m, 1H, Cp–H), 6.25 (m, 1H, Cp–H), 6.19 (m, 1H, Cp–H), 5.88 (m, 1H, Cp–H), 5.74 (m, 1H, Cp–H), 5.73 (m, 1H, Cp–H), 5.58 (m, 1H, 8-H), 4.89 (m, 1H, 7-H), 4.83 (m, 1H, 7-H′), 2.59 (s, 6H, 11-H), 2.35 (s, 3H, 17-H), 2.33 (s, 3H, 18-H) ppm. ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, isomer **B**): δ = 148.0 (C-9), 139.7 (C-6), 134.2 (C-5), 131.2 (C-3), 130.7 (C-15), 124.3 (C-12), 122.4, 122.2, 122.0, 118.0, 117.0, 114.8 (C-1/C-2/C-4/C-13/C-14/C-16), 108.6 (C-7), 104.3 (C-8), 41.0 (C-11), 15.7 (C-17), 15.3 (C-18) ppm. IR (KBr): $\tilde{\nu}$ = 3096 (w), 2935 (m), 2869 (m), 2795 (m), 1617 (vs), 1564 (s), 1463 (s), 1356 (s), 1147 (m), 1075 (m), 1062 (m), 862 (m), 814 (s), 774 (s) cm^{-1}.

4.7.5. [Dimethylaminobutadien-1,3-diyl-bis(3-tert-butylcyclopentadienyl)]hafnium dichloride (**12b**)

The reaction of 2.50 g (12.7 mmol) of the reagent **10b** with 2.03 g (6.3 mmol) of hafnium tetrachloride gave a close to 1:1 mixture of the *rac*- and *meso*-isomers of **12b** (isomer **A** and isomer **B**), yield after recrystallization from diethyl ether: 400 mg (11%), m.p. 78 °C (decomp.). Anal. Calc. for $C_{24}H_{33}NHfCl_2$ (M = 584.93): C, 49.28; H, 5.69; N, 2.39. Found: C, 49.64; H, 5.85; N, 3.67%. ^{1}H NMR (dichloromethane-d_2, 599.87 MHz, isomer **A**): δ = 6.25 (m, 1H, Cp–H), 6.22 (m, 1H, Cp–H), 6.12 (m, 1H, Cp–H), 5.96 (m, 1H, Cp–H), 5.93 (m, 1H, Cp–H), 5.79 (m, 1H, Cp–H), 5.55 (m, 1H, 8-H), 4.92 (m, 1H, 7-H), 4.81 (m, 1H, 7-H′), 2.60 (s, 6H, 11-H), 1.34 (s, 9H, 18-H), 1.31 (s, 9H, 20-H) ppm. ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, isomer **A**): δ = 147.9 (C-9), 145.6 (C-15), 144.1 (C-3), 139.6 (C-6), 130.2 (C-5), 114.0, 113.0, 111.9, 110.6, 110.4, 106.2 (C-1/ C-2/C-4/C-13/C-14/C-16), 109.0 (C-7), 103.5 (C-8), 41.5 (C-11), 31.2 (C-18), 31.1 (C-20), 30.8 (C-17/C-19) ppm. ^{1}H NMR (dichloromethane-d_2, 599.87 MHz, isomer **B**): δ = 6.11 (m, 1H, Cp–H), 6.09 (m, 1H, Cp–H), 6.01 (m, 1H, Cp–H), 5.98 (m, 1H, Cp–H), 5.95 (m, 1H, Cp–H), 5.80–5.79 (m, 1H, Cp–H), 5.56 (m, 1H, 8-H), 4.90 (m, 1H, 7-H), 4.80 (m, 1H, 7-H′), 2.59 (s, 6H, 11-H), 1.33 (s, 9H, 18-H), 1.32 (s, 9H, 20-H) ppm. ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, isomer **B**): δ = 147.8 (C-9), 145.2 (C-15), 143.9 (C-3), 139.5 (C-6), 130.1 (C-5), 111.7, 111.6, 111.4, 111.1, 108.6, 106.3 (C-1/ C-2/C-4/C-13/C-14/C-16), 109.1 (C-7), 103.7 (C-8), 41.4 (C-11), 31.2 (C-18), 31.0 (C-20), 30.7 (C-17/C-19) ppm. IR (KBr): $\tilde{\nu}$ = 3109 (w), 3089 (w), 2979 (s), 2914 (s), 2862 (s), 2797 (m), 1620 (s), 1568 (s), 1471 (m), 1367 (s), 1250 (m), 1159 (m), 1061 (m), 1009 (m), 925 (m), 866 (m), 834 (m), 801 (m) cm^{-1}.

