Evidence for Internal Ion Pair Formation upon Insertion of Reactive Alkenes in the Zirconium–Carbon Bond of the $Cp_2Zr(\mu\text{-}C_4H_6)B(C_6F_5)_3$ Metallocene-Boron-Betaine Ziegler Catalyst System

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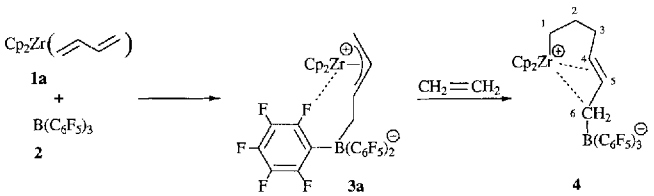
Treatment of the (butadiene)ML_2 complexes **1** [ML_2 = Cp_2Zr (**a**), Cp_2Hf (**b**), and $(\eta\text{-}C_5H_4CH_3)_2Zr$ (**c**)] with $B(C_6F_5)_3$ gives the 1:1 addition products $(CH_2CHCHCH_2{-}B(C_6F_5)_3)ML_2$ (**3a**–**c**). At −40°C the betaine complex **3a** inserts one equivalent of methylenecyclopropane to give the regioisomeric insertion products **5a** and **6a** in a 60:40 ratio. These products exhibit the cyclopropylidene moiety in the α- and β-positions, respectively, relative to zirconium. The corresponding hafnocene complexes **5b** and **6b** are obtained in a 70:30 ratio starting from **3b**. The reaction of **3**(**a**–**c**) with allene gives a single insertion product (**7a**–**c**) in each case where the *exo*-methylene group is in the α-position to the metal center ([2,1]-insertion). The complexes **5**–**7** are chiral. They all exhibit a pronounced π-interaction of the internal $-C^4H{=}C^5H-$ double bond of the σ-ligand chain with the metal center in addition to a metallocene/$-C^6H_2-$[B] ion pair interaction. The relative contributions of these two components to the intramolecular stabilization of the cationic metallocene end of the dipolar complexes **5**–**7** are quite dependent on the steric and electronic properties of the respective metallocene units involved. This is revealed by a comparison of typical ^{13}C-NMR parameters of the complexes **5**–**7** with a pair of suitable model complexes, namely the ethylene insertion product **4** into the betaine system **3a** and its THF adduct **4**·THF.

Introduction

Metallocene Ziegler catalysts have become of great practical importance in recent years[1]. In addition they have found a rather general academic interest since they represent molecular catalysts of a rather small degree of complexity (as compared to e.g. the enzymatic catalyst systems) that in some cases may exhibit very high selectivities at extremely high reaction rates. Thus, the metallocene Ziegler catalysts may become ideal molecular objects to study the general functioning of homogeneous catalysts that are extremely reactive and selective at the same time.

We have recently described a single component metallocene Ziegler catalyst system that may turn out to be ideally suited to study some reaction steps involved in the CC-coupling of simple substrates at such catalyst systems[2]. It is generated by addition of the organometallic Lewis acid tris(pentafluorophenyl)borane (**2**)[3] to (butadiene)zirconocene (**1a**)[4]. The resulting addition product **3a** rapidly polymerizes α-olefins at ambient conditions. At low temperature, the reaction can be stopped after the insertion of e.g. one equivalent of ethene at the stage of product **4**[5]. This compound is chiral. In contrast to **3a** it does not contain measurable zirconium F–C interaction[6]. Therefore, internal ion-pair formation leading to a close zirconium to carbon contact[7] was assumed. We have now carried out a series of additional experiments, including the stoichiometric insertion of reactive olefins other than ethylene, that has provided supporting evidence for this type of internal ion-pair character of these products, and at the same time has revealed subtle differences in the interactions between the metal and the carbon ligand chain within a series of such compounds. Details of a number of representative examples are described in this paper.



Results and Discussion

Generation of the Alkene Insertion Products: In this study we have generated the betaine systems **3** in situ by treatment of the respective (butadiene)metallocenes **1a**–**c** (metallocene = Cp_2Zr (**a**), Cp_2Hf (**b**)[8], $(MeCp)_2Zr$ (**c**)) with $B(C_6F_5)_3$ in [D_8]toluene solution. Although we had previously shown that the metallocene betaines **3** can be isolated as pure compounds[2], the in situ generation was more practical because in this way higher product concentrations were achieved at the low temperatures that were necessary to keep the subsequently formed alkene insertion products

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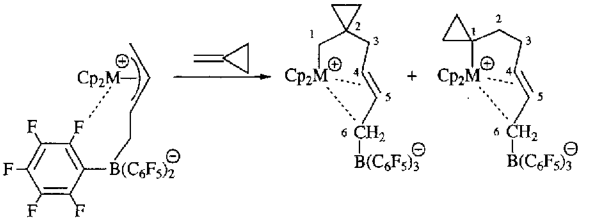
stable. The alkene insertion products turned out to be rather labile and in most cases decomposed rapidly at temperatures above 0 °C. Therefore, these products were not isolated but spectroscopically identified and characterized in [D$_8$]toluene solution. This required the use of a combination of 2D-NMR experiments (usually GCOSY plus a GHSQC experiment[9]) in each case. Together with a suitable pair of reference molecules, namely **4**[5] and its THF donor ligand adduct **4**·THF (see below), this has allowed for a rather detailed description of the primary insertion products of the reactive alkenes into the Zr–C bond of the metallocene betaine systems **3**.

The first reactive olefin used in this study was methylenecyclopropane[10]. It had previously been shown that it is one of the very few disubstituted alkenes that can be coupled at homogeneous metallocene Ziegler type catalysts. Usually, the three-membered ring is opened during the resulting multistep process[11]. Methylenecyclopropane reacts rapidly with the (butadiene)ZrCp$_2$/B(C$_6$F$_5$)$_3$ derived betaine system **3a** at −40 °C. Under these conditions the reaction is stopped after the insertion of one monomer molecule and the three-membered ring structure is retained. The reagent just reacts and inserts as a reactive alkene. Two regioisomeric products can be formed. They are both obtained in a ratio of 60:40. This is very different from the reaction of the betaine **3a** with propene that gave only one regioisomer, namely the complex bearing the methyl group at the 2-position of the resulting six-carbon chain connecting zirconium and boron[5].



3 M = Zr (a), Hf (b) **5** **6**

In the case of the methylenecyclopropane insertion, the major isomer is the one that has the C2 atom as a part of the three-membered ring. The isomers **5a** and **6a** can be distinguished from each other spectroscopically. Both compounds are chiral. Thus the major isomer **5a** exhibits a pair of ^{1}H/^{13}C-NMR signals at δ 5.32, 5.07/110.9, 109.5. The CH$_2$ groups of the cyclopropylidene moiety are diastereotopic (^{13}C-NMR resonance signals at δ 15.7 and 14.8), and so are the pairs of hydrogen atoms at C1 (^{1}H-NMR signals of 1-H, 1-H' at δ −1.35 and 1.64 with ^2J = 13.7 Hz) and C6 (δ −0.02 and 0.79; the signals are broadened due to the adjacent boron nucleus). The ^{13}C-NMR resonance signal of the $-C^6H_2-[B]$ carbon atom of the major regioisomer **5a** is observed at δ 7.0. As we shall see later this is an indication of a zirconium···C^{6}H$_2$–[B] ion-pair type interaction. In addition, the ^{13}C-NMR chemical shifts of the olefinic carbon centers of the $-C^4H{=}C^5H$ moiety (δ 146.0 and 123.7) also indicate that there is a pronounced metal–olefin π-interaction present in complex **5a**[12]. Details of this interaction which seems to be very typical for this class of compounds will be discussed later in this paper when a suitable pair of reference molecules has been described (see below).

