ELSEVIER

Journal of Molecular Catalysis A: Chemical 128 (1998) 85–102

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Observation of the primary Zr–C insertion products in the reaction of the (butadiene)zirconocene/$B(C_6F_5)_3$-betaine Ziegler catalyst system with reactive alkynes

Jörn Karl, Gerhard Erker *

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, 48149 Münster, Germany

Abstract

The (conjugated diene) group 4 metallocenes **1a**–**d** (diene = butadiene, isoprene; metallocene = Cp_2Zr, Cp_2Hf, $MeCp_2Zr$) add $B(C_6F_5)_3$ to yield the metallacyclic M · · · F–C bridged metallocene–borate–betaine complexes **3a**–**d**. These add one equivalent of acetylene to give the chiral metallacyclic insertion products **5a**–**d** that can be described as either intramolecular ion-pair type complexes involving interaction of the negatively polarized terminal –CH=CH–CH_2–[B] group of the resulting σ-ligand system with the positively polarized metallocene moiety of the dipolar betaine product or η^2-internal alkene metallocene complexes, respectively, as it is revealed by a comparison with the related acyclic THF-addition products **10** and **12**. Propyne inserts unselectively into the terminal Zr–C bond of the complexes **3a**–**c**. In each case a 1:1 mixture of the regioisomers **6a**–**c** (methyl at C2) and **7a**–**c** (methyl group at C1) is obtained. © 1998 Elsevier Science B.V.

Keywords: Metallocene–borate–betaines; Homogeneous single component metallocene Ziegler catalysts; Alkyne insertion; Metallocene cations; Metallocene olefin complexes

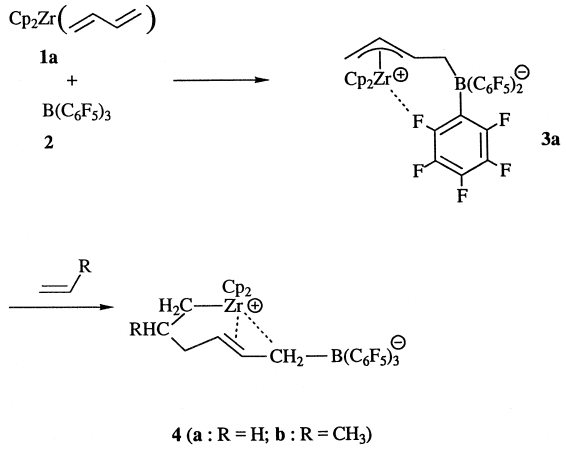
1. Introduction

Tris(pentafluorophenyl)borane (**2**) [1] cleanly adds to (butadiene)zirconocene (**1a**) [2] to yield the metallocene–(μ-C_4H_6)–borate betaine complex **3a** [3,4] (for related recent work by other groups see [5–8]). This system constitutes a very active homogeneous single component Ziegler catalyst for the rapid polymerization of α-olefins. In addition to its practical use in catalytic polyolefin formation the system **3** has allowed for the direct experimental investigation of a variety of aspects of the carbon–carbon coupling process of alkenes at an active Ziegler-type catalyst system. It appears that studies with the Cp_2Zr(butadiene)/$B(C_6F_5)_3$/alkene system comes close to the situation where one may observe an active metallocene Ziegler catalyst 'at work' [9] [1].

* Corresponding author. Fax: +49-251-8339772; e-mail: erker@uni-muenster.de

[1] For remotely related intramolecular insertion reactions see e.g. [10–13]. For other related model systems see e.g. [14–29].

1381-1169/98/$19.00
PII S1381-1169(97)00165-9



4 (a : R = H; b : R = CH_3)

At low temperature complex **3a** inserts one molar equivalent of ethene into the terminal zirconium to carbon bond with formation of the metallacyclic product **4a**. The chiral cyclic structure of **4a** was established unequivocally by NMR spectroscopy. In contrast to the starting material **3a**, that is characterized by the presence of a markedly persistent Zr · · · F–C interaction in solution and in the solid state [3–8] [2], the product **4a** can be described as an intramolecular ion-paired structure [45,46]. In this case the butadiene-derived allyl moiety bonded to boron serves as the donor part in this interaction, the $-B(C_6F_5)_3$ group itself is apparently not involved directly in the formation of the chiral metallacyclic donor–acceptor type structure. With propene an analogous product **4b** (single diastereoisomer) is formed. At higher temperatures ($> -20°C$) the products **4** are not stable; in the presence of excess α-olefin reagent a rapid polymerization reaction with formation of polyethylene and polypropylene, respectively, takes place [3–8].

The (butadiene)$ZrCp_2/B(C_6F_5)_3$ system also reacts rapidly with terminal alkynes at ambient conditions [3]. The resulting oligomers or polymers have not been unequivocally characterized so far. However, we were able to observe in a few cases the primary insertion products by carefully adjusting the reaction conditions at low temperatures and by performing the reactions under these optimized conditions under direct NMR control. The outcome of several typical examples of such insertion reactions of reactive alkynes into a Zr–C bond of the metallocene–betaine Ziegler catalyst system **3** is described in this article [4].

2. Results and discussion

2.1. Generation of the alkyne insertion products

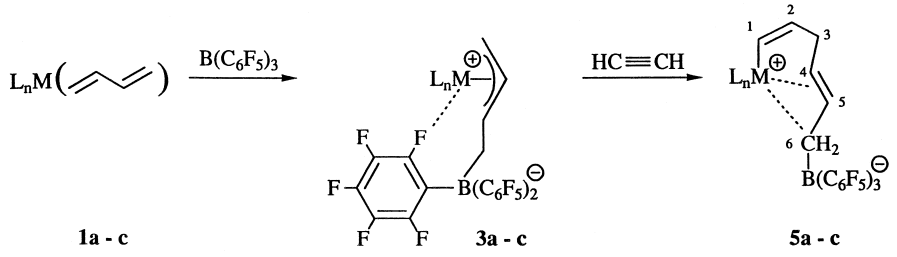
For this study the betaine systems **3** were not isolated but generated in situ in a suitable deuterated solvent (usually toluene-d_8) by the reaction of the respective (conjugated diene) group 4 metallocene complexes (**1**) [2] with an equimolar quantity of $B(C_6F_5)_3$ [1]. Four related (1,3-diene)metallocene complexes were employed, namely (butadiene)zirconocene (**1a**) and -hafnocene (**1b**) as well as the

[2] For related examples of M · · · F–C interactions see e.g. [30–41]; for related reviews see e.g. [42–44].
[3] For other alkyne insertion reactions see e.g. [47–59].
[4] For related betaines see e.g. [60–75].

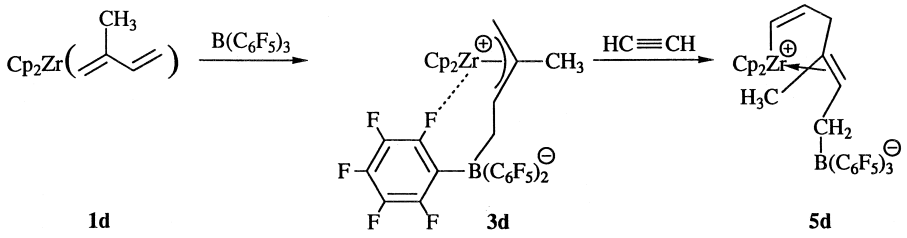
Cp-substituted (butadiene)bis(methylcyclopentadienyl)zirconium system (**1c**). In addition, the corresponding (η^4-isoprene)$ZrCp_2$ system **1d** was chosen as a starting material. The (butadiene)zirconocenes **1a** and **1c** were used as *s-cis-/s-trans*-isomer mixtures at their ambient temperature equilibrium ratio. The equilibrium situation of the other (conjugated diene)metallocene complexes lies far on the side of the *s-cis*-isomers. These were therefore used as such [2].

The reaction of the (butadiene)zirconocene (**1a**)/$B(C_6F_5)_3$-derived betaine system **3a** with acetylene may serve as a typical example of the reactions carried out in this study. First, the metallocene–borate–betaine system **3a** was generated by treatment of (butadiene)$ZrCp_2$ with $B(C_6F_5)_3$ at ambient temperature in toluene-d_8. The solution was then cooled to −35°C. At this temperature acetylene (2–3 ml) was slowly introduced into the solution by means of a glass capillary. Under these conditions the reaction between **3a** and HC≡CH is very clean and goes to completion rapidly. The 1:1 insertion product **5a** is obtained almost exclusively in this solution and it is subsequently characterized by NMR spectroscopy.

For characterization a combination of various NMR techniques was employed [76]. This allowed for an unambiguous structural assignment. Attempts to isolate the product **5a** were unsuccessful so far due to a rapid unspecific decomposition reaction that took place upon raising the temperature of the reaction mixture.



L_nM = Cp_2Zr (**a**), Cp_2Hf (**b**), $(MeC_5H_4)_2Zr$ (**c**)



The ^{13}C NMR spectrum of the product **5a** shows that the ethyne molecule was inserted into the terminal Zr–C bond of **3a** to form a linear chain, elongated by two sp^2-carbon centers. The corresponding C1–C6 ^{13}C NMR resonances are observed at δ 176.0, 142.6, 38.0, 136.6, 129.7 and ca. 4. The C6 signal is very broad due to its direct bonding connection with the boron nucleus of the $B(C_6F_5)_3$ unit. Its chemical shift indicates an ion-pair bonding interaction with the zirconium center and so do the C5 and C4 chemical shifts — this point will be discussed in due detail later (see below). The low field ^{13}C NMR resonance of the C1 carbon center is very typical for zirconium bound alkenyl groups [77–84].

The $-HC^1=C^2H-$ moiety is *cis*-configurated. This is apparent from the ^3J(1-H/2-H) coupling constant of 12 Hz. The $^1H/^{13}C$ connectivities and assignments were secured by two dimensional GCOSY, GHSQC (and in some cases GHMBC) experiments [76]. The most noteworthy feature that becomes apparent from the ^1H and ^{13}C NMR spectra of complex **5a** is that this compound is chiral. Thus, complex **5a** exhibits (in toluene-d_8 at $-35°C$) a 1:1 intensity pair of $^1H/^{13}C$ NMR Cp-resonances at δ 5.18, 5.12/110.9, 110.7 ppm. In addition, the hydrogen atoms at the chain carbon atom C3 are diastereotopic (3-H, 3-H′: δ 2.00, 1.90 ppm), and so are the 6-H, 6-H′ hydrogens (broad signals at δ 0.73 and 0.43 ppm).