4.8. Preparation of the [dialkylaminobutadien-1,3-diyl-bis(cyclopentadienyl)]dimethyl Group 4 metal complexes. General procedure

The respective [dialkylaminobutadien-1,3-diyl-bis(cyclopentadienyl)] Group 4 metal dihalide complex (ca. 1 mmol) was dissolved in ca. 40 ml of diethyl ether and cooled to −40 °C. At this temperature a 1.6 M ethereal methyl lithium solution (ca. 2 mmol) was added dropwise with stirring. The mixture was stirred for 2 h at −40 °C, then warmed to room temperature and stirred for additional 30 min. The lithium chloride precipitate was removed by filtration. The filtrate was concentrated in vacuo until a precipitate began to form. The mixture was then cooled to −30 °C and the precipitated product collected by filtration.

4.8.1. [Dimethylaminobutadien-1,3-diyl-bis(cyclopentadienyl)]dimethyl zirconium (**7a**)

The reaction of 515 mg of complex **4a** (1.34 mmol) with 1.67 ml of a 1.6 M solution of methyl lithium in ether (2.68 mmol) was carried out according to the general procedure described above. It yielded 256 mg (55%) of the product **7a** as a yellow solid, m.p. 140 °C, 197 °C (decomp.). Anal. Calc. for $C_{18}H_{23}NZr$ (M = 344.61): C, 62.74; H, 6.73; N, 4.06. Found: C, 62.28; H, 5.92; N, 4.18%. ^{1}H NMR (chloroform-d_1, 599.99 MHz): δ = 6.61 (m, 2H, 15-H/16-H), 6.54 (m, 2H, 1-H/4-H), 5.76 (m, 4H, 2-H/3-H/14-H/17-H), 5.32 (s, 1H, 8-H), 4.85 (t, 1H, 7-H), 4.65 (t, 1H, 7-H′), 2.58 (s, 6H, 11-H), −0.37 (s, 6H, 18-H/19-H) ppm. ^{13}C NMR (chloroform-d_1, 154.99 MHz): δ = 148.0 (C-9), 140.1 (C-5), 128.3 (C-6), 118.6 (C-13), 116.2 (C-1/C-4), 116.1 (C-15/C-16), 109.8 (C-14/C-17), 107.5 (C-2/C-3), 107.7 (C-7), 103.7 (C-8), 41.4 (C-11), 29.1 (C-18/C-19) ppm. IR (KBr): $\tilde{\nu}$ = 3071 (w), 2909 (m), 2859 (m), 2839 (m), 1601 (vs), 1575 (s), 1391 (s), 1351 (s), 1299 (s), 1260 (vs), 1103 (vs), 1097 (vs), 1037(vs), 860 (s), 818 (vs), 812 (vs), 800 (vs) cm^{-1}.

4.8.2. [Pyrrolidinobutadien-1,3-diyl-bis(cyclopentadienyl)]-dimethylzirconium (**7b**)