The minor regioisomer **6a** is also chiral and thus exhibits the ^{1}H/^{13}C NMR signals of a pair of diastereotopic Cp ligands (δ 5.18, 5.04/112.4, 112.3). Again, the methylene groups of the three-membered ring are diastereotopic (δ 20.0 and 19.5), as are the $-C^6H_2-[B]$ hydrogen atoms (δ −0.12 and 0.39). The ^{13}C NMR signals of the $-C^4H{=}C^5H$ group in **6a** (δ 140.1 and 130.5) are closer together than in the isomer **5a**.

The analogous insertion reaction of methylenecyclopropane takes place starting from the [Cp$_2$Hf(μ-C$_4$H$_6$)B(C$_6$F$_5$)$_3$] betaine **3b**. Again, two regioisomers **5b** (with C2 being part of the three-membered ring) and **6b** are formed, now in a 70:30 ratio. Again, both regioisomers are chiral and should be regarded as internal ion-paired/alkene-coordinated compounds (see Table 1 for a compilation of characteristic ^{13}C-NMR data).

Table 1. Selected ^{13}C-NMR data of the alkene insertion products **4-7** [a]

	Metallocene	C1	C2	C3	C4	C5	C6
5a	Cp$_2$Zr	55.7	37.2	43.2	146.0	123.7	7.0
6a	Cp$_2$Zr	[b]	51.0	29.7	140.1	130.5	[b]
5b	Cp$_2$Hf	56.8	28.4	43.9	140.7	129.2	14.1
6b	Cp$_2$Hf	49.6	42.5	32.2	135.3	134.6	[b]
7a	Cp$_2$Zr	192.9	52.9	31.0	141.2	126.9	7
7b	Cp$_2$Hf	199.3	45.0	32.4	135.8	133.3	16
7c	(MeCp)$_2$Zr	197.1	50.7	29.6	137.2	131.3	8
4	Cp$_2$Zr [c]	49.2	42.6	34.7	146.4	123.6	4
4·THF	Cp$_2$Zr [d]	71.4	35.2	39.8	124.9	137.3	29.3

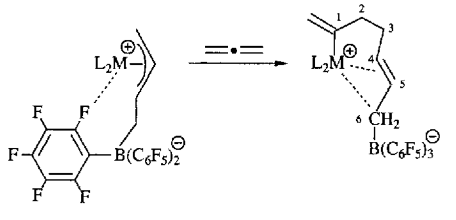
[a] In [D$_8$]toluene at 233 K unless otherwise noted, complexes **5** contain the substituent at C2, **6** at C1. – [b] Not located. – [c] From ref. [5], 238 K. – [d] [D$_8$]THF, 299 K.

We next employed allene in the insertion reaction. It was known from Jordan's and Horton's work that allene had a tendency to form (π-allyl)metallocene cations when treated with [(MeCp)$_2$ZrH(THF)$^+$] or [Cp*$_2$ZrCH$_3^+$], respectively[13]. Thus, in these cases, the reactive hydride or alkyl anion equivalent added to the central sp-carbon atom of the cumulene reagent.

This is distinctly different in the case of the reaction of the betaine system **3** with the allene reagent. Complex **3a** reacts instantaneously with allene at −35 °C in [D$_8$]toluene solution. The reaction is strictly stoichiometric under these conditions and stops after the insertion of one molar equivalent of allene. A single organometallic insertion product (**7a**) is obtained. The product is chiral, as is evident from the observation of the ^{1}H/^{13}C-NMR signals of a pair of diastereotopic η-cyclopentadienyl ligands at zirconium (δ 5.23, 5.22/111.5, 111.3 at 238 K in [D$_8$]toluene, 600/150 MHz).

The persistent chirality of the product under these conditions again indicates that a metallacyclic structure has been obtained. From the characteristic ^{13}C-NMR features (Table 1, for a detailed discussion see below) ion-pairing/

internal coordination between the $-C^4H=C^5H-C^6H_2-[B]$ end of the resulting σ-ligand carbon chain and the electrophilic positively polarized zirconium center must be assumed. The ^{19}F NMR spectrum of **7a** shows three typical features at δ −134.0, −165.8 and −160.7 for the *o*-, *m*-, and *p*-fluorine substituents of the $B(C_6F_5)_3$ group with no indication for signal broadening at low temperature due to metal···F−C interaction. The chemical shift difference between the *m*-F and *p*-F resonance of $\Delta \approx 5$ ppm is in the range that has been proposed to be indicative for the presence of $Zr\cdots C^6H_2-B(C_6F_5)_3$ ion pairing[14].



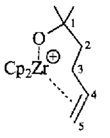
3 **7**

$L_2M = Cp_2Zr$ (a), Cp_2Hf (b), $(MeCp)_2Zr$ (c)

The most noteworthy observation in the reaction between the betaine **3a** and allene at low temperature is that a single regioisomeric insertion product is formed, and that it is the isomer that contains an *exo*-methylene group at the C1 position of the linear six-carbon-containing σ-ligand chain. This clearly follows from the spectroscopic characterization of the product **7a**. The ^{13}C-NMR spectrum exhibits the very characteristic low field signal of the quat. $C^1=CH_2$ alkenyl carbon bound to zirconium at δ 192.9[15]. The ^{13}C-NMR resonance of the adjacent $=CH_2$ group is observed at δ 125.2. The ^1H-NMR resonances of the $C^1=CH_2$ *exo*-methylene group are very different at δ 5.38 and 3.87, which is probably due to a pronounced anisotropy effect caused by the chiral metallocene−σ-ligand framework.

The betaine complexes **3b** and **3c** react with allene analogously. In each case a single regioisomeric mono-insertion product is obtained, which is chiral (**7b**, **7c**). In both these cases the *exo*-methylene group in the product is located at the α-position to the metallocene. The chirality is due to internal ion pairing and $-C^4H=C^5H$ coordination to zirconium although there are subtle differences in the strength of this coordination between the different metallocene product systems (see Table 1 and the discussion below). All these mono-insertion products are rather unstable. They rapidly decompose unspecifically when allowed to warm to ca. 0°C. Therefore, they were not isolated as yet.

Assessment of the Internal Coordination Features in the Products **5**−**7**: The persistent chirality of the systems **5**−**7** indicates the presence of cyclic product structures that contain an internal ion pair or coordinative interaction of the $-C^4H=C^5H-C^6H_2-[B]$ end group of the σ-ligand chain with the zirconium center. This pronounced intramolecular interaction is probably due to the dipolar character of the $L_2M^+-[X]-CH=CH-CH_2-[B]^-$ chain. The resulting high electrophilicity at the metallocene end of the product betaine structure at the same time opens up an attractive possibility for internal olefin coordination (i.e. of the $-C^4H=C^5H$ double bond) to the incipient metallocene cation. To qualitatively assess the participation of the $-C^4H=C^5H$ coordination to zirconium relative to simple ion pairing between zirconium and the $-C^6H_2-[B]$ end of the dipole a suitable spectroscopic reference system had to be developed.



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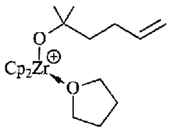
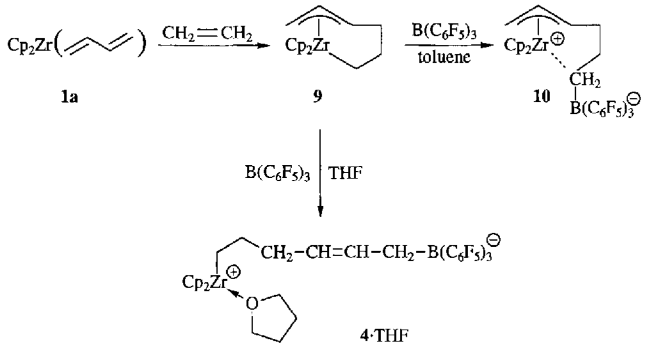


8·THF

Jordan has recently demonstrated that ^{13}C NMR spectroscopy is a powerful tool to detect intramolecular olefin coordination to a zirconocene cation[16][17]. When a pair of related (ω-alkenyloxy)zirconocene cations (e.g. **8**/**8**·THF) was investigated, the transition between the system with a free alkenyl group (**8**·THF) and the internally coordinated alkenyl ligand (**8**) was monitored by a very characteristic alteration in the ^{13}C NMR chemical shift pattern. In the uncoordinated alkenyl situation (i.e. complex **8**·THF) the $-C^4H=C^5H_2$ ^{13}C NMR chemical shifts are at δ 138.1 and 115.1. The alkenyl coordinated situation (i.e. complex **8**) is characterized by a ^{13}C NMR shift situation relative to the uncoordinated situation where the internal $-C^4H$ resonance is shifted substantially to a larger δ value (158.8) and the $=C^5H$ ^{13}C NMR resonance in the opposite direction to a smaller δ value (94.3). Thus, in the model compound **8** internal coordination of the terminal alkenyl group is monitored by very pronounced ^{13}C NMR coordination shifts of the $-C^4H=C^5H_2$ carbon atoms in opposite directions: $\Delta\delta \approx -20$ ppm for $-C^4H=$ and $\Delta\delta \approx +20$ ppm for $=C^5H_2$.