Apparently, the chirality of **5a** originates from a ring formation by means of an intramolecular ion-pair association phenomenon. Monitoring the ^{19}F NMR spectra from 238 K down to a limiting temperature of 193 K did not reveal any indication for zirconium $\cdots$ F–C interaction [3–8,30–44]. Only three ^{19}F resonances are observed of the freely rotating $B-C_6F_5$ moieties (at δ −165.2 (*m*-F), −160.1 (*p*-F), and −133.7 (*o*-F)) [5]. The ^{13}C NMR shift situation of the $C^6H_2-C^5H=C^4CH$ group indicates that the ring structure of complex **5a** originates from a pronounced internal ion-pair type interaction of this part of the C_6-chain, that is adjacent to boron, with the very electrophilic zirconium center.

Ethyne insertion reactions were also carried out under similar conditions with the (butadiene)metallocene derived metallocene–borate betaine systems **3b** and **3c** and with the (isoprene)zirconocene complex **3d**. In each case the analogous chiral cyclic acetylene insertion products were obtained. In the case of the product **5c** the characteristic asymmetry of the metallacyclic system is revealed by the observation of a set of eight different MeCp methine ^{13}C NMR resonances (in toluene-d_8, −10°C at δ 114.8, 114.7, 111.5, 111.3, 110.4, 109.3, 106.7, 106.0).

A priori, the reaction of the isoprene-derived system could have presented us with a selectivity problem. However, it turns out that the addition of $B(C_6F_5)_3$ to the coordinated isoprene ligand in the complex **1d** occurs exclusively at the $-CH=CH_2$ terminus of the conjugated diene (for related regioselectivities in reactions involving (isoprene)group 4 metallocene complexes see e.g. [86]). The resulting betaine complex **3d** then subsequently inserts the acetylene reagent at the opposite end of the former isoprene moiety [6] leading to the selective formation of the product **5d** that exhibits the isoprene-derived methyl substituent at carbon atom C4 of the resulting carbon ligand chain.

We next treated the metallocene–borate–betaine complexes **3a**–**c** with propyne. The same type of insertion products were obtained as in the reactions with ethyne. However, it turned out that here the insertion was unselective with regard to the regiochemistry of the 1-alkyne insertion. In each case a 1:1 mixture of the regioisomeric insertion products **6a**–**c** (methyl group attached at carbon atom C2) and **7a**–**c** (CH_3 group bonded to C1) was obtained. The regioisomers are readily distinguished by their respective ^1H and ^{13}C NMR resonances of the propyne derived building blocks. Thus, complex **6a** ($L_nM=Cp_2Zr$) exhibits a ^1H NMR singlet of the 1-H hydrogen at δ 4.74 ppm (in toluene-d_8 at 238 K, 600 MHz) and the corresponding C1 signal at δ 168.2, whereas the 1-H resonance is missing for the regioisomer **7a** (2-H signal at δ 5.2 ppm) and the C1 signal here is observed at δ 182.9. Complete assignments of the $^1H/^{13}C$ NMR spectra of the complexes **6a**–**c** and **7a**–**c** were achieved using a combination of the 2D NMR experiments mentioned above.

[5] The *m*-F/*p*-F chemical shift difference of **5a** is 5.1 ppm. It has been argued that this might indicate that the adjacent carbon (here: $-C^6H_2-$[B]) is involved in ion-pair formation [85].

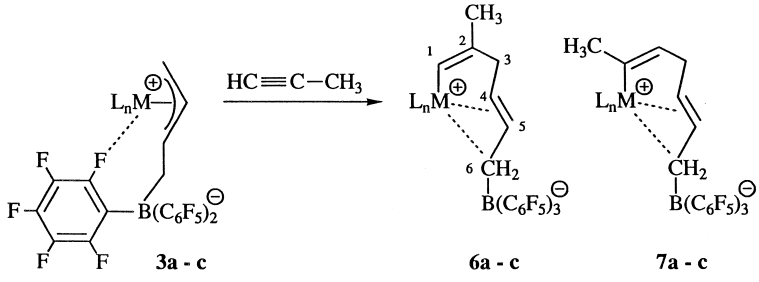
[6] Selective 1,4-addition is often observed in a variety of template reactions involving the (conjugated diene)group 4 metallocene complexes. For typical examples see: [87–95].

Table 1
Selected ^{13}C NMR data[a] of the pairs of regioisomeric propyne insertion products **6a–c** (2-CH_3) and **7a–c** (1-CH_3)

Compd	L_nM	C1	C2	C3	C4	C5	C6	CH_3
6a	Cp_2Zr	168.2	150.4	40.7	132.9	128.0	~4	27.2
7a		182.9	135.6	37.0	130.3	135.0	~6	30.2
6b	Cp_2Hf	173.6	146.8	41.1	132.0	130.6	~8	27.7
7b		192.4	126.0	36.0	123.2	145.3	~21	29.0
6c	$(MeCp)_2Zr$	175.4	150.4	41.3	131.1	131.7	~6	27.3
7c		187.9	135.2	40.8	126.0	140.0	~21	30.4

[a] In toluene-d_8 at 238 K, 150 MHz.

Again in each case a set of chiral products is obtained (e.g. **6a/7a**: $^1H/^{13}C$ NMR signals of the two pairs of diastereotopic Cp-ligands observed at δ 5.23, 5.22, 5.21, 5.14/111.9, 111.3, 110.9, 110.7) which again indicates the presence of cyclic structures by internal ion-pair formation. The ^{13}C NMR data again indicate that the C4–C6 section of the C1–C6 carbon ligand chain is involved, although the relative contribution of the $C^4=C^5$ double bond vs. the C^6H_2–[B] interaction with the zirconium center seems to vary with the specific metal/ligand combination involved (see Table 1, see below for a general discussion of the $C^4H=C^5H-C^6H_2$–[B] interaction with the zirconium center). Again there is no indication of Zr · · · F–C interaction in the complexes **6** and **7** from the ^{19}F NMR spectra.



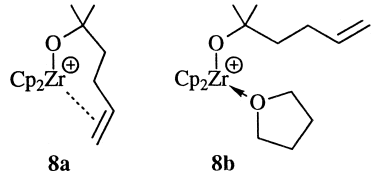
L_nM = Cp_2Zr (**a**), Cp_2Hf (**b**), $(MeC_5H_4)_2Zr$ (**c**)

2.2. Spectroscopic characterization of the intramolecular ion-pair association

From the NMR spectra of the complexes **5** (and also the **6/7** pairs) it appears that the chiral metallacyclic structures of these complexes are likely to arise from internal ion-pair formation. In this case the whole $-C^4H=C^5H-C^6H_2$–[B] unit appears to be involved, although the relative strength of the $-C^4H=C^5H-$/Zr vs. the $-C^6H_2$–[B]/Zr interaction may be unequally pronounced with the different specific examples generated in the course of this study. To gain a deeper understanding of the involvement of 'simple' –CH=CH–olefin-coordination vs. ion-pair metal/ligand interaction of the zirconium with the carbanion-like $-CH_2$–[B] moiety we undertook the following additional investigation.

Starting point of this part of the study was an observation made by Jordan et al. concerning a series of (ω-alkenyloxy)zirconocene cation complexes [96,97] (see also [98]). For the example of the

complex **8a** they found ^{13}C NMR resonances of the coordinated $-CH=CH_2$ group at δ 158.8 and 94.3 in a non-coordinating solvent. Upon addition of THF these values were changed to δ 138.1 and 115.1, respectively, indicating the formation of the uncoordinated (alkenyloxy)(THF)zirconocene cation reference **8b**. Thus it appears that intramolecular coordination of an alkenyl unit may lead to a very pronounced downfield shift of the ^{13}C NMR resonance of the alkene methine group that is arranged towards the zirconocene terminus of the ligand chain (i.e. the 'proximal' $-CH=$ group) whereas the 'distal' carbon atom of the $C=C$ double bond receives an equally pronounced upfield shift upon complexation to the metallocene cation.



8a **8b**

This spectroscopic tool has turned out to be of value in characterizing the metal–olefin interaction in a number of systems that were generated in the course of our present study. For this purpose we had to find ways of arriving at the THF-adducts of the organometallic systems described above to serve as a reference of the uncoordinated alkene situation. This was achieved by the addition of a suitable quantity of tetrahydrofuran to the freshly generated insertion product or by means of an alternative independent synthetic route (see below).

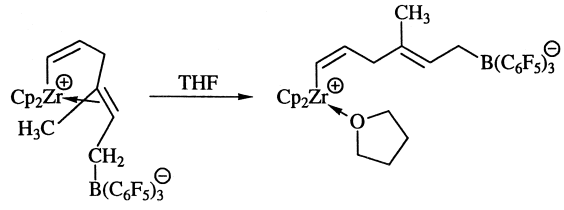
The straightforward procedure of adding THF to the ethyne-insertion product, previously generated in toluene-d_8 solution, was applied in the case of the (isoprene)zirconocene/$B(C_6F_5)_3$/HC≡CH coupling product **5d**. After addition of THF-d_8 the achiral donor-ligand adduct **10d** was obtained ($^1H/^{13}C$ NMR Cp-signal at δ 6.00/114.0). A comparison of the ^{13}C NMR chemical shifts of the C1–C6 ligand chain between the donor-ligand free system **5d** and the THF-adduct **10d**, derived from it (see Table 2), is very instructive. It reveals that the $-C^6H_2-$[B] section of the chain does not significantly change its characteristic ^{13}C NMR chemical shift upon cyclization — so it is likely that in this case the $-C^6H_2$ group is not involved. It appears that the only significant changes take place at the $-C^4H=C^5H-$ carbon carbon double bond. Formal removal of the THF apparently leads to

Table 2
A comparison of characteristic ^{13}C NMR data of internally coordinated zirconocene–alkenylborate–betaine complexes and their acyclic THF donor ligand containing analogues

Compd	C1	C2	C3	C4	C5	C6	Solvent
5d	177.8	144.8	44.3	177.0	112.6	~ 22	[a]
10d	185.8	149.8	46.0	129.0	132.1	16.0	[b]
5a	176.0	142.6	38.0	136.6	129.7	~ 4	[a]
10a[c]	174.5	144.0	40.6	124.2	136.8	29.4	[d]
10a′[c]	185.7	149.2	40.4	122.5	139.6	29.4	[d]
11	176.7	144.2	38.0	149.2	120.6	~ 22[e]	[a]
12	185.7	147.4	39.5	126.5	133.9	24.0[f]	[b]