The reaction of 627 mg (1.52 mmol) of complex **4b** with methyl lithium (3.04 mmol) in ether gave 271 mg (48%) of complex **7b**, m.p. 78 °C (decomp.). Anal. Calc. for $C_{20}H_{25}NZr$ (M = 370.65): C, 64.81; H, 6.80; N, 3.78. Found: C, 64.95; H, 6.26; N, 4.26%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.60 (m, 2H, Cp–H), 6.50 (m, 2H, Cp–H), 5.86 (m, 2H, Cp–H), 5.72 (m, 2H, Cp–H), 5.19 (s, 1H, 8-H), 4.79 (ps, 1H, 7-H), 4.61 (ps, 1H, 7-H′), 3.02–2.96 (m, 4H, 11-H), 1.89–1.81 (m, 4H, 12-H), −0.37 (s, 6H, 18-H/19-H) ppm. ^{13}C NMR (chloroform-d_1, 50.32 MHz): δ = 145.8 (C-9), 139.9 (C-5), 127.8, 118.7 (C-6/C-13), 115.9, 115.6, 109.3, 106.9 (C–Cp), 107.9 (C-7), 99.3 (C-8), 49.3 (C-11), 29.1 (C-18/C-19), 25.1 (C-12) ppm. IR (KBr): $\tilde{\nu}$ = 3082 (m), 2960 (s), 2950 (s), 2921 (s), 1603 (vs), 1538 (s), 1359 (s), 1331 (s), 1289 (s), 1163 (m), 1057 (s), 1036 (s), 806 (vs), 802 (vs), 798 (vs) cm^{-1}.

4.8.3. [Morpholinobutadien-1,3-diyl-bis(cyclopentadienyl)]dimethyl zirconium (**7d**)

The reaction of 178 mg (0.42 mmol) of **4d** with methyl lithium (0.84 mmol) in ether gave 92 mg (57%) of complex **7d**, m.p. 101 °C (decomp.). Anal. Calc. for $C_{20}H_{25}NOZr$ (M = 386.65): C, 62.13; H, 6.52; N, 3.62. Found: C, 62.37; H, 6.42; N, 4.05%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.61–6.55 (m, 4H, Cp–H), 5.79–5.73 (m, 4H, Cp–H), 5.43 (ps, 1H, 8-H), 4.91 (ps, 1H, 7-H), 4.71 (ps, 1H, 7-H′), 3.72–3.67 (m, 4H, 12-H), 2.83–2.79 (m, 4H, 11-H), −0.35 (s, 6H, 18-H/19-H) ppm. ^{13}C NMR (dichloromethane-d_2, 50.32 MHz): δ = 149.8 (C-9), 136.1 (C-5), 127.5 (C-6), 117.2 (C-13), 116.7, 116.6, 110.4, 108.8 (C–Cp), 107.9 (C-7), 105.7 (C-8), 67.2 (C-12), 50.5 (C-11), 29.3 (C-18/C-19) ppm. IR (KBr): $\tilde{\nu}$ = 3083 (w), 2951 (m), 2853 (m), 1613 (m), 1262 (s), 1114 (s), 1020 (s), 955 (s), 875 (s), 824 (vs), 799 (vs) cm^{-1}.

4.8.4. [Dimethylaminobutadien-1,3-diyl-bis(cyclopentadienyl)]dimethyl hafnium (**8a**)

The reaction of 557 mg (1.18 mmol) of **5a** with methyl lithium (2.36 mmol) in ether gave 417 mg (82%) of the product **5a** as a beige colored solid, m.p. 146 °C (decomp.). Anal. Calc. for $C_{18}H_{23}NHf$ (M = 431.88): C, 50.06; H, 5.37; N, 3.24. Found: C, 50.43; H, 5.06; N, 3.30%. ^{1}H NMR (chloroform-d_1, 200.13 MHz): δ = 6.48 (m, 2H, Cp–H), 6.42 (m, 2H, Cp–H), 5.71–5.67 (m, 4H, Cp–H), 5.35 (s, 1H, 8-H), 4.83 (ps, 1H, 7-H), 4.69 (ps, 1H, 7-H′), 2.59 (s, 6H, 11-H), −0.56 (s, 6H, 18-H/19-H) ppm. ^{13}C NMR (chloroform-d_1, 50.32 MHz): δ = 147.9 (C-9), 140.0 (C-5), 127.4 (C-6), 120.9 (C-13), 115.4, 115.3, 109.2, 106.7 (C-1/C-2/C-3/C-4/C-14/C-15/C-16/C-17), 108.1 (C-7), 103.5 (C-8), 41.4 (C-11), 35.3 (C-18/C-19). IR (KBr): $\tilde{\nu}$ = 3086 (m), 3071 (m), 2917 (s), 2910 (s), 2862 (s), 2837 (s), 2785 (m), 1602 (vs), 1488 (s), 1392 (s), 1352 (s), 1299 (s), 1132 (s), 1103 (vs), 1038 (vs), 860 (s), 822 (s), 810 (vs), 804 (vs) cm^{-1}.