Apparently, a suitable pair of reference systems relevant to our study would be the ethylene insertion product **4** into the betaine system **3a** and its THF adduct **4**·THF. We were able to generate the required complex **4**·THF by means of an alternative synthetic route. We had previously shown that (butadiene)zirconocene (**1a**) reacts rapidly with ethene to yield the metallacyclic (π-allyl)metallocene complex **9**[18]. Treatment of **9** with $B(C_6F_5)_3$ in a non-coordinating solvent, as expected gives rise to cleavage of the zirconium-sp^3-carbon σ-bond to generate **10** (for details see the Experimental Section). In the presence of a sufficient amount of the donor ligand tetrahydrofuran the reaction between **9** and $B(C_6F_5)_3$ takes a different course. In $[D_8]$THF solution the Lewis acid tris(pentafluorophenyl)borane (**2**) exclusively adds to the terminal carbon center of the π-allyl group with a clean generation of the THF adduct of complex **4** (i.e. **4**·THF).

As expected, complex **4**·THF is no longer chiral ($^1H/^{13}C$ NMR Cp signals at δ 6.53/115.6). Also THF addition to the zirconium center has resulted in a change of the $-C^1H_2-$ ^{13}C NMR chemical shift from δ 49.2 (**4**) to 71.4 (**4**·THF). The $-C^2H_2-C^3H_2-$ resonances are only marginally changed whereas the $-C^4H=C^5H-[B]$ unit has experienced a major alteration of its ^{13}C NMR chemical shifts



upon formally going from **4** to its donor ligand adduct **4**·THF. In **4**·THF the $-C^4H$ = ^{13}C NMR resonance occurs at δ 124.9, the $=C^5H$ signal is at δ Symbol '137.3. Thus, a comparison between the pairs of compounds **4**·THF and **4** reveals ^{13}C NMR coordination shifts of $\Delta\delta \approx -21$ ppm for $-C^4H=$ and $\Delta\delta \approx +\ 14$ ppm for $=C^5H-$ which are in the same direction and of the same order of magnitude as observed for Jordan's example (**8/8**·THF, see above). We thus conclude that there is a pronounced internal $-C^4H=C^5H-$ alkene coordination present in the ethene insertion product **4**, that is easily detected from its very characteristic ^{13}C NMR spectra. In addition, there is also evidence for a zirconium···$C^6H_2-[B]$ interaction in **4**. The corresponding $-C^6H_2-$ ^{13}C NMR resonance in **4** is at δ 4 , which is changed to δ 29.3 in its THF adduct. We thus conclude, that a comparison of the ^{13}C NMR spectra of **4** and its THF adduct (**4**·THF) clearly indicates a pronounced interaction of the $C^4H=C^5H-C^6H_2-$ part of the σ-ligand system in **4** with the electrophilic metal center. The $C^4H=C^5H-$/Zr coordinative interaction appears to be strongly supplemented with a $CH_2-[B]$/Zr ion pair interaction (or vice versa).

It is remarkable how well these data fit the situation encountered in the product **5a** obtained from the reaction between the betaine **3a** and methylenecyclopropane. The $-C^4H=C^5H-$ ^{13}C-NMR chemical shifts of the major regioisomer **5a** at δ 146.0 and 123.7 (see Table 2) are practically identical to the corresponding C^4/C^5 resonances of complex **4** (δ 146.4/123.6). Also the $-C^6H_2-[B]$ ^{13}C NMR resonances of both **4** and **5a** are very similar (see Table 1). This indicates an almost indistinguishable internal coordination situation for these two complexes. Attaching the cyclopropylidene-derived substituents at C2 of the σ-ligand chain does apparently not influence or disturb the typical coordination mode of the $-C^4H=C^5H-C^6H_2-[B]$ unit to the incipient metallocene cation.

Slight differences are observed for the other regioisomer. From the data compilated in Table 1 it appears that the $-C^4H=C^5H-$ group of **6a** exhibits slightly smaller ^{13}C NMR coordination shifts of both the $-C^4H=$ ($\Delta\delta \approx -14$ ppm relative to ca. -21 ppm for **5a**) and the $=C^5H-$ group ($\Delta\delta \approx +7$ ppm relative to ca. $+14$ ppm for **5a**). Thus it appears that the presence of the bulky α-substituents in **6a** makes the internal alkene coordination to the metallocene unit slightly less favourable.

A similar effect is observed when the Cp_2Hf unit is introduced. In this case, the $-C^4H=C^5H-$ ^{13}C NMR chemical shifts of the major isomer **5b** are almost identical to those previously found for the minor **6a** zirconocene isomer. The $-C^6H_2-[B]$ resonance at δ 14.1 (**5a**: δ 7.0) indicates a slightly reduced metallocene···$CH_2[B]$ ion pair interaction. Again, the internal $-C^4H=C^5H-$ coordination is further diminished in the minor isomer **6b** (δ 135.3/134.6).

Siminar effects are observed in the **7a**−**7c** series of complexes. Again, very pronounced coordination shifts of the $-C^4H=C^5H-$ group are observed (**7a**: δ 141.2/126.9) that become equally smaller upon either going to the hafnocene system **7b** (δ 135.8/133.3) or to the bis(methylcyclopentadienyl)zirconium system **7c** (δ 137.2/131.3). Thus it appears that here the electronic influence of the varied electrophilicity of the respective metallocene unit on the internal alkene coordination becomes visible.

Conclusions

The first point that merits attention is the observed regiochemistry of the alkene insertion into the Zr−C bond of the starting material **3a**. Insertion of methylenecyclopropane gives rise to the formation of both regioisomers **5** and **6** in contrast to the selective [1,2]-insertion of propene[5]. The lower regioselectivity of the methylenecyclopropane insertion reaction is probably due to the much higher reactivity of the strained alkene; we assume that it results from a normal reactivity/selectivity behavior of this organometallic alkene insertion system.

Allene reacts with the complexes **3** selectively by [2,1]-insertion. This is opposite of what is usually observed in organometallic allene CC-coupling reactions involving nucleophilic hydrocarbyl additions at early transition metal centers, that mostly represent [1,2]-additions leading to 2-substituted (π-allyl)metal complexes[13]. In the case of a group 4 bent metallocene [1,2]-insertion of allene would inevitably first lead to a σ-allyl complex[19], that would only subsequently rearrange to the more stable (π-allyl)metallocene isomer. The insertion step itself would, therefore, not profit energetically from π-allyl complex formation.