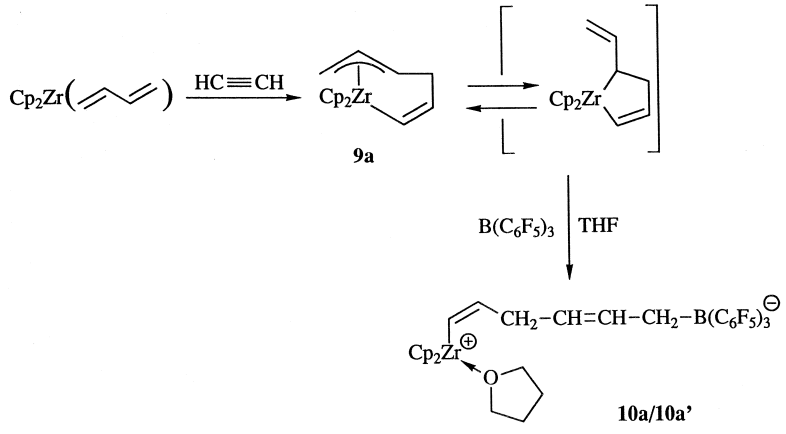
[a] Toluene-d_8.
[b] Toluene-d_8/THF-d_8 2:1.
[c] Two isomers are obtained.
[d] THF-d_8.
[e] C8, C6: 27.0, C7: 27.8.
[f] C8, C6: 37.8, C7: 29.8 ppm.

coordination of this double bond to the zirconium cation. Quite analogously as observed in Jordan's case (**8a′** → **8a**) [96,97] bonding of this C=C double bond to the Cp_2ZrR^+ cation results in a very significant shifting of the ^{13}C NMR resonance of the 'proximate' –CH= moiety to low field (coordination shift $\Delta\delta = +38$ ppm (see Table 2)) and at the same time a very substantial high field shift of the corresponding ^{13}C NMR resonance of the 'distal' =CH– group ($\Delta\delta \approx -20$ ppm, see Table 2). Thus it appears as if the interaction between the C1–C6 ligand chain in the donor–ligand free complex **5d** is dominated by coordination of the internal olefin to the electrophilic zirconium center.



5d **10d**

The THF-donor–ligand stabilized system **10a** was, for the sake of chemical variety, generated by an interesting alternative route, namely treatment of the (butadiene)zirconocene/ethyne addition product **9a** [99–101] with $B(C_6F_5)_3$ in THF-d_8 solution. In this case a close to 1:1 mixture of two isomers is obtained, which we assign them tentatively as *cis*- and *trans*-isomers (**10a**, **10a′**) with regard to the configuration at the $-C^4H=C^5H-$ double bond.

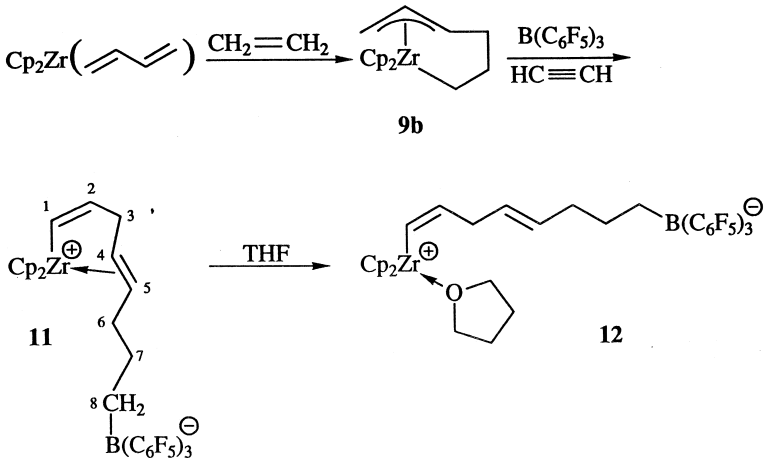


9a **10a/10a'**

In the case of **5a**, coordination of the $-C^4H=C^5H-$ double bond to the zirconium center is again indicated by the typical ^{13}C NMR coordination shift values, that were determined relative to the **10a**/**10a′** standard as a reference ($\Delta\delta$ $-C^4H=$: $+12/+14$ ppm, $\Delta\delta$ $=C^5H-$: $-7/-10$ ppm). But here, the formation of the chiral cyclic system **5a** is also accompanied by a significant high field shift of the $-C^6H_2-$[B] ^{13}C NMR signal ($\Delta\delta = -25$ ppm). This probably indicates that in the case of **5a** the whole boron–bound allyl group (i.e. $-C^4H=C^5H-C^6H_2-$) is involved in the intramolecular coordinative interaction of this specific ligand system with the zirconium center in the betaine system. As the carbon atom C6 is tetracoordinate this situation must probably be regarded as a pronounced internal ion-pair type interaction [45,46].

Eventually, we have prepared a related betaine system that may serve as a reference for this interpretation. One of a variety of suitable reference systems would be designed in such a way that the $-CH_2-B(C_6F_5)_3$ borate end of the betaine dipole would be isolated from the internal –CH=CH– double bond by a number of methylene groups. In such a situation we would expect that only the carbon–carbon double bond could coordinate to zirconium (i.e. providing an 'ordinary' olefin–metallocene coordination) without the interference of the $-CH_2-$[B]/Zr ion-pair bonding contribution.

On the basis of our experience with the **9a** + $B(C_6F_5)_3$ reaction (see above) we prepared such a complex by treatment of the (butadiene)zirconocene/ethylene addition product **9b** [99–101] with $B(C_6F_5)_3$ and acetylene. Treatment of **9b** with these reagents in this order at low temperature in the absence of a coordinating donor solvent resulted in the formation of the chiral hydrocarbyl-bridged metallocene–borate–betaine system **11** ($^1H/^{13}C$ NMR Cp-resonances in toluene-d_8 at 238 K, 600/150 MHz: δ 5.22, 5.09/111.6, 111.3). Subsequent addition of THF-d_8 resulted in the formation of the achiral THF adduct **12** ($^1H/^{13}C$ NMR resonances at δ 6.10/114.5) that was used as a suitable reference to NMR spectroscopically characterize the consequences of internal alkene coordination to the positively polarized zirconocene moiety. As can be seen from the data listed in Table 2 the ^{13}C NMR chemical shift of the distant $-CH_2-$[B] methylene group is practically not influenced by the coordination situation, whereas the $-C^4H=C^5H-$ olefinic group exhibits a pronounced ^{13}C NMR coordination shift upon binding of this group to the zirconocene unit ($\Delta\delta$ $-C^4H=$: +23 ppm, $\Delta\delta$ $=C^5H-$: −13 ppm).



3. Conclusions

The metallocene–borate–betaine system **3** [3–8] is in several ways unique and noteworthy. It represents a novel class of neutral homogeneous one component metallocene Ziegler catalyst systems [102] [7]. It is very easily available, can in principle be isolated as a well defined molecular compound, but is most conveniently being generated in situ under the desired general reaction conditions by simply combining equimolar equivalents of the (conjugated diene)metallocene catalyst precursor and the strong organometallic Lewis acid tris(pentafluorophenyl)borane. We had shown previously that

[7] Reviews: [103–105], and references cited in these articles.

reactive alkene monomers can then be inserted into the active zirconium–carbon bond of the complexes **3** [9]; multiple repetition of this process leads to chain growth and eventually chain transfer and the formation of the respective α-olefin polymer [3–8]. One great advantage of our system **3** is undoubtedly that almost any insertion process can be stopped for a while after the first step by carefully adjusting the actual reaction conditions, and thus the characteristics of the initial carbon carbon coupling process at the active catalyst system at the metallocene–betaine stage can be studied experimentally. This is a situation where we get very close to directly study the course taken in CC-coupling [9,14–29] at the enormously active metallocene Ziegler catalyst systems experimentally, and these studies will probably provide us with a sound experimental basis for a deeper understanding of the functioning and the rules by which extremely active and at the same time very selective chemical catalyst systems are operating.

The reason for a brief pause of the insertion reaction sequence after the first steps in the systems **3**/**5** lies probably in the ability of the product system to internally coordinate weakly the end of the σ-ligand chain [8]. In a few cases this interaction may be described as an internal ion-pairing process, but in a number of cases it is to be regarded as mainly internal η^2-olefin complex formation. The specific systems in the course of this investigation, which are described above, will certainly be of help to identify such metal/alkene π-interactions at other metallocene cation systems in the future. Their spectroscopic characteristics match those found and described by Jordan et al. [96,97] so well, that the typical NMR coordination shifts will serve to identify such bonding situations more easily.

It was a bit surprising to see the ready ability of internal alkene moieties, even of trisubstituted olefin groups to coordinate to the positively polarized zirconocene centers in the situation provided by the systems **5** (and **11**). In this ability the zirconocene cations appear to match a variety of Lewis acids used in organic synthesis [107]. On the other hand it is known that the common homogeneous group 4 metallocene based Ziegler catalyst systems have a very limited tolerance concerning the spectrum of monomers that they are able to convert by catalytical carbon carbon coupling [102–105]. We are hopeful that further studies with derivatives and relatives of the systems described above in this article will help us to overcome the present limitations of the homogeneous metallocene Ziegler catalyst systems and may lead to a much broader synthetic application of these fascinating catalyst systems in the future [108–120].

4. Experimental section

All reactions were carried out under an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. The (conjugated diene)metallocenes [2], the reagents **9** [99–101], and the organometallic Lewis acid tris(pentafluorophenyl)borane (**2**) [1] were prepared according to literature procedures. The NMR spectra were recorded at a Varian Unity Plus Spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz). The following 2D NMR sequences were applied: GHSQC (gradient pulsed heteronuclear single quantum coherence; an inverse C,H correlation is determined), GHMBC (gradient pulsed heteronuclear multiple bond coherence; an inverse long-range C,H correlation is determined), GCOSY (gradient pulsed correlated spectroscopy;

[8] The $-C^4H=C^5H-$ plane will be oriented normal to the $-C^1H=C^2R-$plane to allow for an optimum overlap with the bent metallocene valence orbitals [106].

gives a H,H correlation) [76]. The starting materials **3** were generated in situ in the respective deuterated solvent by equimolar reaction of the respective (conjugated diene)metallocene complex with the $B(C_6F_5)_3$ reagent [3–8].

*4.1. Reaction of the complexes **3** with alkynes, general procedure*

An aliquot of a toluene-d_8 solution (1–2 ml) containing ca. 0.10 mmol of the in situ generated metallocene–borate–betaine complex **3** is transferred to a 5 mm NMR tube and cooled to the required temperature, usually between −10 and −35°C. The alkyne (2–3 ml, 0.09–0.13 mmol) (i.e. ethyne or propyne) is then passed as a gas into the solution by means of a thin glass capillary. The resulting product (**5**) is then analyzed and characterized by NMR spectroscopy at the temperature indicated, in each case including GCOSY and GHSQC experiments, and, if quaternary carbon centers are present, an additional GHMBC experiment.