4.8.5. [Pyrrolidinobutadien-1,3-diyl-bis(cyclopentadienyl)]dimethyl hafnium (**8b**)

The reaction of 472 mg (0.95 mmol) of complex **5b** with 1.90 mmol of methyl lithium in ether gave 334 mg (77%) of **8b**, m.p. 67 °C (decomp.). Anal. Calc. for $C_{20}H_{25}NHf$ (M = 457.92): C, 52.46; H, 5.50; N, 3.06. Found: C, 52.32; H, 6.71; N, 3.33%. ^{1}H NMR (dichloromethane-d_2, 200.13 MHz): δ = 6.50 (m, 2H, Cp–H), 6.38 (m, 2H, Cp–H), 5.80 (m, 2H, Cp–H), 5.67 (m, 2H, Cp–H), 5.23 (ps, 1H, 8-H), 4.75 (ps, 1H, 7-H), 4.63 (ps, 1H, 7-H′), 3.03–2.97 (m, 4H, 11-H), 1.87–1.81 (m, 4H, 12-H), −0.55 (s, 6H, 18-H/19-H) ppm. ^{13}C NMR (dichloro-

methane-d_2, 50.32 MHz): δ = 148.6 (C-9), 140.8 (C-5), 127.3, 119.4, (C-6/ C-13), 115.7, 115.2, 107.7, 107.0 (C–Cp), 109.0 (C-7), 99.3 (C-8), 49.6 (C-11), 35.2 (C-18/C-19), 25.4 (C-12) ppm. IR (KBr): $\tilde{\nu}$ = 3086 (w), 3076 (w), 2957 (m), 2897 (m), 1607 (s), 1550 (m), 1394 (m), 1261 (m), 1099 (m), 1069 (m), 1029 (m), 807 (s), 801(s) cm^{-1}.

*4.8.5.1. [Dimethylaminobutadien-1,3-diyl-bis(cyclopentadienyl)]bis(dimethylamido)zirconium (**9a**).* Complex **4a** (770 mg, 2.0 mmol) and lithium dimethylamide (204 mg, 4.0 mmol) were combined as solids and cooled to −78 °C, then 30 ml of precooled diethyl ether was added. The mixture was allowed to warm to room temperature with stirring and then stirred over night. Solvent was removed in vacuo. The residue was taken up with 30 ml of pentane and filtered. The clear filtrate was concentrated in vacuo and the product crystallized at −30 °C to yield 523 mg (65%) of **9a**. Anal. Calc. for $C_{20}H_{29}N_3Zr$ (M = 402.22): C, 59.65; H, 7.262; N, 10.43. Found: C, 58.81; H, 7.52; N, 10.60%. ^{1}H NMR (benzene-d_6, 599.9 MHz): δ = 6.27 (m, 2H, 14-H/15-H), 6.23 (m, 2H, 2-H/3-H), 5.90 (m, 2H, 13-H/16-H), 5.88 (m, 2H, 1-H/4-H), 5.48 (s, 1H, 8-H), 5.09 (m, 1H, 7-H), 4.94 (m, 1H, 7-H′), 2.88 (s, 12H, Zr(NMe_2), 2.33 (s, 6H, C(NMe_2)). ^{13}C NMR (benzene-d_6, 150.8 MHz, 298K): δ = 148.9 (C-9), 141.8 (C-6), 132.1 (C-5), 124.7 (C-12), 113.4 (C-2/C-3), 113.3 (C-14/C-15), 109.0 (C-13/C-16), 107.7 (C-7), 106.5 (C-1/C-4), 104.0 (C-8), 49.5 (C-17/C-18)/C-19/C-20), 41.4 (C-10/C-11).