Let us next consider the intramolecular coordination of the $-C^4HC^5H-C^6H_2-[B]$ unit in the products **4**−**7**. We think that our study convincingly shows that both possible modes of internal $Zr/C^4H=C^5H-C^6H_2-[B]$ interaction are involved and used for internal stabilization of the electrophilic zirconocene center in these dipolar complexes, namely internal ion pair interaction between zirconium and the nucleophilic borate $-C^6H_2$ carbon *and* intramolecular π-coordination of the internal $-C^4H=C^5H-$ double bond to the positively charged metallocene moiety. A comparison of the characteristic ^{13}C NMR features reveals a very sensitive response of this $Zr/-CH=CH-$ π-interaction to the steric and electronic features around the metallocene unit. In the methylenecyclopropane insertion product series the 2,2-disubstituted major products **5** appear to bind the olefin slightly stronger than their 1,1-disubstituted isomers (see Table 1). Hafnium complexes show a slightly less favoured π-interaction[20]. The same trend is seen in the **7a**-**7c** series.

In the specific coordinative situation encountered here, the Cp_2Zr unit binds the internal alkene slightly better than Cp_2Hf. Increasing the electron density at the metal center by additional methyl substituents (**7c**) leads to a typical ^{13}C NMR response indicating a slight reduction of the Zr/$-C^4H{=}C^5H-$ π-interaction (see Table 1).

The homogeneous metallocene Ziegler catalyst systems are rather bad catalysts for the conversion of most internal alkenes. Therefore, it is remarkable that we have now found a number of systems such as the complexes **4**−**7** where intramolecular π-coordination of a 1,2-disubstituted alkene (that here is, of course, part of the σ-ligand system) to the metallocene apparently leads to a substantial stabilization of the observed product. It could be that coordination of disubstituted alkenes to group 4 metallocene cations might not create such an unfavourable situation as previously thought. Investigations aimed at finding out which step actually makes the involvement of 1,1- and 1,2-dialkyl-substituted alkenes in homogeneous Ziegler catalysis so disfavoured, namely the alkene coordination or actually the carbon−carbon coupling step, are currently being carried out in our laboratory.

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Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The complexes **4**−**7** were generated in a suitable deuterated solvent under the conditions given below and characterized by NMR spectroscopy using a Varian Unity plus NMR spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz). Usually the following 2D-NMR experiments were used in addition to 1D NMR measurements: GHSQC (gradient pulsed heteronuclear single quantum coherence), GHMBC (gradient pulsed heteronuclear multiple bond coherence), GCOSY (gradient pulsed correlated spectroscopy)[9]. Due to the instability of the insertion products at higher temperature (≥0°C) no attempt was made to isolate the products **4**−**7**. Although complexes **3** were isolated by us previously[2] they were in situ generated from the respective Cp_2M(butadiene) starting material and $B(C_6F_5)_3$. Complex **9** was prepared as previously described by us[18]. We thank Professor *P. Binger* for a gift of methylenecyclopropane.

Reaction of the Group 4 Metallocene-(μ-C_4H_6)-borate Betaines **3** *with Alkenes. − General Procedure:* The betaine **3** (0.10 mmol) was generated by treatment of the respective (butadiene)metallocene with $B(C_6F_5)_3$ in a 1:1 molar ratio in 1−2 ml of [D$_8$]toluene. The mixture was transferred to a 5-mm NMR tube and cooled to −40°C. The reactive olefin was then introduced into the solution as a gas (2−3 ml, ca. 0.1 mmol) by means of a thin glass capillary. The resulting product was then characterized by NMR spectroscopic techniques at the temperature indicated.

Reaction of the Betaine **3a** *with Methylenecyclopropane. − Formation of* **5a** *and* **6a**: (Butadiene)zirconocene **1a** (25 mg, 0.09 mmol) was reacted with 52 mg (0.1 mmol) of $B(C_6F_5)_3$ in [D$_8$]toluene. Subsequent treatment with 2−3 ml of gaseous methylenecyclopropane at −40°C gave a 60:40 mixture of **5a** and **6a**. Upon warming complex **6a** decomposed at −20°C, **5a** at 0°C. The spectroscopic characterization was, therefore, carried out at −40°C. Major isomer (**5a**): ^{1}H-NMR (599.9 MHz, 233 K, [D$_8$]toluene): δ = 6.36 (m, 1 H, 4-H), 5.67 (m, 1 H, 5-H), 5.32 (s, 5 H, Cp), 5.07 (s, 5 H, Cp), 1.64 (d, $^2J_{HH}$ = 13.7 Hz, 1 H, 1-H′), 1.50 (t, $^{2/3}J_{HH}$ = 12.0 Hz, 1 H, 3-H′), 0.79 (br. s, 1 H, 6-H′), 0.59 (m, 1 H, 3-H), 0.15, 0.11, 0.03, −0.25 (each m, each 1 H, 7-H,H′, 8-H,H′), −0.02 (br. s, 1 H, 6-H), −1.35 (d, $^2J_{HH}$ = 13.7 Hz, 1 H, 1-H). − ^{13}C-NMR (150.8 MHz, 233 K, [D$_8$]toluene): δ = 148.4 (d, $^1J_{CF}$ = 240 Hz, *o*-$B(C_6F_5)_3$), 146.0 (CH, C-4), 139.0 (d, $^1J_{CF}$ = 240 Hz, *p*-$B(C_6F_5)_3$), 137.4 (d, $^1J_{CF}$ = 240 Hz, *m*-$B(C_6F_5)_3$), 123.7 (CH, C-5), 114.4 (C, *ipso*-$B(C_6F_5)_3$), 110.9 (CH, Cp), 109.5 (CH, Cp), 55.7 (CH$_2$, C-1), 43.2 (CH$_2$, C-3), 37.2 (C, C-2), 14.8, 15.7 (each CH$_2$, C-7,8), 7.0 (br CH$_2$, C-6) . − GCOSY (599.9 MHz, 233 K, [D$_8$]toluene): δ = 6.36 (4-H)/5.67 (5-H), 1.50 (3-H′), 0.59 (3-H), 5.67 (5-H)/0.79 (6-H′), 1.64 (1-H′)/−1.35 (1-H), 1.50 (3-H′)/0.59 (3-H), 0.79 (6-H′)/−0.02 (6-H), 0.15, 0.11, 0.03, −0.25 (7-H,H′, 8-H,H′, all mutually coupled) . − GHSQC (599.9 MHz, 233 K, [D$_8$]toluene): δ = 146.0/5.63 (C-4), 123.7/5.67 (C-5), 110.9/5.07 (Cp), 109.5/5.32 (Cp), 55.7/1.64, −1.35 (C-1), 43.2/1.50, 0.59 (C-3), 15.7/0.03, −0.25, 14.8/0.15, 0.11 (C-7, C-8), 7.0/0.79, −0.02 (C-6) . − GHMBC (599.9 MHz, 233 K, [D$_8$]toluene): δ = 37.2 (C-2)/1.64 (1-H′), 1.50 (3-H′), −1.35(1-H), 14.8 (C-6 or C-7)/1.64 (1-H′), 1.50 (3-H′) . − ^{19}F-NMR (564.3 MHz, 233 K, [D$_8$]toluene): δ = −167.3 (t, $^3J_{FF}$ = 21 Hz, 6 F, *m*-F), −162.2 (t, $^3J_{FF}$ = 21 Hz, 3 F, *p*-F), −135.1 (d, $^3J_{FF}$ = 22 Hz, 6 F, *o*-F of $B(C_6F_5)_3$) . Minor isomer (**6a**): ^{1}H-NMR (599.9 MHz, 233 K, [D$_8$]toluene): δ = 6.07 (m, 1 H, 5-H), 6.01 (m, 1 H, 4-H), 5.18 (s, 5 H, Cp), 5.04 (s, 5 H, Cp), 1.22 (m, 1 H, 3-H′), 1.06 (m, 2 H, 3-H, 2-H′), 0.39 (br. s, 1 H, 6-H′), 0.28 (m, 1 H, 2-H), 0.10, −0.16, −0.45 (each m, 1 H, 1-H, 2-H, 7-H,H′, 8-H,H′), −0.12 (br. s, 1 H, 6-H). − ^{13}C-NMR (150.8 MHz, 233 K, [D$_8$]toluene): δ = 140.1 (CH, C-4), 130.5 (CH, C-5), 112.4 (CH, Cp), 112.3 (CH, Cp), 51.0 (CH$_2$, C-2), 29.7 (CH$_2$, C-3), 20.0, 19.5 (each CH$_2$, C-7,8) . − GCOSY (599.9 MHz, 233 K, [D$_8$]toluene): δ = 6.07 (5-H)/6.01 (4-H), 0.39 (6-H′), 6.01 (4-H)/1.23 (3-H′), 1.06 (3-H), 1.22 (3-H′)/1.06 (2-H′), 0.28 (2-H), 1.06 (2-H′, 3-H′)/0.28 (2-H), 0.39 (6-H′)/−0.12 (6-H), 0.10, −0.16, −0.45 (2x) (7-H,H′, 8-H,H′, all mutually coupled). − GHSQC (599.9 MHz, 233 K, [D$_8$]toluene): δ = 140.1/6.01 (C-4), 130.5/6.07 (C-5), 112.4, 112.3/5.18, 5.04 (Cp), 51.0/1.06, 0.28 (C-2), 29.7/1.06, 1.22 (C-3), 20.0/−0.45, 19.5/0.10, −0.16 (C-7, C-8). (C-1) and (C-6) were not detected. The other C resonances were detected only by GHSQC. - ^{19}F-NMR (564.3 MHz, 233 K, [D$_8$]toluene): δ = −166.0 (t, $^3J_{FF}$ = 21 Hz, 6 F, *m*-F), −162.3 (t, $^3J_{FF}$ = 21 Hz, 3 F, *p*-F), −135.6 (d, $^3J_{FF}$ = 22 Hz, 6 F, *o*-F of $B(C_6F_5)_3$) .