*4.2. Reaction of **3a** with acetylene, formation of **5a***

3a was generated by treatment of 25 mg (0.09 mmol) of (butadiene)zirconocene (**1a**) with 52 mg (0.10 mmol) of $B(C_6F_5)_3$ in toluene-d_8. Subsequent treatment with 2–3 ml of gaseous HC≡CH (0.09–0.13 mmol) at −35°C gave **5a**. ^{1}H-NMR (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.36$ (m, 1H, 4-H), 5.69 (m, 2H, 5-H, 2-H), 5.20 (dd, $^3J_{HH} = 12.1$, $^4J_{HH} = 2.7$ Hz, 1H, 1-H), 5.18 (s, 5H, CpH), 5.12 (s, 5H, CpH), 2.00 (m, 1H, 3-H^1), 1.90 (m, 1H, 3-H), 0.73 (br, 1H, 6-H^1), 0.43 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 238 K, toluene-d_8): $\delta = 176.0$ (CH, C-1), 148.3 (d, $^1J_{CF} = 246$ Hz, *o*-$B(C_6F_5)_3$), 142.6 (CH, C-2), 139.0 (d, $^1J_{CF} = 264$ Hz, *p*-$B(C_6F_5)_3$), 137.3 (d, $^1J_{CF} = 255$ Hz, *m*-$B(C_6F_5)_3$), 136.6 (CH, C-4), 129.7 (CH, C-5), 110.9 (CH, Cp), 110.7 (CH, Cp), 38.0 (CH_2, C-3), ≈ 4 (C-6) ppm. GCOSY(599.9 MHz, 238 K, toluene-d_8): $\delta = 6.36$ (4-H)/5.69 (5-H), 2.00 (3-H^1), 1.90 (3-H); 5.69 (2-H, 5-H)/5.20 (1-H), 2.00 (3-H′), 0.76 (6-H, H^1); 2.00 (3-H′)/1.90 (3-H); 0.73 (6-H^1)/0.43 (6-H) ppm. GHSQC(599.9 MHz, 238 K, toluene-d_8): $\delta = 176.0/5.20$ (C-1), 142.6/5.69 (C-2), 136.6/6.36 (C-4), 129.7/5.69 (C-5), 110.9, 110.7/5.18, 5.12 (CpH), 38.0/2.00, 1.90 (C-3), 4.0/0.73, 0.46 (C-6) ppm; the C-6 resonance was only observed in the GHSQC experiment, ipso-C of $B(C_6F_5)_3$ not located. ^{19}F-NMR (564.3 MHz, 238 K, toluene-d_8): $\delta = -165.2$ (tr, $^3J_{FF} = 21$ Hz, 6F, *m*-F), −160.1 (tr, $^3J_{FF} = 23$ Hz, 3F, *p*-F), −133.7 (d, $^3J_{FF} = 21$ Hz, 6F, *o*-F) ppm.

*4.3. Formation of the THF-adducts **10a / 10a′***

30 mg (0.10 mmol) of bis(cyclopentadienyl)(1-3:6-η-hexa-2,5-diendiyl)zirconium **9a** was reacted with 52 mg (0.10 mmol) of $B(C_6F_5)_3$ in THF-d_8. The resulting mixture of the isomeric addition products **10a** and **10a′** (1:1) was characterized by NMR spectroscopy. Isomer **10a**: ^{1}H-NMR (599.9 MHz, 303 K, THF-d_8): $\delta = 6.22$ (s, 10H, CpH), 6.00 (m, 1H, 2-H), 5.75 (d, $^3J_{HH} = 12.8$ Hz, 1H, 1-H), 5.58 (m, 1H, 5-H), 4.69 (m, 1H, 4-H), 2.24 (m, 2H, 3-H), 2.09 (m, 2H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 303 K, THF-d_8): $\delta = 174.5$ (CH, $^1J_{CH} = 116$ Hz, C-1), 148.7 (d, $^1J_{CF} = 242$ Hz, *o*-$B(C_6F_5)_3$), 144.0 (CH, $^1J_{CH} = 148$ Hz, C-2), 139.7 (d, $^1J_{CF} = 240$ Hz, *p*-$B(C_6F_5)_3$), 137.9 (d, $^1J_{CF} = 243$ Hz, *m*-$B(C_6F_5)_3$), 136.8 (CH, C-5), 128.3 (C, ipso-$B(C_6F_5)_3$), 124.2 (CH, $^1J_{CH} = 148$ Hz, C-4), 113.3 (CH, $^1J_{CH} = 174$ Hz, Cp), 40.6 (CH_2, $^1J_{CH} = 125$ Hz, C-3), 29.4 (br, CH_2, C-6) ppm. GCOSY(599.9 MHz, 303 K, THF-d_8) $\delta = 6.00$ (2-H)/5.75 (1-H), 2.24 (3-H,H^1); 5.85 (5-H)/4.69

(4-H), 2.09 (6-H,H[1]); 4.69 (4-H)/2.24 (3-H, H[1]) ppm. GHSQC(599.9 MHz, 303 K, THF-d_8) $\delta = 174.5/5.75$ (C-1), 144.0/6.00 (C-2), 136.8/5.85 (C-5), 124.2/4.69 (C-4), 113.3/6.22 (CpH), 40.6/2.24 (C-3), 29.4/2.09 (C-6) ppm. Isomer **10a′**: ^{1}H-NMR (599.9 MHz, 303 K, THF-d_8): $\delta = 6.53$ (s, 10H, CpH), 6.31 (m, 1H, 2-H), 5.66 (m, 1H, 5-H), 5.38 (d, $^3J_{HH} = 11.0$ Hz, 1H, 1-H), 4.75 (m, 1H, 4-H), 2.31 (br, 2H, 3-H), 2.13 (br, 2H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 303 K, THF-d_8): $\delta = 185.7$ (CH, $^1J_{CH} = 110$ Hz, C-1), 149.2 (CH, $^1J_{CH} = 150$ Hz, C-2), 148.7 (d, $^1J_{CF} = 242$ Hz, *o*-B(C_6F_5)$_3$), 139.7 (d, $^1J_{CF} = 240$ Hz, *p*-B(C_6F_5)$_3$), 139.6 (CH, C-5), 137.9 (d, $^1J_{CF} = 243$ Hz, *m*-B(C_6F_5)$_3$), 128.3 (C, ipso-B(C_6F_5)$_3$), 122.5 (CH, $^1J_{CH} = 148$ Hz, C-4), 115.0 (CH, $^1J_{CH} = 175$ Hz, Cp), 40.4 (CH_2, $^1J_{CH} = 126$ Hz, C-3), 29.4 (br CH_2, C-6) ppm. GCOSY(599.9 MHz, 303 K, THF-d_8) $\delta = 6.31$ (2-H)/5.38 (1-H), 2.31 (3-H,H[1]); 5.66 (5-H)/4.75 (4-H), 2.13 (6-H,H[1]); 4.75 (4-H)/2.31 (3-H,H[1]) ppm. GHSQC(599.9 MHz, 303 K, THF-d_8) $\delta = 185.7/5.38$ (C-1), 149.2/6.31 (C-2), 139.6/5.66 (C-5), 122.5/4.75 (C-4), 115.0/6.22 (CpH), 40.4/2.31 (C-3), 29.4/2.13 (C-6) ppm. ^{19}F-NMR (564.3 MHz, 303 K, THF-d_8): $\delta = -169.2$ (br, 12F, *m*-F), -166.8 (br, 6F, *p*-F), -132.4 (br, 12F, *o*-F) ppm (the ^{19}F-NMR set of resonances of both isomers is identical).

4.4. Reaction of *3b* with acetylene, formation of *5b*

3b, in situ generated by treatment of 20 mg (0.06 mmol) of (η^4-butadiene)bis(η^5-cyclopentadienyl)hafnium (**1b**) with 32 mg (0.06 mmol) of B(C_6F_5)$_3$, was treated in toluene-d_8 with 2–3 ml (0.09–0.13 mmol) of gaseous HC≡CH at -35°C to yield **5b**. ^{1}H-NMR (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.25$ (m, 1H, 4-H), 5.85 (m, 2H, 5-H, 2-H), 5.56 (dd, $^3J = 12.7$ Hz, $^4J = 2.3$ Hz, 1H, 1-H), 5.15 (s, 5H, CpH), 5.06 (s, 5H, CpH), 2.01 (m, 2H, 3-H,H[1]), 0.80 (br, 1H, 6-H[1]), 0.37 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 238 K, toluene-d_8): $\delta = 180.9$ (CH, C-1), 148.2 (d, $^1J_{CF} = 242$ Hz, *o*-B(C_6F_5)$_3$), 139.0 (d, $^1J_{CF} = 260$ Hz, *p*-B(C_6F_5)$_3$), 138.8 (CH, C-2), 137.3 (d, $^1J_{CF} = 255$ Hz, *m*-B(C_6F_5)$_3$), 134.9 (CH, C-4), 131.5 (CH, C-5), 122.8 (br C, ipso-B(C_6F_5)$_3$), 110.4 (CH, Cp), 110.1 (CH, Cp), 38.2 (CH_2, C-3), ≈ 8 (C-6) ppm. GCOSY (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.25$ (4-H)/5.85 (5-H), 2.01 (3-H,H[1]); 5.85 (2-H, 5-H)/5.56 (1-H), 2.01 (3-H,H[1]), 0.80 (6-H[1]), 0.37 (6-H); 0.80 (6-H[1])/0.37 (6-H) ppm. GHSQC (599.9 MHz, 238 K, toluene-d_8): $\delta = 180.9/5.56$ (C-1), 138.8/5.85 (C-2), 134.9/6.25 (C-4), 131.5/5.85 (C-5), 110.4/5.15 (CpH), 110.1/5.06 (CpH), 38.2/2.01 (C-3), 8.0/0.80, 0.37 (C-6) ppm (C-6 resonance was only detected in the GHSQC experiment). ^{19}F-NMR (564.3 MHz, 238 K, toluene-d_8): $\delta = -165.4$ (tr, $^3J_{FF} = 22$ Hz, 6F, *m*-F), -160.3 (tr, $^3J_{FF} = 22$ Hz, 3F, *p*-F), -133.5 (d, $^3J_{FF} = 23$ Hz, 6F, *o*-F) ppm.