*4.8.5.2. X-ray crystal structure analysis of complex **9a**.* Single crystals from pentane at −30 °C: Formula $C_{20}H_{29}N_3Zr$, M = 402.68, yellow crystal 0.30 × 0.25 × 0.10 mm, a = 20.818(1) Å, b = 8.438(1) Å, c = 21.598(1) Å, V = 3794.0(5) Å^3, ρ_{calc} = 1.410 g cm^{-3}, μ = 5.86 cm^{-1}, empirical absorption correction (0.844 ⩽ T ⩽ 0.944), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 0.71073 Å, T = 198 K, ω and φ scans, 21,307 reflections collected (h, k, l), [(sin θ)/λ] = 0.66 Å^{-1}, 4522 independent (R_{int} = 0.042) and 3716 observed reflections [$I \geqslant 2\sigma(I)$], 208 refined parameters, R = 0.032, wR^2 = 0.079, maximum residual electron density 0.46 (−0.62) e Å^{-3}, hydrogens calculated and refined as riding atoms.

*4.8.6. X-ray crystal structure analysis of the CpZrCl$_3$(morpholine) dimer **14***

Formula $C_{18}H_{28}Cl_6N_2O_2Zr_2$, M = 699.56, yellow crystal 0.25 × 0.20 × 0.10 mm, a = 9.585(1) Å, b = 7.105(1) Å, c = 17.942(1) Å, β = 91.72(1) Å, V = 1221.3(2) Å^3, ρ_{calc} = 1.902 g cm^{-3}, μ = 15.29 cm^{-1}, empirical absorption correction via ψ scan data (0.701 ⩽ T ⩽ 0.862), Z = 2, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 2546 reflections collected (h, $-k$, $+l$), [(sin θ)/λ] = 0.62 Å^{-1}, 2469 independent (R_{int} = 0.025) and 1993 observed reflections [$I \geqslant 2\sigma(I)$], 139 refined parameters, R = 0.025, wR^2 = 0.057, maximum residual electron density 0.46 (−0.33) e Å^{-3}, hydrogen at N10 from difference Fourier map and refined free, others calculated and refined as riding atoms.

*4.8.7. Reaction of complex **13f** with HB(C$_6$F$_5$)$_2$, formation of bis(vinylcyclopentadienyl)zirconium dichloride (**17**) and the aminoborane **18***

The zirconium complex **13f** (112 mg, 202 μmol) was dissolved in 10 ml of toluene. A solution of 140 mg (404 μmol) of $HB(C_6F_5)_2$ in 5 ml of toluene was added dropwise with stirring at ambient temperature. The mixture was stirred for 12 h at room temperature. Solvent was removed in vacuo and the residue extracted with pentane (2 × 15 ml). Bis(vinylcyclopentadienyl)$ZrCl_2$ (**17**, 175 mg, 96% yield) was recovered from the combined pentane extracts. The residue from the pentane extraction was dried in vacuo and identified as **18** (68 mg, 98% recovered). Complex **17**: ^{1}H NMR (benzene-d_6, 599.87 MHz): δ = 6.33 (dd, 1H, 6-H, $^3J_{cis}$ = 10.7 Hz, $^3J_{trans}$ = 16.8 Hz), 6.02 (m, 2H, 2-H/3-H), 5.80 (m, 2H, 1-H/4-H), 5.29 (dd, 1H, 7-H, ^2J = 1.1 Hz, $^3J_{trans}$ = 16.8 Hz), 5.02 (dd, 1H, 7-H′, ^2J = 1.1 Hz, $^3J_{cis}$ = 10.7 Hz) ppm. ^{13}C NMR (benzene-d_6, 150.84 MHz): δ = 130.0 (C-6), 127.1 (C-5), 115.8 (C-7), 115.3 (C-2/C-3), 114.6 (C-1/C-4) ppm.

Compound **18**: ^{1}H NMR (benzene-d_6, 599.87 MHz): δ = 6.86–6.79 (m, 4H, *o*-, *m*-Ph), 6.77 (m, 1H, *p*-Ph), 2.72 (s, 3H, CH_3) ppm. ^{13}C NMR (benzene-d_6, 150.84 MHz): δ = 147.3 (*ipso*-), 129.4 (*m*-), 127.4 (*p*-), 125.8 (*o*-Ph), 43.2 (CH_3) ppm. C_6F_5 resonances not located. ^{11}B NMR (benzene-d_6, 64.2 MHz): δ = 35.4 ppm. ^{19}F NMR (benzene-d_6, 282.4 MHz): δ = −162.8, −161.4, −151.9, −151.0, −131.5 ppm.