Reaction of **3b** *with Methylenecyclopropane. − Generation of* **5b** *and* **6b**: **3b** was generated by treatment of 20 mg (0.06 mmol) of (butadiene)hafnocene **1b** with 32 mg (0.06 mmol) of $B(C_6F_5)_3$ in [D$_8$]toluene. Subsequent addition of 2−3 ml of gaseous methylenecyclopropane at −40°C gave a 70:30 mixture of **5b** (decomp. at temperatures above 0°C) and **6b** (decomp. at temperatures above −20°C). Major isomer (**5b**): ^{1}H-NMR (599.9 MHz, 233 K, [D$_8$]toluene): δ = 6.22 (m, 1 H, 4-H), 5.99 (m, 1 H, 5-H), 5.30 (s, 5 H, Cp), 5.14 (s, 5 H, Cp), 1.54 (d, $^2J_{HH}$ = 14.5 Hz, 1 H, 1-H′), 1.49 (t, $^{2/3}J_{HH}$ = 11.6 Hz, 1 H, 3-H′), 0.74 (br. s, 1 H, 6-H′), 0.69 (m, 1 H, 3-H′), 0.55 (br. s, 1 H, 6-H), 0.14, 0.08, 0.04, -0.22, (each m, each 1 H, 7-H,H′, 8-H,H′), −1.46 (d, $^2J_{HH}$ = 14.5 Hz, 1 H, 1-H). − ^{13}C-NMR (150.8 MHz, 233 K, [D$_8$]toluene): δ = 148.4 (d, $^1J_{CF}$ = 240 Hz, *o*-$B(C_6F_5)_3$), 140.7 (CH, C-4), 139.0 (d, $^1J_{CF}$ = 240 Hz, *p*-$B(C_6F_5)_3$), 137.4 (d, $^1J_{CF}$ = 240 Hz, *m*-$B(C_6F_5)_3$), 129.2 (CH, C-5), 111.1 (CH, Cp), 109.6 (CH, Cp), 56.8 (CH$_2$, C-1), 43.9 (CH$_2$, C-3), 28.4 (C, C-2), 16.3, 14.1 (each CH$_2$, C-7, C-8), 14.1 (br CH$_2$, C-6). − GCOSY (599.9 MHz, 233 K, [D$_8$]toluene): δ = 6.22 (4-H)/5.99 (5-H), 1.49 (3-H′), 0.69 (3-H), 5.99 (5-H)/0.74 (6-H′), 1.54

(1-H′)/−1.46 (1-H), 1.49 (3-H′)/0.69 (3-H), 0.74 (6-H′)/0.55 (6-H), 0.14, 0.08, 0.04, −0.22 (7-H,H′, 8-H,H′, all mutually coupled). – GHSQC (599.9 MHz, 233 K, $[D_8]$toluene): δ = 140.7/6.22 (C-4), 129.2/5.99 (C-5), 111.1/5.14 (Cp), 109.6/5.30 (Cp), 56.8/1.54, −1.46 (C-1), 43.9/1.49, 0.69 (C-3), 16.3/0.04, −0.22, 14.1/0.14, 0.08 (C-7, C-8), 14.1/0.74, 0.55 (C-6). – GHMBC (599.9 MHz, 233 K, $[D_8]$toluene): δ = 140.7 (C-4)/1.49 (3-H′), 129.2 (C-5)/1.49 (3-H′), 43.9 (C-3)/−1.46 (1-H), 28.7 (C-2)/1.49 (3-H′), −1.46 (1-H), 14.1 (C-7 or C-8)/1.49 (3-H′). – ^{19}F-NMR (564.3 MHz, 233 K, $[D_8]$toluene): δ = −167.5 (t, $^{3}J_{FF}$ = 21 Hz, 6 F, *m*-F), −162.6 (t, $^{3}J_{FF}$ = 21 Hz, 3 F, *p*-F), −135.2 (d, $^{3}J_{FF}$ = 22 Hz, 6 F, *o*-F of $B(C_6F_5)_3$) . Minor isomer (**6b**): ^{1}H-NMR (599.9 MHz, 233 K, $[D_8]$toluene): δ = 6.49 (m, 1 H, 5-H), 5.86 (m, 1 H, 4-H), 5.21 (s, 5 H, Cp), 5.11 (s, 5 H, Cp), 1.29 (m, 2 H, 3-H,H′), 1.12 (br. s, 1 H, 6-H′), 0.63 (m, 1 H, 2-H′), 0.53 (m, 1 H, 2-H), 0.36 (br. s, 1 H, 6-H), 0.08, −0.04, −0.07, −0.22 (each m, each 1 H, 7-H,H′, 8-H,H′). – ^{13}C-NMR (150.8 MHz, 233 K, $[D_8]$toluene): δ = 148.4 (d, $^{1}J_{CF}$ = 240 Hz, *o*-$B(C_6F_5)_3$), 139.0 (d, $^{1}J_{CF}$ = 240 Hz, *p*-$B(C_6F_5)_3$), 137.4 (d, $^{1}J_{CF}$ = 240 Hz, *m*-$B(C_6F_5)_3$), 135.3 (CH, C-4), 134.6 (CH, C-5), 112.6 (CH, Cp), 111.8 (CH, Cp), 49.6 (C, C-1), 42.5 (CH_2, C-2), 32.2 (CH_2, C-3), 20.4, 17.6 (each CH_2, C-7, C-8). – GCOSY (599.9 MHz, 233 K, $[D_8]$toluene) δ = 6.49 (5-H)/5.86 (4-H), 0.36 (6-H), 5.86 (4-H)/1.29 (3-H,H′), 1.29 (3-H,H′)/0.63 (2-H′), 0.53 (2-H), 1.12 (6-H′)/0.36 (6-H), 0.63 (2-H′)/0.53 (2-H), 0.08, −0.04, −0.07, −0.22 (7-H,H′, 8-H,H′, all mutually coupled). – GHSQC (599.9 MHz, 233 K, $[D_8]$toluene): δ = 135.3/5.86 (C-4), 134.6/6.49 (C-5), 112.6/5.21 (Cp), 111.8/5.11 (Cp), 42.5/0.63, 0.53 (C-2), 32.2/1.29 (C-3), 20.4/0.08, −0.04, 17.6/−0.07, −0.22 (C-7, C-8). – GHMBC (599.9 MHz, 233 K, $[D_8]$toluene): δ = 134.6 (C-5)/1.29 (3-H,H′), 0.63 (2-H′), 0.53 (2-H), 49.6 (C-1)/1.29 (3-H,H′) . (C-6)-resonance and *ipso*-C of C_6F_5 not detected. - ^{19}F-NMR (564.3 MHz, 233 K, $[D_8]$toluene): δ = -167.7 (t, $^{3}J_{FF}$ = 21 Hz, 6 F, *m*-F), −162.9 (t, $^{3}J_{FF}$ = 21 Hz, 3 F, *p*-F), −135.4 (d, $^{3}J_{FF}$ = 22 Hz, 6 F, *o*-F of $B(C_6F_5)_3$) .