4.5. Reaction of *3c* with acetylene, formation of *5c*

Reaction of 30 mg (0.10 mmol) of (η^4-butadiene)bis(η^5-methylcyclopentadienyl)zirconium (**1a**) and 52 mg (0.10 mmol) of B(C_6F_5)$_3$ in toluene-d_8 gave **3c**, which was reacted with 2–3 ml (0.09–0.13 mmol) of gaseous acetylene at -10°C to give **5c**. ^{1}H-NMR (599.9 MHz, 263 K, toluene-d_8): $\delta = 6.13$ (m, 1H, 4-H), 5.89 (m, 1H, 5-H), 5.77 (m, 1H, 2H), 5.38 (m, 1H, 1-H), 5.34, 5.32 (3x), 5.20, 5.13, 4.71, 4.49 (each m, each 1H, each CpH), 1.97 (m, 1H, 3-H[1]), 1.87 (m, 1H, 3-H), 1.40, 1.39 (each s, each 3H, each CpMe), 0.85 (br, 1H, 6-H[1]), 0.56 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 263 K, toluene-d_8): $\delta = 175.7$ (CH, C-1), 148.4 (d, $^1J_{CF} = 248$ Hz, *o*-B(C_6F_5)$_3$), 143.0 (CH, C-2), 139.4 (d, $^1J_{CF} = 255$ Hz, *p*-B(C_6F_5)$_3$), 137.4 (d, $^1J_{CF} = 253$ Hz, *m*-B(C_6F_5)$_3$), 134.4 (CH, C-4), 132.7 (CH, C-5), 114.8, 114.7, 111.5, 111.3, 110.4, 109.3, 106.7, 106.0 (each CH, each Cp), 38.0 (CH_2, C-3), 14.9, 14.7 (CH_3, CpMe), ≈ 6 (C-6) ppm. GCOSY (599.9 MHz, 263 K, toluene-d_8): $\delta = 6.13$ (4-H)/5.89 (5-H), 1.97 (3-H[1]), 1.87 (3-H); 5.89

(5-H)/0.85 (6-H^1), 0.56 (6-H); 5.77 (2-H)/5.38 (1-H); 1.97 (3-H^1)/1.87 (3-H); 0.85 (6-H^1)/0.56 (6-H) ppm. GHSQC (599.9 MHz, 263 K, toluene-d_8): δ = 175.7/5.38 (C-1), 143.0/5.77 (C-2), 134.4/6.13 (C-4), 132.7/5.89 (C-5), 114.8/5.34 (CpH), 114.7/5.32 (CpH), 111.5/4.71 (CpH), 111.3/5.13 (CpH), 110.4/5.20 (CpH), 109.3/5.32 (CpH), 106.7/4.49 (CpH), 106.0/5.32 (CpH), 38.0/1.97, 1.87 (C-3), 14.9, 14.7/1.49, 1.39 (MeCp), 6.0/0.85, 0.56 (C-6) ppm (C-6 resonance located in GHSQC, quat. CpMe resonances and ipso-C of C_6F_5 not located). ^{19}F-NMR (564.3 MHz, 263 K, toluene-d_8): δ = −165.5 (tr, $^3J_{FF}$ = 21 Hz, 6F, *m*-F), −160.4 (tr, $^3J_{FF}$ = 21 Hz, 3F, *p*-F), −133.6 (d, $^3J_{FF}$ = 20 Hz, 6F, *o*-F) ppm.

*4.6. Reaction of **3d** with acetylene, formation of **5d***

Reaction of 29 mg (0.10 mmol) of bis(η^5-cyclopentadienyl)(η^4-isoprene)zirconium (**1d**) and 52 mg (0.10 mmol) of B(C_6F_5)$_3$ in toluene-d_8 gave **3d**, subsequent treatment with 2–3 ml (0.09–0.13 mmol) of acetylene at −35°C gave **5d**. ^{1}H-NMR (599.9 MHz, 253 K, toluene-d_8): δ = 5.85 (m, 1H, 2-H), 5.47 (br, 1H, 5-H), 5.33 (dd, ^3J = 12.8 Hz, ^4J = 3.2 Hz, 1H, 1-H), 5.21, 5.08 (each s, each 5H, each CpH), 2.45 (d, ^2J = 15.6 Hz, 1H, 3-H^1), 1.81 (dd, ^2J = 15.6 Hz, ^3J = 5.7 Hz, 1H, 3-H), 1.29 (br, 1H, 6-H^1), 1.14 (s, 3H, CH_3), −0.56 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 253 K, toluene-d_8): δ = 177.8 (CH, C-1), 177.0 (C, C-4), 148.4 (d, $^1J_{CF}$ = 248 Hz, *o*-B(C_6F_5)$_3$), 144.8 (CH, C-2), 139.2 (d, $^1J_{CF}$ = 255 Hz, *p*-B(C_6F_5)$_3$), 137.4 (d, $^1J_{CF}$ = 255 Hz, *m*-B(C_6F_5)$_3$), 112.6 (CH, C-5), 112.4, 111.4 (each CH, each Cp), 44.3 (CH_2, C-3), 19.8 (CH_3), ≈ 22 (C-6) ppm. GCOSY (599.9 MHz, 253 K, toluene-d_8): δ = 5.85 (2-H)/5.33 (1-H), 1.81 (3-H); 5.47 (5-H)/1.29 (6-H^1); 2.45 (3-H^1)/1.81 (3-H); 1.29 (6-H^1)/-0.56 (6-H) ppm. GHSQC (599.9 MHz, 253 K, toluene-d_8): δ = 177.8/5.33 (C-1), 144.8/5.85 (C-2), 112.6/5.47 (C-5), 112.4/5.11 (CpH), 111.4/5.08 (CpH), 44.3/2.45, 1.81 (C-3), 19.8/1.14 (CH_3), 22.0/1.29, −0.56 (C-6) ppm. GHMBC(599.9 MHz, 253 K, toluene-d_8): δ = 177.8 (C-1)/5.88 (2-H), 1.81 (3-H), 177.0 (C-4)/1.14 (7-H), 112.6 (C-5)/1.81 (3-H), 1.14 (CH_3), 44.3 (C-3)/1.14 (CH_3) ppm (C-6-resonance and ipso-C of C_6F_5 not observed. ^{19}F-NMR (564.3 MHz, 253 K, toluene-d_8): δ = −165.7 (tr, $^3J_{FF}$ = 21 Hz, 6F, *m*-F), −160.5 (tr, $^3J_{FF}$ = 21 Hz, 3F, *p*-F), −131.8 (d, $^3J_{FF}$ = 20 Hz, 6F, *o*-F) ppm.

*4.7. Formation of the THF-adduct **10d***

5d was generated in toluene-d_8 analogously as described above, then 0.5 ml of THF-d_8 was added to the solution at −35°C in the NMR tube to give **10d**. ^{1}H-NMR (599.9 MHz, 263 K, toluene-d_8:THF-d_8 2:1): δ = 6.46 (m, 1H, 2-H), 6.00 (s, 10H, CpH), 5.65 (m, 1H, 5-H), 4.98 (d, ^3J = 10.8 Hz, 1H, 1-H), 2.51 (br, 2H, 6-H, H^1), 2.21 (m, 2H, 3-H, H^1), 1.50 (s, 3H, CH_3) ppm. ^{13}C-NMR (150.8 MHz, 263 K, toluene-d_8:THF-d_8 2:1): δ = 185.8 (CH, C-1), 149.0 (d, $^1J_{CF}$ = 240 Hz, *o*-B(C_6F_5)$_3$), 149.8 (CH, C-2), 139.6 (d, $^1J_{CF}$ = 240 Hz, *p*-B(C_6F_5)$_3$), 137.6 (d, $^1J_{CF}$ = 240 Hz, *m*-B(C_6F_5)$_3$), 132.1 (CH, C-5), 129.0 (C-4), 114.0 (CH, Cp), 46.0 (CH_2, C-3), 16.6 (CH_3), 16.0 (br CH_2, C-6) ppm. GCOSY (599.9 MHz, 263 K, toluene-d_8:THF-d_8 2:1) δ = 6.46 (2-H)/4.98 (1-H), 2.21 (3-H, H^1); 5.65 (5-H)/2.51 (6-H, H^1) ppm. GHSQC(599.9 MHz, 263 K, toluene-d_8:THF-d_8 2:1) δ = 185.8/4.98 (C-1), 149.8/6.46 (C-2), 132.1/5.65 (C-5), 114.0/6.00 (CpH), 46.0/2.21 (C-3), 16.6/1.50 (CH_3), 16.0/2.51 (C-6) ppm. GHMBC (599.9 MHz, 263 K, toluene-d_8:THF-d_8 2:1) δ = 185.8 (C-1)/6.46 (2-H), 149.8 (C-2)/4.96 (1-H), 2.21 (3-H, H^1), 132.1 (C-5)/2.51 (6-H, H^1), 1.21 (3-H, H^1), 1.50 (CH_3), 129.0 (C-4)/2.51 (6-H, H^1), 22.1 (3-H, H^1), 1.50 (7-H), 46.0 (C-3)/1.50 (CH_3), 16.6 (CH_3)/5.67 (5-H) ppm (ipso-C of C_6F_5 not observed). ^{19}F-NMR (564.3 MHz, 263 K, toluene-d_8:THF-d_8 2:1): δ = −169.7 (tr, $^3J_{FF}$ = 21 Hz, 6F, *m*-F), −167.4 (tr, $^3J_{FF}$ = 21 Hz, 3F, *p*-F), −135.6 (d, $^3J_{FF}$ = 21 Hz, 6F, *o*-F) ppm.