*4.8.8. Reaction of complex **13c** with HB(C$_6$F$_5$)$_2$, preparation of **19A/B***

Complex **13c** (70 mg, 137 μmol) was dissolved in 15 ml of toluene. A solution of 95 mg (274 μmol) of $HB(C_6F_5)_2$ in 5 ml of toluene was added dropwise with stirring. The mixture was stirred for 48 h at room temperature. Solvent was removed in vacuo and the residue washed with pentane (2 × 5 ml). The remaining solid was dried in vacuo to yield 134 mg (81%) of a 2:3 mixture of the *rac*- and *meso*-isomers of product **19** (isomers **19A** and **19B**), m.p. 109 °C (decomp.). Anal. Calc. for $C_{48}H_{34}N_2B_2F_{20}ZrCl_2$ (M = 1202.5): C, 47.94; H, 2.85; N, 2.33. Found: C, 48.23; H, 3.69; N, 2.25%. ^{1}H NMR (benzene-d_6, 599.87 MHz, isomer **A**): δ = 6.41 (m, 1H, Cp–H), 6.09 (m, 1H, Cp–H), 5.97 (m, 1H, Cp–H), 5.64 (m, 1H, Cp–H), 4.74 (dd, 1H, 6-H, $^3J_{7\text{-H}}$ = 6.8 Hz, $^3J_{7\text{-H}'}$ = 12.6 Hz), 2.95 (m, 2H, 8-H), 2.59 (m, 2H, 12-H), 2.34 (dd, 1H, 7-H, $^3J_{6\text{-H}}$ = 6.8 Hz, $^2J_{7\text{-H}'}$ = 12.6 Hz), 1.66 (t, 1H, 7-H′, $^3J_{6\text{-H}}$ = $^2J_{7\text{-H}}$ = 12.6

Hz), 1.16 (m, 2H, 9-H), 0.95 (m, 2H, 10-H), 0.64 (m, 2H, 11-H) ppm. ^{13}C NMR (benzene-d_6, 150.84 MHz, isomer **A**): δ = 129.2 (C-5), 123.9, 118.6, 114.1, 107.5 (C-1/C-2/C-3/C-4), 69.1 (C-6), 56.9 (C-8), 47.7 (C-12), 21.6 (C-9/C-11), 21.2 (C-10), 19.4 (br, C-7) ppm. C_6F_5 resonances not located. ^{1}H NMR (benzene-d_6, 599.87 MHz, isomer **B**): δ = 6.18 (m, 1H, Cp–H), 6.10 (m, 1H, Cp–H), 5.98 (m, 1H, Cp–H), 5.67 (m, 1H, Cp–H), 4.75 (dd, 1H, 6-H, $^3J_{7\text{-H}}$ = 6.8 Hz, $^3J_{7\text{-H}'}$ = 12.9 Hz), 2.95 (m, 2H, 12-H), 2.43 (m, 2H, 8-H), 2.42 (m, 1H, 7-H), 1.69 (t, 1H, 7-H′, $^3J_{6\text{-H}}$ = 12.9 Hz), 0.95 (m, 2H, 9-H), 0.86 (m, 2H, 10-H), 0.02 (m, 2H, 11-H) ppm. ^{13}C NMR (benzene-d_6, 150.84 MHz, isomer **B**): δ = 128.8 (C-5), 120.1, 117.8, 117.4, 108.7 (C-1/C-2/C-3/C-4), 69.5 (C-6), 56.9 (C-8), 47.4 (C-12), 22.1 (C-9), 21.7 (C-11), 21.2 (C-10), 19.4 (br, C-7) ppm. ^{11}B NMR (benzene-d_6, 64.2 MHz, both isomers): δ = 2.76 ppm. ^{19}F NMR (benzene-d_6, 282.4 MHz, both isomers): δ = −162.4, −162.3, −156.2, −154.7, −128.3, −127.3 ppm. IR (KBr): $\tilde{\nu}$ = 2961 (m), 2949 (m), 2866 (w), 1645 (m), 1635 (m), 1533 (m), 1517 (s), 1464(vs), 1283 (m), 1262 (m), 1099 (s), 970 (s), 817 (s) cm $^{-1}$.