Reaction of **3a** *with Allene. – Formation of* **7a**: Complex **3a** was generated by treatment of (butadiene)zirconocene **1a** (25 mg, 0.09 mmol) with $B(C_6F_5)_3$ (52 mg, ca. 0.10 mmol) in $[D_8]$toluene. Allene (2-3 ml, ca. 0.1 mmol) was introduced as a gas at −35°C to yield the insertion product **7a**, that was characterized spectroscopically. – ^{1}H-NMR (599.9 MHz, 238 K, $[D_8]$toluene): δ = 6.03 (m, 1 H, 4-H), 5.88 (m, 1 H, 5-H), 5.38 (s, 1 H, 7-H′), 5.23 (s, 5 H, Cp), 5.22 (s, 5 H, Cp), 3.87 (s, 1 H, 7-H), 1.97 (m, 2 H, 2-H,H′), 1.25 (m, 1 H, 3-H′), 1.17 (m, 1 H, 3-H), 0.39 (br, 1 H, 6-H′), 0.28 (br, 1 H, 6-H). – ^{13}C-NMR (150.8 MHz, 238 K, $[D_8]$toluene): δ = 192.9 (C, C-1), 148.3 (d, $^{1}J_{CF}$ = 239 Hz, *o*-$B(C_6F_5)_3$), 141.2 (CH, C-4), 139.0 (d, $^{1}J_{CF}$ = 255 Hz, *p*-$B(C_6F_5)_3$), 137.3 (d, $^{1}J_{CF}$ = 255 Hz, *m*-$B(C_6F_5)_3$), 126.9 (CH, C-5), 125.2 (CH_2, C-7), 111.5 (CH, Cp), 111.3 (CH, Cp), 106.8 (br., C, *ipso*-$B(C_6F_5)_3$), 52.9 (CH_2, C-2), 31.0 (CH_2, C-3), ≈ 7 (CH_2, C-6). – GCOSY (599.9 MHz, 238 K, $[D_8]$toluene): δ = 6.03 (4-H)/5.88 (5-H), 1.25 (3-H′), 1.17 (3-H), 5.88 (5-H)/0.39 (6-H′), 0.28 (6-H), 5.38 (7-H′)/3.87 (7-H), 1.97 (2-H,H′)/1.25 (3-H′), 1.17 (3-H), 1.25 (3-H′)/1.17 (3-H), 0.39 (6-H′)/0.28 (6-H). – GHSQC (599.9 MHz, 238 K, $[D_8]$toluene): δ = 141.2/6.03 (C-4), 126.9/5.88 (C-5), 125.2/5.38, 3.87 (C-7), 111.5, 111.3/5.23, 5.22 (Cp), 52.9/1.97 (C-2), 31.0/1.25, 1.17 (C-3), 7.0/0.39, 0.28 (C-6) . The C-6 resonance could only be detected by GHSQC. – ^{19}F-NMR (564.3 MHz, 238 K, $[D_8]$toluene): δ = −165.8 (t, $^{3}J_{FF}$ = 21 Hz, 6 F, *m*-F), −160.7 (t, $^{3}J_{FF}$ = 21 Hz , 3 F, *p*-F), −134.0 (d, $^{3}J_{FF}$ = 21 Hz, 6 F, *o*-F of $B(C_6F_5)_3$) .

Reaction of **3b** *with Allene. – Formation of* **7b**: (Butadiene)hafnocene **1b** (20 mg, 0.06 mmol) was treated with 32 mg (0.06 mmol) of $B(C_6F_5)_3$ in $[D_8]$toluene to give the betaine **3b** which was then reacted with allene (2-3 ml) at −35°C to give **7b**. – ^{1}H-NMR (599.9 MHz, 238 K, $[D_8]$toluene): δ = 6.28 (m, 1 H, 5-H), 5.89 (m, 1 H, 4-H), 5.66 (s, 1 H, 7-H′), 5.25 (s, 5 H, Cp), 5.17 (s, 5 H, Cp), 3.91 (s, 1 H, 7-H), 1.88 (m, 1 H, 2-H′), 1.81 (m, 1 H, 2-H), 1.38 (m, 1 H, 3-H′), 1.24 (m, 1 H, 3-H), 0.75 (br. s, 1 H, 6-H′), 0.45 (br. s, 1 H, 6-H). – ^{13}C-NMR (150.8 MHz, 238 K, $[D_8]$toluene): δ = 199.3 (C, C-1), 148.3 (d, $^{1}J_{CF}$ = 252 Hz, *o*-$B(C_6F_5)_3$), 139.0 (d, $^{1}J_{CF}$ = 248 Hz, *p*-$B(C_6F_5)_3$), 137.3 (d, $^{1}J_{CF}$ = 240 Hz, *m*-$B(C_6F_5)_3$), 135.8 (CH, C-4), 133.3 (CH, C-5), 126.6 (CH_2, C-7), 111.2 (CH, Cp), 111.7 (CH, Cp), 45.0 (CH_2, C-2), 32.4 (CH_2, C-3), ≈ 16 (br. CH_2, C-6). – GCOSY (599.9 MHz, 238 K, $[D_8]$toluene): δ = 6.28 (5-H)/5.89 (4-H), 0.75 (6-H), 5.89 (4-H)/1.38 (3-H′), 1.24 (3-H), 5.66 (7-H′)/3.91 (7-H), 1.88 (2-H′)/1.81 (2-H), 1.38 (3-H′), 1.24 (3-H), 1.81 (2-H)/1.38 (3-H′), 1.24 (3-H), 1.38 (3-H′)/1.24 (3-H), 0.79 (6-H′)/0.45 (6-H). – GHSQC (599.9 MHz, 238 K, $[D_8]$toluene): δ = 135.8/5.89 (C-4), 133.3/6.28 (C-5), 126.6/5.66, 3.91 (C-7), 111.7/5.25 (Cp), 111.2/5.17 (Cp), 45.0/1.88, 1.81 (C-2), 32.4/1.38, 1.24 (C-3), 16.0/0.75, 0.45 (C-6). The (C-6) resonance could only be detected by GHSQC, *ipso*-C of $B(C_6F_5)_3$ not detected. – ^{19}F-NMR (564.3 MHz, 238 K, $[D_8]$toluene): δ = −165.5 (t, $^{3}J_{FF}$ = 21 Hz, 6 F, *m*-F), −160.6 (t, $^{3}J_{FF}$ = 21 Hz, 3 F, *p*-F), −133.5 (d, $^{3}J_{FF}$ = 20 Hz, 6 F, *o*-F of $B(C_6F_5)_3$) .