4.8. Generation of **11**

30 mg (0.10 mmol) of bis(cyclopentadienyl)(1-3:6-η-hexendiyl)zirconium (**9b**) was treated with 52 mg (0.10 mmol) of $B(C_6F_5)_3$ in toluene-d_8 and then subsequently reacted with 2–3 ml (0.09–0.13 mmol) of acetylene at −35°C to give **11**. ^{1}H-NMR (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.33$ (m, 1H, 4-H), 5.77 (m, 1H, 2-H), 5.22 (s, 5H, CpH), 5.13 (1H, 1-H), 5.09 (s, 5H, CpH), 4.96 (m, 1H, 5-H), 2.14 (m, 1H, 3-H^1), 2.10 (m, 1H, 3-H), 1.76 (m, 1H, 8-H^1), 1.60 (m, 1H, 8-H), 1.39 (m, 1H, 7-H^1), 1.24 (m, 1H, 7-H), 0.40 (m, 1H, 6-H^1), −2.91 (m, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 238 K, toluene-d_8): $\delta = 176.7$ (CH, C-1), 149.0 (d, $^1J_{CF} = 242$ Hz, *o*-$B(C_6F_5)_3$), 149.2 (CH, C-4), 144.2 (CH, C-2), 139.6 (d, $^1J_{CF} = 250$ Hz, *p*-$B(C_6F_5)_3$), 137.3 (d, $^1J_{CF} = 250$ Hz, *m*-$B(C_6F_5)_3$), 120.6 (CH, C-5), 111.6, 111.3 (each CH, each Cp), 38.0 (CH_2, C-3), 27.8 (CH_2, C-7), 27.0 (CH_2, C-6), ≈ 22 (C-8) ppm. GCOSY (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.33$ (4-H)/4.96 (5-H), 2.14 (3-H^1); 5.77 (2-H)/5.13 (1-H), 2.14 (3-H^1), 4.96 (5-H), 0.40 (6-H^1), −2.91 (6-H); 2.14 (3-H^1)/2.10 (3-H); 1.76 (8-H^1)/1.60 (8-H), 1.39 (7-H^1), 1.24 (7-H); 1.60 (8-H)/1.39 (7-H^1), 1.24 (7-H); 1.39 (7-H^1)/1.24 (7-H), 0.40 (6-H^1), −2.91 (6-H); 1.24 (7-H)/0.40 (6-H^1), −2.91 (6-H); 0.40 (6-H^1)/−2.91 (6-H) ppm. GHSQC (599.9 MHz, 238 K, toluene-d_8): $\delta = 176.7/5.13$ (C-1), 149.2/6.33 (C-4), 144.2/5.77 (C-2), 120.6/4.96 (C-5), 111.6/5.22 (CpH), 111.3/5.09 (CpH), 38.0/2.14, 2.10 (C-3), 27.8/1.39, 1.24 (C-7), 27.0/0.40, −2.91 (C-6), 22.0/1.76, 1.60 (C-8) ppm (C-8 assigned by GHSQC, ipso-C of C_6F_5 not found). ^{19}F-NMR (564.3 MHz, 238 K, toluene-d_8): $\delta = -166.9$ (tr, $^3J_{FF} = 21$ Hz, 6F, *m*-F), −163.5 (tr, $^3J_{FF} = 23$ Hz, 3F, *p*-F), −134.0 (d, $^3J_{FF} = 22$ Hz, 6F, *o*-F) ppm.

4.9. Generation of the THF-adduct **12**

Complex **11** was generated analogously as described above. Subsequent addition of 0.5 ml of THF-d_8 at −35°C gave **12**. ^{1}H-NMR (599.9 MHz, 263 K, toluene-d_8:THF-d_8 2:1): $\delta = 6.54$ (m, 1H, 2-H), 6.10 (s, 10H, CpH), 5.50 (m, 1H, 5-H), 5.34 (m, 1H, 4-H), 5.13 (d, $^3J_{HH} = 11.1$ Hz, 1H, 1-H), 2.26 (m, 2H, 3-H, H^1), 2.15 (m, 2H, 6-H, H^1), 1.48 (br, 2H, 8-H, H^1), 1.16 (m, 2H, 7-H, H^1) ppm. ^{13}C-NMR (150.8 MHz, 263 K, toluene-d_8:THF-d_8 2:1): $\delta = 185.7$ (CH, C-1), 149.0 (d, $^1J_{CF} = 240$ Hz, *o*-$B(C_6F_5)_3$), 147.4 (CH, C-2), 139.6 (d, $^1J_{CF} = 240$ Hz, *p*-$B(C_6F_5)_3$), 137.6 (d, $^1J_{CF} = 240$ Hz, *m*-$B(C_6F_5)_3$), 133.9 (CH, C-5), 126.5 (CH, C-4), 114.5 (CH, Cp), 39.5 (CH_2, C-3), 37.8 (CH_2, C-6), 29.8 (CH_2, C-7), 24.0 (C-8) ppm. GCOSY (599.9 MHz, 263 K, toluene-d_8:THF-d_8 2:1) $\delta = 6.54$ (2-H)/5.13 (1-H), 2.26 (3-H,H^1); 5.50 (5-H)/5.34 (4-H), 2.15 (6-H,H^1); 5.34 (4-H)/2.26 (3-H,H^1); 2.15 (6-H,H^1)/1.16 (7-H,H^1); 1.48 (8-H,H^1)/1.16 (7-H,H^1) ppm. GHSQC (599.9 MHz, 263 K, toluene-d_8:THF-d_8 2:1) $\delta = 185.7/5.13$ (C-1), 147.4/6.54 (C-2), 133.9/5.50 (C-5), 126.5/5.34 (C-4), 114.5/6.10 (CpH), 39.5/2.26 (C-3), 37.8/2.15 (C-6), 29.8/2.15 (C-7), 24.0/1.48 (C-8) ppm. (C-8 assigned by GHSQC, ipso-C of C_6F_5 not observed. ^{19}F-NMR (564.3 MHz, 263 K, toluene-d_8:THF-d_8 2:1): $\delta = -169.7$ (tr, $^3J_{FF} = 21$ Hz, 6F, *m*-F), −167.4 (tr, $^3J_{FF} = 21$ Hz, 3F, *p*-F), −135.6 (d, $^3J_{FF} = 21$ Hz, 6F, *o*-F) ppm.

4.10. Reaction of **3a** with propyne, formation of **6a / 7a**

3a was generated by treatment of 25 mg (0.09 mmol) of (η^4-butadiene)bis(η^5-cyclopentadienyl)zirconium (**1a**) with 52 mg (0.10 mmol) of $B(C_6F_5)_3$ in toluene-d_8, then 2–3 ml (0.09–0.13 mmol) of gaseous propyne was added at −35°C to give a 1:1 mixture of the regioisomers **6a** and **7a**. Isomer **6a**: ^{1}H-NMR (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.23$ (m, 1H, 4-H), 5.64 (m, 1H, 5-H), 5.23, 5.22, 5.21, 5.14 (each s, each 5H, each CpH of **6a** and **7a**), 4.74 (s, 1H, 1-H), 1.92

(m, 1H, 3-H[1]), 1.79 (m, 1H, 3-H), 1.36 (s, 3H, 2-CH_3), 0.74 (br, 1H, 6-H[1]), 0.36 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 238 K, toluene-d_8): $\delta = 168.2$ (CH, C-1), 150.4 (C, C-2), 148.2 (d, $^1J_{CF} = 235$ Hz, *o*-B(C_6F_5)$_3$), 139.0 (d, $^1J_{CF} = 261$ Hz, *p*-B(C_6F_5)$_3$), 137.4 (d, $^1J_{CF} = 259$ Hz, *m*-B(C_6F_5)$_3$), 132.9 (CH, C-4), 128.0 (CH, C-5), 111.9, 111.3, 110.9, 110.7 (each CH, each Cp of **6a** and **7a**), 40.7 (CH_2, C-3), 27.2 (2-CH_3), ≈ 4 (br CH_2, C-6) ppm. GCOSY (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.23$ (4-H)/5.64 (5-H), 1.92 (3-H[1]), 1.79 (3-H); 5.64 (5-H)/0.74 (6-H[1]), 0.36 (6-H); 1.92 (3-H[1])/1.79 (3-H); 0.74 (6-H[1])/0.36 (6-H) ppm. GHSQC (599.9 MHz, 238 K, toluene-d_8): $\delta = 168.2/4.74$ (C-1), 132.9/6.23 (C-4), 128.0/5.64 (C-5), 111.9/5.23 (CpH), 111.3/5.21 (CpH), 110.9/5.22 (CpH), 110.7/5.14 (CpH), 40.7/1.92, 1.73 (C-3), 27.2/1.36 (2-CH_3), 4.0/0.74, 0.36 (C-6) ppm. GHMBC (599.9 MHz, 238 K, toluene-d_8): $\delta = 168.2$ (C-1)/1.92 (3-H[1]), 1.79 (3-H), 1.36 (2-CH_3), 150.4 (C-2)/1.92 (3-H[1]), 1.79 (3-H), 1.36 (2-CH_3), 132.9 (C-4)/1.92 (3-H[1]), 1.79 (3-H) ppm. The Cp signals cannot be assigned to the respective isomers. The C-6 resonance was detected in the GHSQC experiment; ipso-C signals of C_6F_5 not observed.

Isomer **7a**: ^{1}H-NMR (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.23$ (m, 1H, 4-H), 6.09 (m, 1H, 5-H), 5.23, 5.22, 5.21, 5.14 (each s, each 5H, each CpH of **6a** and **7a**), 5.20 (1H, 2-H), 1.92 (m, 1H, 3-H[1]), 1.79 (m, 1H, 3-H), 1.02 (s, 3H, 1-CH_3), 0.74 (br, 1H, 6-H[1]), 0.58 (br, 1H, 6-H) ppm. ^{13}C-NMR(150.8 MHz, 238 K, toluene-d_8): $\delta = 182.9$ (C, C-1), 148.2 (d, $^1J_{CF} = 235$ Hz, *o*-B(C_6F_5)$_3$), 139.0 (d, $^1J_{CF} = 261$ Hz, *p*-B(C_6F_5)$_3$), 137.4 (d, $^1J_{CF} = 259$ Hz, *m*-B(C_6F_5)$_3$), 135.6 (CH, C-2), 135.0 (CH, C-5), 130.3 (CH, C-4), 111.9, 111.3, 110.9, 110.7 (each CH, Cp of **6a** and **7a**), 37.0 (CH_2, C-3), 30.2 (1-CH_3), ≈ 6 (br CH_2, C-6) ppm. GCOSY (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.23$ (4-H)/6.09 (5-H), 1.92 (3-H[1]), 1.79 (3-H); 6.09 (5-H)/0.74 (6-H[1]), 0.58 (6-H); 5.20 (2-H)/1.92 (3-H[1]), 1.79 (3-H); 1.92 (3-H[1])/1.79 (3-H); 0.74 (6-H[1])/0.58 (6-H) ppm. GHSQC (599.9 MHz, 238 K, toluene-d_8): $\delta = 135.6/5.20$ (C-2), 135.0/6.09 (C-5), 130.3/6.23 (C-4), 111.9/5.23 (CpH), 111.3/5.21 (CpH), 110.9/5.22 (CpH), 110.7/5.14 (CpH), 37.0/1.92, 1.79 (C-3), 30.2/1.02 (1-CH_3), 6.0/0.74, 0.58 (C-6) ppm. GHMBC (599.9 MHz, 238 K, toluene-d_8): $\delta = 182.9$ (C-1)/5.20 (2-H), 1.92 (3-H[1]), 1.79 (3-H), 1.02 (7-H), 135.6 (C-2)/1.92 (3-H[1]), 1.79 (3-H), 1.02 (1-CH_3), 130.3 (C-4)/1.92 (3-H[1]), 1.79 (3-H) ppm. ^{19}F-NMR (564.3 MHz, 238 K, toluene-d_8, both isomers): $\delta = -165.8$ (tr, $^3J_{FF} = 21$ Hz, 6F, *m*-F), −165.7 (tr, $^3J_{FF} = 21$ Hz, 6F, *m*-F), −160.7 (tr, $^3J_{FF} = 21$ Hz, 3F, *p*-F), −160.6 (tr, $^3J_{FF} = 21$ Hz, 3F, *p*-F), −134.5 (d, $^3J_{FF} = 21$ Hz, 6F, *o*-F), −134.2 (d, $^3J_{FF} = 21$ Hz, 6F, *o*-F) ppm.