*4.8.9. Reaction of complex **13d** with HB(C_6F_5)$_2$, preparation of **20AlB***

Analogously as described above the reaction of complex **13d** (98 mg, 190 μmol) with HB(C_6F_5)$_2$ (132 mg, 380 μmol) in a total of 20 ml of toluene gave 150 mg (65%) of a 3:4 mixture of the *rac*- and *meso*-isomers of product **20** (isomers **20A** and **20B**), m.p. 97 °C (decomp.). Anal. Calc. for $C_{46}H_{30}N_2O_2B_2F_{20}ZrCl_2$ (M = 1206.4): C, 45.80; H, 2.51; N, 2.32. Found: C, 46.24; H, 2.85; N, 2.09%. ^{1}H NMR (benzene-d_6, 599.87 MHz, isomer **A**): δ = 6.28 (m, 1H, Cp–H), 6.00 (m, 1H, Cp–H), 5.91 (m, 1H, Cp–H), 5.55 (m, 1H, Cp–H), 4.69 (dd, 1H, 6-H, $^3J_{7\text{-H}}$ = 7.0 Hz, $^3J_{7\text{-H}'}$ = 12.4 Hz), 3.52 (m, 1H, 9-H), 3.22 (m, 3H, 8-H/8-H′/10-H), 3.11 (m, 1H, 9-H′), 3.10 (m, 1H, 11-H), 2.89 (m, 1H, 10-H′), 2.28 (dd, 1H, 7-H, $^3J_{6\text{-H}}$ = 7.0 Hz, $^2J_{7\text{-H}'}$ = 12.4 Hz), 2.26 (m, 1H, 11-H′), 1.76 (m, 1H, 7-H′) ppm. ^{13}C NMR (benzene-d_6, 150.84 MHz, isomer **A**): δ = 136.9 (C-5), 122.7, 118.9, 115.4, 108.5 (C-1/C-2/C-3/C-4), 69.4 (C-6), 68.2 (C-9), 62.1 (C-10), 55.6 (C-8), 48.9 (C-11), 19.2 (C-7) ppm. ^{1}H NMR (benzene-d_6, 599.87 MHz, isomer **B**): δ = 6.12 (m, 1H, Cp–H), 5.95–5.94 (m, 1H, Cp–H), 5.92 (m, 1H, Cp–H), 5.56 (m, 1H, Cp–H), 4.71 (dd, 1H, 6-H, $^3J_{7\text{-H}}$ = 6.9 Hz, $^3J_{7\text{-H}'}$ = 13.0 Hz), 3.29 (m, 2H, 9-H/9-H′), 3.01 (m, 1H, 11-H), 2.74 (m, 1H, 11-H′), 2.34 (dd, 1H, 7-H, $^3J_{6\text{-H}}$ = 6.9 Hz, $^2J_{7\text{-H}'}$ = 13.0 Hz), 2.26 (m, 2H, 10-H/10-H′), 2.10 (m, 2H, 8-H/8-H′), 1.74 (m, 1H, 7-H′) ppm. ^{13}C NMR (benzene-d_6, 150.84 MHz, isomer **B**): δ = 138.6 (C-5), 120.4, 117.7, 117.2, 109.1 (C-1/C-2/C-3/C-4), 69.7 (C-6), 67.7 (C-9), 61.8 (C-10), 55.6 (C-8), 50.3 (C-11), 19.2 (C-7) ppm. ^{11}B NMR (benzene-d_6, 64.2 MHz, both isomers): δ = 2.52 ppm. ^{19}F NMR (benzene-d_6, 282.4 MHz, both isomers): δ = −162.1, −160.5, −154.7, −151.3, −127.7, −122.9 ppm. IR (KBr): $\tilde{\nu}$ = 2978 (m), 2962 (s), 2874 (m), 1656 (s), 1527 (vs), 1470 (vs), 1403 (s), 1269 (vs), 1320 (s), 1098 (vs), 980 (vs), 814 (s), 742 (s), 696 (s) cm^{-1}.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 236337–236342. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

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