Reaction of **3c** *with Allene. – Formation of* **7c**: Treatment of 30 mg (0.10 mmol) of (butadiene)$Zr(\eta\text{-}C_5H_4CH_3)_2$ **1c** with 52 mg (0.10 mmol) of $B(C_6F_5)_3$ in $[D_8]$toluene gave **3c**, which was subsequently reacted with allene (2-3 ml) at −10°C to give **7c**. - ^{1}H-NMR (599.9 MHz, 263 K, $[D_8]$toluene): δ = 6.12 (m, 1 H, 5-H), 5.86 (m, 1 H, 4-H), 5.69, 5.63, 5.60, 5.34, 5.29, 5.09, 4.91, 4.55 (each m, each 1 H, C_5H_4-), 5.38 (d, $^{2}J_{HH}$ = 2.1 Hz, 1 H, 7-H′), 3.93 (d, $^{2}J_{HH}$ = 2.1 Hz, 1 H, 7-H), 1.81 (m, 2 H, 2-H′, 2-H), 1.38, 1.36 (each s, each 3 H, each $CpCH_3$), 1.29 (m, 1 H, 3-H′), 0.99 (m, 1 H, 3-H), 1.04 (br. s, 1 H, 6-H′), 0.11 (br. s, 1 H, 6-H). – ^{13}C-NMR (150.8 MHz, 263 K, $[D_8]$toluene): δ = 197.1 (C, C-1), 148.4 (d, $^{1}J_{CF}$ = 244 Hz, *o*-$B(C_6F_5)_3$), 139.1 (d, $^{1}J_{CF}$ = 253 Hz, *p*-$B(C_6F_5)_3$), 137.4 (d, $^{1}J_{CF}$ = 252 Hz, *m*-$B(C_6F_5)_3$), 137.2 (CH, C-4), 131.3 (CH, C-5), 123.0 (CH_2, C-7), 117.6, 115.1, 113.1, 112.2, 111.1, 108.6, 107.9, 103.6 (each CH, C_5H_4-), 50.7 (CH_2, C-2), 29.6 (CH_2, C-3), 14.6, 14.3 (each CH_3, $CpCH_3$), ≈ 8 (C-6). – GCOSY (599.9 MHz, 263 K, $[D_8]$toluene): δ = 6.12 (5-H)/5.86 (4-H), 0.11 (6-H), 5.86 (4-H)/1.29 (3-H′), 0.99 (3-H), 5.38 (7-H′)/3.93 (7-H), 1.81 (2-H,H′)/1.29 (3-H′), 0.99 (3-H), 1.29 (3-H′)/0.99 (3-H), 1.04 (6-H′)/0.11 (6-H). – GHSQC (599.9 MHz, 263 K, $[D_8]$toluene): δ = 137.2/5.86 (C-4), 131.3/6.12 (C-5), 123.0/5.38, 3.93 (C-7), 117.6/5.34 (C_5H_4-), 115.1/5.69 (C_5H_4-), 113.1/5.29 (C_5H_4-), 112.2/5.09 (C_5H_4-), 111.1/4.91 (C_5H_4-), 108.6/5.63 (C_5H_4-), 107.9/5.60 (C_5H_4-), 103.6/4.55 (C_5H_4-), 50.7/1.81 (C-2), 29.6/1.29, 0.99 (C-3), 14.6, 14.3/1.38, 1.36 ($CpCH_3$), 8.0 (C-6)/1.04, 0.11 (C-6). Signals of the quat. Cp-C not found. – ^{19}F-NMR (564.3 MHz, 263 K, $[D_8]$toluene): δ = −165.6 (t, $^{2}J_{FF}$ = 21 Hz, 6 F, *m*-F), −160.7 (t, $^{3}J_{FF}$ = 21 Hz, 3 F, *p*-F), −133.9 (d, $^{2}J_{FF}$ = 20 Hz, 6 F, *o*-F of $B(C_6F_5)_3$) .

Reaction of Bis(η-cyclopentadienyl)(1-3:6-η-hexenylene)zirconium **9** *with Tris(pentafluorophenyl)borane in Toluene. – Formation of* **10**: 30 mg (0.10 mmol) of **9** was dissolved in ca. 1 ml of $[D_8]$toluene and combined with a solution of 52 mg (0.10 mmol) of $B(C_6F_5)_3$ in ca. 1 ml of $[D_8]$toluene and then immediately cooled to −35°C. The NMR spectra showed the presence of **10** admixed with a small amount of its isomer **4**. Complex **10** decomposed rapidly at temperatures above 0°C and was, therefore, not isolated but only characterized spectroscopically in $[D_8]$toluene solution. – ^{1}H-NMR (599.9 MHz, 238 K, $[D_8]$toluene): δ = 5.29 (s, 5 H, Cp), 5.12 (m, 1 H, 2-H), 5.06 (s, 5 H, Cp), 4.62 (m, 1 H, 3-H), 1.80 (d, $^{3}J_{HH}$ = 10.7 Hz, 1 H, 4-H′), 1.68 (dd, $^{2/3}J_{HH}$ = 4.2, 13.2 Hz, 1 H, 1-H′), 1.48 (m, 1 H, 5-H′), 1.40 (dd, $^{2/3}J_{HH}$ = 4.2, 7.9 Hz, 1 H, 1-H), 1.20

(m, 1 H, 5-H), 0.98 (m, 1 H, 4-H), −0.17 (br. s, 1 H, 6-H′), −3.05 (br. s, 1 H, 6-H). – ^{13}C-NMR (150.8 MHz, 238 K, [D_8]toluene): δ = 148.4 (d, $^1J_{CF}$ = 219 Hz, *o*-B(C_6F_5)$_3$), 138.9 (d, $^1J_{CF}$ = 252 Hz, *p*-B(C_6F_5)$_3$), 137.2 (d, $^1J_{CF}$ = 257 Hz, *m*-B(C_6F_5)$_3$), 131.7 (CH, C-2), 119.7 (CH, C-3), 112.7 (br C, *ipso*-B(C_6F_5)$_3$), 110.4, 109.7 (each CH, Cp), 48.2 (CH_2, C-1), 37.7 (CH_2, C-4), 35.2 (CH_2, C-5), 18.0 (C-6). – GCOSY (599.9 MHz, 238 K, [D_8]toluene): δ = 5.12 (2-H)/4.62 (3-H), 1.68 (1-H′), 1.40 (1-H), 4.62 (3-H)/1.80 (4-H′), 0.98 (4-H), 1.80 (4-H′)/1.48 (5-H′), 0.98 (4-H), 1.68 (1-H′)/1.40 (1-H), 1.48 (5-H′)/1.20 (5-H), −3.05 (6-H), 1.20 (5-H)/0.98 (4-H), −0.17 (6-H′), −3.05 (6-H). – GHSQC (599.9 MHz, 238 K, [D_8]toluene): δ = 131.7/5.12 (C-2), 119.7/4.62 (C-3), 110.4/5.29 (Cp), 109.7/5.06 (Cp), 48.2/1.68, 1.40 (C-1), 37.7/1.80, 0.98 (C-4), 32.5/1.48, 1.20 (C-5), 18.6/−0.17, −3.05 (C-6). The (C-6) atom was only detected by GHSQC. – ^{19}F-NMR (564.3 MHz, 238 K, [D_8]toluene): δ = −165.9 (br, 6 F, *m*-F), −161.6 (br, 3 F, *p*-F), −133.3 (br, 6 F, *o*-F of B(C_6F_5)$_3$). The ^{19}F-NMR signals were broad but did not get sharp and resolved at 188 K.