*4.11. Reaction of **3b** with propyne, formation of **6b** and **7b***

Treatment of 24 mg (0.07 mmol) of (η^4-butadiene)bis(η^5-cyclopentadienyl)hafnium (**1b**) with 40 mg (0.08 mmol) of B(C_6F_5)$_3$ in toluene-d_8 gave **3b**. Subsequent reaction with 2–3 ml (0.09–0.13 mmol) of propyne at −35°C gave a 1:1 mixture of the regioisomers **6b** and **7b**. Isomer **6b**: ^{1}H-NMR (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.19$ (m, 1H, 4-H), 5.81 (m, 1H, 5-H), 5.24, 5.22, 5.19, 5.08 (each s, each 5H, each CpH of **6b** and **7b**), 5.10 (s, 1H, 1-H), 1.96 (m, 1H, 3-H[1]), 1.90 (m, 1H, 3-H), 1.38 (s, 3H, 2-CH_3), 0.81 (br, 1H, 6-H[1]), 0.27 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 238 K, toluene-d_8): $\delta = 173.6$ (CH, C-1), 148.3 (d, $^1J_{CF} = 251$ Hz, *o*-B(C_6F_5)$_3$), 146.8 (C, C-2), 139.0 (d, $^1J_{CF} = 251$ Hz, *p*-B(C_6F_5)$_3$), 137.3 (d, $^1J_{CF} = 250$ Hz, *m*-B(C_6F_5)$_3$), 132.0 (CH, C-4), 130.6 (CH, C-5), 112.4, 111.7, 110.4, 110.1 (each CH, each Cp of **6b** and **7b**), 41.1 (CH_2, C-3), 27.7 (2-CH_3), ≈ 8 (C-6) ppm. GCOSY (599.9 MHz, 238 K, toluene-d_8): $\delta = 6.19$ (4-H)/5.81 (5-H), 1.96 (3-H[1]), 1.90 (3-H); 5.81 (5-H)/0.81 (6-H[1]); 1.96 (3-H[1])/1.90 (3-H); 0.81 (6-H[1])/0.27 (6-H) ppm. GHSQC (599.9 MHz, 238 K, toluene-d_8): $\delta = 173.6/5.10$ (C-1), 132.0/6.19 (C-4), 130.6/5.81 (C-5), 112.4/5.19 (CpH), 111.7/5.24 (CpH), 110.4/5.08 (CpH), 110.1/5.22 (CpH), 41.1/1.96, 1.90

(C-3), 27.7/1.38 (2-CH_3), 8.0/0.81, 0.27 (C-6) ppm. GHMBC (599.9 MHz, 238 K, toluene-d_8): δ = 173.6 (C-1)/1.38 (2-CH_3), 146.8 (C-2)/1.38 (2-CH_3), 41.1 (C-3)/1.38 (2-CH_3) ppm.

Isomer **7b**: ^{1}H-NMR (599.9 MHz, 238 K, toluene-d_8): δ = 6.60 (m, 1H, 5-H), 5.81 (m, 1H, 4-H), 5.24, 5.22, 5.19, 5.08 (each s, each 5H, each CpH of **6b** and **7b**), 5.12 (1H, 2-H), 1.87 (m, 2H, 3-H, H^1), 1.48 (br, 1H, 6-H^1), 1.13 (d, $^4J_{HH}$ = 1.4 Hz, 3H, 1-CH_3), 0.84 (br, 1H, 6-H) ppm. ^{13}C-NMR(150.8 MHz, 238 K, toluene-d_8): δ = 192.4 (C, C-1), 148.3 (d, $^1J_{CF}$ = 251 Hz, *o*-B(C_6F_5)$_3$), 145.3 (CH, C-5), 139.0 (d, $^1J_{CF}$ = 251 Hz, *p*-B(C_6F_5)$_3$), 137.3 (d, $^1J_{CF}$ = 250 Hz, *m*-B(C_6F_5)$_3$), 126.0 (CH, C-2), 123.2 (CH, C-4), 112.4, 111.7, 110.4, 110.1 (each CH, each Cp of **6b** and **7b**), 36.0 (CH_2, C-3), 29.0 (1-CH_3, C-7), ≈ 21 (C-6) ppm. GCOSY (599.9 MHz, 238 K, toluene-d_8): δ = 6.60 (5-H)/5.81 (4-H), 0.84 (6-H); 5.81 (4-H)/1.87 (3-H,H^1); 5.12 (2-H)/1.87 (3-H,H^1); 1.48 (6-H^1)/0.84 (6-H) ppm. GHSQC (599.9 MHz, 238 K, toluene-d_8): δ = 145.3/6.60 (C-5), 126.0/5.12 (C-2), 123.2/5.81 (C-4), 112.4/5.19 (CpH), 111.7/5.24 (CpH), 110.4/5.08 (CpH), 110.1/5.22 (CpH), 36.0/1.87 (C-3), 29.0/1.13 (1-CH_3), 21.0/1.48, 0.84 (C-6) ppm. GHMBC (599.9 MHz, 238 K, toluene-d_8): δ = 192.4 (C-1)/1.13 (1-CH_3), 126.0 (C-2)/1.13 (1-CH_3) ppm. The C-6 resonances were only detected in the GHSQC experiment. The ipso-C signals of C_6F_5 were not detected. The Cp signals could not be assigned to the respective regioisomers. ^{19}F-NMR (564.3 MHz, 238 K, toluene-d_8, both isomers): δ = −165.7 (tr, $^3J_{FF}$ = 20 Hz, 6F, *m*-F), −165.4 (tr, $^3J_{FF}$ = 20 Hz, 6F, *m*-F), −160.8 (tr, $^3J_{FF}$ = 21 Hz, 3F, *p*-F), −160.3 (tr, $^3J_{FF}$ = 21 Hz, 3F, *p*-F), −134.0 (d, $^3J_{FF}$ = 20 Hz, 6F, *o*-F), −133.5 (d, $^3J_{FF}$ = 20 Hz, 6F, *o*-F) ppm.

*4.12. Reaction of **3c** with propyne, formation of **6c** / **7c***

3c was generated by treatment of 30 mg (0.10 mmol) of (η^4-butadiene)bis(η^5-methylcyclopentadienyl)-zirconium (**1a**) with 52 mg (0.10 mmol) of B(C_6F_5)$_3$ in toluene-d_8. Subsequent treatment with 2–3 ml (0.09–0.13 mmol) of propyne at −10°C gave a 1:1 mixture of the regioisomers **6c** and **7c**. Isomer **6c**: ^{1}H-NMR (599.9 MHz, 263 K, toluene-d_8): δ = 6.04 (m, 1H, 4-H), 5.81 (m, 1H, 5-H), 5.56, 5.44, 5.35 (3x), 5.31, 5.26, 5.21, 5.16, 5.14, 5.12, 4.88, 4.82, 4.80, 4.72, 4.39 (each m, each 1H, each CpH of **6c** and **7c**), 4.91 (s, 1H, 1-H), 1.89 (m, 1H, 3-H^1), 1.77 (m, 1H, 3-H), 1.41 (s, 6H, CpMe), 1.30 (s, 3H, 2-CH_3), 0.75 (br, 1H, 6-H^1), 0.55 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 263 K, toluene-d_8): δ = 175.4 (CH, C-1), 148.6 (d, $^1J_{CF}$ = 244 Hz, *o*-B(C_6F_5)$_3$), 150.4 (C, C-2), 139.4 (d, $^1J_{CF}$ = 242 Hz, *p*-B(C_6F_5)$_3$), 137.4 (d, $^1J_{CF}$ = 246 Hz, *m*-B(C_6F_5)$_3$), 131.7 (CH, C-5), 131.1 (CH, C-4), 116.0, 115.1, 115.0, 114.5, 114.4, 113.8 (2x), 113.2, 111.5 (2x), 110.5, 110.0, 109.4, 107.2, 106.6, 105.8 (each CH, each Cp of **6c** and **7c**), 41.3 (CH_2, C-3), 27.3 (2-CH_3), 14.7 (CH_3, CpMe), ≈ 6 (C-6) ppm. GCOSY (599.9 MHz, 263 K, toluene-d_8): δ = 6.04 (4-H)/5.81 (5-H), 1.89 (3-H^1), 1.77 (3-H); 5.81 (5-H)/0.55 (6-H); 1.89 (3-H^1)/1.77 (3-H); 0.75 (6-H^1)/0.55 (6-H) ppm. GHSQC (599.9 MHz, 263 K, toluene-d_8): δ = 175.4/4.91 (C-1), 131.7/5.81 (C-5), 131.1/6.04 (C-4), 41.3/1.89, 1.77 (C-3), 27.3/1.30 (2-CH_3), 14.7/1.41 (MeCp), 6.0/0.75, 0.55 (C-6) ppm. GHMBC (599.9 MHz, 263 K toluene-d_8): δ = 175.4 (C-1)/1.30 (2-CH_3), 150.4 (C-2)/1.30 (2-CH_3), 131.1 (C-4)/1.30 (2-CH_3) ppm. The Cp signals could not be assigned to the respective regioisomers.