Reaction of **9** *with B(C_6F_5)$_3$* in Tetrahydrofuran. – Formation of **4**·THF: **9** (300 mg, 0.99 mmol) and B(C_6F_5)$_3$ (520 mg, 1.02 mmol) were allowed to react in 2 ml of THF at ambient temperature. After a few minutes the solvent was removed in vacuo and the residue stirred with 10 ml of toluene at room temperature overnight. Solvent was decanted from the solid and the residue dried in vacuo to give a light brown colored powder (yield 684 mg, 68%, mp 43°C decomp.) that contained several equivalents of THF that could not be removed in vacuo, even at prolonged drying times. Therefore, the product **4**·THF was only characterized spectroscopically in [D_8]THF solution. – ^{1}H-NMR (599.9 MHz, 299 K, [D_8]THF): δ = 6.53 (s, 10 H, Cp), 5.47 (m, 1 H, 5-H), 4.68 (m, 1 H, 4-H), 2.07 (br. d, $^3J_{HH}$ = 7.1 Hz, 2 H, 6-H), 1.63 (m, 2 H, 3-H), 1.40 (m, 2 H, 2-H), 1.37 (m, 2 H, 1-H). – ^{13}C-NMR (150.8 MHz, 299 K, [D_8]THF): δ = 148.9 (d, $^1J_{CF}$ = 240 Hz, *o*-B(C_6F_5)$_3$), 139.2 (d, $^1J_{CF}$ = 246 Hz, *p*-B(C_6F_5)$_3$), 137.3 (CH, $^1J_{CH}$ = 145 Hz, C-5), 137.0 (d, $^1J_{CF}$ = 248 Hz, *m*-B(C_6F_5)$_3$), 128.6 (*ipso*-B(C_6F_5)$_3$), 124.9 (CH, $^1J_{CH}$ = 148 Hz, C-4), 115.6 (CH, $^1J_{CH}$ = 174 Hz, Cp), 71.4 (CH_2, $^1J_{CH}$ = 118 Hz, C-1), 39.8 (CH_2, $^1J_{CH}$ = 125 Hz, C-3), 35.2 (CH_2, $^1J_{CH}$ = 125 Hz, C-2), 29.3 (br. CH_2, C-6). – GCOSY (599.9 MHz, 299 K, [D_8]THF): δ = 5.47 (5-H)/4.68 (4-H), 2.07 (6-H), 4.68 (4-H)/1.63 (3-H), 1.63 (3-H)/1.40 (2-H), 1.40 (2-H)/1.37 (1-H). – GHSQC (599.9 MHz, 299 K, [D_8]THF): δ = 1.37.3/5.47 (C-5), 124.9/4.68 (C-4), 115.6/6.53 (Cp), 71.4/1.37 (C-1), 39.8/1.63 (C-3), 35.2/1.49 (C-2), 29.3/2.07 (C-6). – ^{19}F-NMR (564.3 MHz, 303 K, [D_8]THF): δ = −169.2 (t, $^3J_{FF}$ = 21 Hz, 6 F, *m*-F), −166.8 (t, $^3J_{FF}$ = 21 Hz, 3 F, *p*-F), −132.3 (d, $^3J_{FF}$ = 21 Hz, 6 F, *o*-F of B(C_6F_5)$_3$). – IR (KBr): $\tilde{\nu}$ = 2963, 2935, 2910, 1645, 1512, 1458, 1269, 1084, 980, 814, 737 cm^{-1}.

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[1] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99. M. Aulbach, F. Küber, *Chemie Unserer Zeit* **1994**, *28*, 197; H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* **1995**, *107*, 1255; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143; M. Bochmann, *J. Chem. Soc., Dalton Trans.* **1996**, 255, and references cited in these articles.

[2] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem.* **1995**, *107*, 1867; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1755.

[3] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245.

[4] G. Erker, C. Krüger, G. Müller, *Adv. Organomet. Chem.* **1985**, *24*, 1, and references cited therein.

[5] B. Temme, J. Karl, G. Erker, *Chem. Eur. J.* **1996**, *2*, 919.

[6] For other examples of M···F−C interactions see e.g. J. S. Thompson, T. Sorrell, T. J. Marks, J. A. Ibers, *J. Am. Chem. Soc.* **1979**, *101*, 4193; P. W. Murray-Rust, W. C. Stallins, C. T. Monti, R. K. Preston, J. P. Glusker, *J. Am. Chem. Soc.* **1983**, *105*, 3206; R. M. Catala, D. Cruz-Garritz, A. Hills, D. L. Hughes, R. L. Richards, P. Sosa, H. Torrens, *J. Chem. Soc., Chem. Commun.* **1987**, 261; Z. Lin, J.-F. LeMarechal, M. Sabat, T. J. Marks, *J. Am. Chem. Soc.* **1987**, *109*, 4127; D. Stalke, K. H. Whitmire, *J. Chem. Soc., Chem. Commun.* **1990**, 833; X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1991**, *10*, 840; A. D. Horton, A. G. Orpen, *Organometallics* **1991**, *10*, 3910; A. R. Siedle, R. A. Newmark, W. M. Lamanna, J. C. Huffman, *Organometallics* **1993**, *12*, 1491; J. Ruwwe, G. Erker, R. Fröhlich, *Angew. Chem.* **1996**, *108*, 108, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 80; H. Plenio, R. Diodone, *Chem. Ber.* **1996**, *129*, 1211; H. Plenio, R. Diodone, D. Badura, *Angew. Chem.* **1997**, *109*, 130; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 156; J. D. Dunitz, R. Taylor, *Chem. Eur. J.* **1997**, *3*, 89.

[7] X. Yang, C. L. Stern, T. J. Marks, *Angew. Chem.* **1992**, *104*, 1406, *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375; X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015; L. Jia, X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 842.

[8] C. Krüger, G. Müller, G. Erker, U. Dorf, K. Engel, *Organometallics* **1985**, *4*, 215.

[9] S. Braun, H. Kalinowski, S. Berger in *100 and More Basic NMR Experiments*, VCH, Weinheim, **1996**, and references cited therein.

[10] R. Köster, S. Arora, P. Binger, *Angew. Chem.* **1969**, *81*, 186; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 205.

[11] L. Jia, X. Yang, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 1547; L. Jia, X. Yang, A. M. Seyam, I.D.L. Albert, P.-F. Fu, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 7900.

[12] A similar interaction was noticed in the insertion products of alkynes into the Zr-C bond of **3a**: J. Karl, G. Erker, *J. Mol. Catal.* submitted.

[13] R. F. Jordan, R. E. LaPointe, P. K. Bradley, N. Baenziger, *Organometallics* **1989**, *8*, 2892. A. D. Horton, *Organometallics* **1992**, *11*, 3271.

[14] A. D. Horton, J. de With, A. J. van der Linden, H. van de Weg, *Organometallics* **1996**, *15*, 2672.

[15] G. Erker, K. Kropp, J. L. Atwood, W. E. Hunter, *Organometallics* **1983**, *2*, 1555; P. Czisch, G. Erker, *J. Organomet. Chem.* **1983**, *253*, C9; P. Czisch, G. Erker, H.-G. Korth, R. Sustmann, *Organometallics* **1984**, *3*, 945; I. Hyla-Kryspin, R. Gleiter, C. Krüger, R. Zwettler, G. Erker, *Organometallics* **1990**, *9*, 517; G. Erker, R. Zwettler, C. Krüger, I. Hyla-Kryspin, R. Gleiter, *Organometallics* **1990**, *9*, 524; Y. Raoult, R. Choukroun, D. Gervais, G. Erker, *J. Organomet. Chem.* **1990**, *399*, C1.

[16] Z. Wu, R. F. Jordan, J. L. Petersen, *J. Am. Chem. Soc.* **1995**, *117*, 5867.

[17] See also: C. P. Casey, S. L. Hallenbeck, D. W. Pollock, C. R. Landis, *J. Am. Chem. Soc.* **1995**, *117*, 9770; A. D. Horton, A. G. Orpen, *Organometallics* **1992**, *11*, 8.

[18] G. Erker, K. Engel, U. Dorf, J. L. Atwood, W. E. Hunter, *Angew. Chem.* **1982**, *94*, 915, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 914; U. Dorf, K. Engel, G. Erker, *Angew. Chem.* **1982**, *94*, 916, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 914; K. Engel, doctoral thesis, Univ. Bochum **1983**.

[19] This is due to the special stereoelectronic features of the bent metallocene unit: H. H. Brintzinger, L. S. Bartell, *J. Am. Chem. Soc.* **1970**, *92*, 1105; J. W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[20] $Hf-C(sp^3)$ σ-bonds are by ca. 5 kcal/mol stronger than $Zr-C(sp^3)$ bonds, but the opposite appears to be true for the corresponding π-interactions; see ref.[8] and J. K. Kochi, in *Organometallic Mechanisms and Catalysis*, Academic Press New York **1978**, p. 237–245, and references cited therein. J. A. Connor, *Topics Curr. Chem.* **1977**, *71*, 71.

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