Isomer **7c**: ^{1}H-NMR (599.9 MHz, 263 K, toluene-d_8): δ = 6.36 (m, 1H, 5-H), 5.96 (m, 1H, 4-H), (CpH: see isomer **6c**), 5.31 (v, 1H, 2-H), 1.89, (m, 1H, 3-H^1), 1.77 (m, 1H, 3-H), 1.41 (s, 6H, CpMe), 1.31 (br, 1H, 6-H^1), 1.00 (s, 3H, 1-CH_3), 0.43 (br, 1H, 6-H) ppm. ^{13}C-NMR (150.8 MHz, 263 K, toluene-d_8): δ = 187.9 (C, C-1), 148.6 (d, $^1J_{CF}$ = 244 Hz, *o*-B(C_6F_5)$_3$), 139.4 (d, $^1J_{CF}$ = 242 Hz, *p*-B(C_6F_5)$_3$), 137.5 (d, $^1J_{CF}$ = 246 Hz, *m*-B(C_6F_5)$_3$), 135.2 (CH, C-2), 140.0 (CH, C-5), 126.0 (CH, C-4), (Cp: see isomer **6c**), 40.8 (CH_2, C-3), 30.4 (1-CH_3), ≈ 21 (C-6), 14.6 (CH_3, CpMe) ppm. GCOSY (599.9 MHz, 263 K, toluene-d_8): δ = 6.36 (5-H)/5.96 (4-H), 1.31 (6-H^1), 0.43 (6-H); 5.96

(4-H)/1.89 (3́-H), 1.77 (3-H); 5.31 (2-H)/1.89 (3-H^1), 1.77 (3-H); 1.89 (3-H^1)/1.77 (3-H); 1.31 (6-H^1)/0.43 (6-H) ppm. GHSQC (599.9 MHz, 263 K, toluene-d_8): $\delta = 135.2/5.31$ (C-2), 140.0/6.36 (C-5), 126.0/5.96 (C-4), 40.8/1.89, 1.77 (C-3), 30.4/1.00 (1-CH_3), 21.0/1.31, 0.43 (C-6), 14.6/1.41 (MeCp) ppm. GHMBC (599.9 MHz, 263 K, toluene-d_8): $\delta = 187.9$ (C-1)/1.00 (1-CH_3), 135.2 (C-2)/1.00 (1-CH_3) ppm. C-6 resonance only detected in the GHSQC experiment, quat. Cp and ipso-C of C_6F_5 not observed. ^{19}F-NMR (564.3 MHz, 263 K, toluene-d_8, both isomers): $\delta = -165.7$ (tr, $^3J_{FF} = 20$ Hz, 6F, *m*-F), -165.5 (tr, $^3J_{FF} = 20$ Hz, 6F, *m*-F), -160.8 (tr, $^3J_{FF} = 21$ Hz, 3F, *p*-F), -160.5 (tr, $^3J_{FF} = 21$ Hz, 3F, *p*-F), -133.8 (d, $^3J_{FF} = 20$ Hz, 6F, *o*-F), -133.6 (d, $^3J_{FF} = 20$ Hz, 6F, *o*-F) ppm.

Acknowledgements

Financial support from the Fonds der Chemischen Industrie, the Ministerium für Wissenschaft und Forschung des Landes Nordrhein–Westfalen, and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

[1] A.G. Massey, A.J. Park, J. Organomet. Chem. 2 (1964) 245.
[2] G. Erker, C. Krüger, G. Müller, Adv. Organomet. Chem. 24 (1985) 1.
[3] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, Angew. Chem. 107 (1995) 1867; Angew. Chem. Int. Ed. Engl. 34 (1995) 1755.
[4] J. Karl, G. Erker, R. Fröhlich, J. Organomet. Chem. 535 (1997) 59.
[5] K. Mashima, S. Fujikawa, A. Nakamura, J. Am. Chem. Soc. 115 (1993) 10990.
[6] K. Mashima, S. Fujikawa, H. Urata, E. Tanaka, A. Nakamura, J. Chem. Soc. Chem. Commun. (1994) 1623.
[7] K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka, A. Nakamura, Organometallics 14 (1995) 2633.
[8] D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, Organometallics 14 (1995) 3132.
[9] B. Temme, J. Karl, G. Erker, Chem. Eur. J. 2 (1996) 919.
[10] B. Temme, G. Erker, R. Fröhlich, M. Grehl, Angew. Chem. 106 (1994) 1570; Angew. Chem. Int. Ed. Engl. 33 (1994) 1480.
[11] B. Temme, G. Erker, R. Fröhlich, M. Grehl, J. Chem. Soc., Chem. Commun. (1994) 1713.
[12] G. Erker, W. Ahlers, R. Fröhlich, J. Am. Chem. Soc. 117 (1995) 5853.
[13] W. Ahlers, B. Temme, G. Erker, R. Fröhlich, T. Fox, J. Organomet. Chem. 527 (1997) 191.
[14] R.F. Jordan, D.F. Taylor, J. Am. Chem. Soc. 111 (1989) 778.
[15] R.F. Jordan, R.E. LaPointe, P.K. Bradley, N. Baenziger, Organometallics 8 (1989) 2892.
[16] R.F. Jordan, P.K. Bradley, N.C. Baenziger, R.E. LaPointe, J. Am. Chem. Soc. 112 (1990) 1289.
[17] A.S. Guram, R.F. Jordan, Organometallics 9 (1990) 2190.
[18] R.F. Jordan, D.F. Taylor, N.C. Baenziger, Organometallics 9 (1990) 1546.
[19] A.S. Guram, R.F. Jordan, Organometallics 10 (1991) 3470.
[20] Y.W. Alelyunas, Z. Guo, R.E. LaPointe, R.F. Jordan, Organometallics 12 (1993) 544.
[21] A.S. Guram, Z. Guo, R.F. Jordan, J. Am. Chem. Soc. 115 (1993) 4902.
[22] Z. Guo, D.C. Swenson, R.F. Jordan, Organometallics 13 (1994) 1424.
[23] S. Rodewald, R.F. Jordan, J. Am. Chem. Soc. 116 (1994) 4491.
[24] Y.W. Alelyunas, N.C. Baenziger, P.K. Bradley, R.F. Jordan, Organometallics 13 (1994) 148.
[25] C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, Organometallics 12 (1993) 4473.
[26] C. Pellechia, A. Grassi, A. Immirzi, J. Am. Chem. Soc. 115 (1993) 1160.
[27] C. Pellecchia, A. Immirzi, D. Pappalardo, A. Peluso, Organometallics 3 (1994) 3773.
[28] C. Pellecchia, A. Grassi, A. Zambelli, Organometallics 13 (1994) 298.
[29] C. Pellecchia, A. Immirzi, A. Zambelli, J. Organomet. Chem. 479 (1994) C9.
[30] J.S. Thompson, T. Sorrell, T.J. Marks, J.A. Ibers, J. Am. Chem. Soc. 101 (1979) 4193.
[31] P.W. Murray-Rust, W.C. Stallins, C.T. Monti, R.K. Preston, J.P. Glusker, J. Am. Chem. Soc. 105 (1983) 3206.
[32] 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.

[33] Z. Lin, J.-F. LeMarechal, M. Sabat, T.J. Marks, J. Am. Chem. Soc. 109 (1987) 4127.
[34] D. Stalke, K.H. Whitmire, J. Chem. Soc., Chem. Commun. (1990) 833.
[35] X. Yang, C.L. Stern, T.J. Marks, Organometallics 10 (1991) 840.
[36] A.D. Horton, A.G. Orpen, Organometallics 10 (1991) 3910.
[37] A.R. Siedle, R.A. Newmark, W.M. Lamanna, J.C. Huffman, Organometallics 12 (1993) 1491.
[38] J. Ruwwe, G. Erker, R. Fröhlich, Angew. Chem. 108 (1996) 108; Angew. Chem. Int. Ed. Engl. 35 (1996) 80.
[39] H. Plenio, R. Diodone, Chem. Ber. 129 (1996) 1211.
[40] H. Plenio, R. Diodone, D. Badura, Angew. Chem. 109 (1997) 130; Angew. Chem. Int. Ed. Engl. 36 (1997) 156.
[41] J.D. Dunitz, R. Taylor, Chem. Eur. J. 3 (1997) 89.
[42] T.G. Richmond, Coord. Chem. Rev. 105 (1990) 221.
[43] R.J. Kulawiec, R.H. Crabtree, Coord. Chem. Rev. 99 (1990) 89.
[44] W. Beck, K. Sünkel, Chem. Rev. 88 (1988) 1405.
[45] X. Yang, C.L. Stern, T.J. Marks, Angew. Chem. 104 (1992) 1406; Angew. Chem. Int. Ed. Engl. 31 (1992) 1375.
[46] X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10015.
[47] J.J. Eisch, A.M. Piotrowski, S.K. Brownstein, E.J. Gabe, L.L. Florence, J. Am. Chem. Soc. 107 (1985) 7219.
[48] A.S. Guram, R.F. Jordan, D.F. Taylor, J. Am. Chem. Soc. 113 (1991) 1833.
[49] D. Röttger, G. Erker, R. Fröhlich, S. Kotila, Chem. Ber. 129 (1996) 5.
[50] H. Yamazaki, J. Chem. Soc., Chem. Commun. (1976) 841.
[51] S. Yoshikawa, J. Kiji, J. Furukawa, J. Macromol. Chem. 178 (1977) 1077.
[52] M. Akita, H. Yasuda, A. Nakamura, Bull. Chem. Soc. Jpn. 57 (1984) 480.
[53] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.
[54] K.H. den Haan, Y. Wielstra, J.H. Teuben, Organometallics 6 (1987) 2053.
[55] M. Ishikawa, J. Ohskita, Y. Ito, A. Minato, J. Organomet. Chem. 346 (1988) C58.
[56] H.J. Heeres, J.H. Teuben, Organometallics 10 (1991) 1980.
[57] A.D. Horton, A.G. Orpen, Angew. Chem. 104 (1992) 912; Angew. Chem. Int. Ed. Engl. 31 (1992) 876.
[58] A.D. Horton, A.G. Orpen, Organometallics 11 (1992) 8.
[59] A.D. Horton, J. Chem. Soc., Chem. Commun. (1992) 185.
[60] G.G. Hlatky, H.W. Turner, R.R. Eckman, J. Am. Chem. Soc. 111 (1989) 2728.
[61] M. Bochmann, G. Karger, A.J. Jaggar, J. Chem. Soc., Chem. Commun. (1990) 1038.
[62] A.D. Horton, J.H.G. Frijns, Angew. Chem. 103 (1991) 181; Angew. Chem. Int. Ed. Engl. 30 (1991) 1152.
[63] D.M. Amorose, R.A. Lee, J.L. Petersen, Organometallics 10 (1991) 2191.
[64] X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623.
[65] C. Sishta, R.M. Hathorn, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 1112.
[66] G.G. Hlatky, R.R. Eckman, H.W. Turner, Organometallics 11 (1992) 1413.
[67] C.J. Schaverien, Organometallics 11 (1992) 3476.
[68] M. Bochmann, Angew. Chem. 104 (1992) 1206; Angew. Chem. Int. Ed. Engl. 31 (1992) 1181.
[69] J.J. Eisch, S.I. Pombrik, G.-X. Zheng, Organometallics 12 (1993) 3856.
[70] D.J. Gillis, M.J. Tudoret, M.C. Baird, J. Am. Chem. Soc. 115 (1993) 2543.
[71] F. Calderazzo, G. Pampaloni, L. Rocchi, U. Englert, Organometallics 13 (1994) 2592.
[72] J.L. Kiplinger, T.G. Richmond, C.E. Osterberg, Chem. Rev. 94 (1994) 373.
[73] R.E.v.H. Spence, W.E. Piers, Organometallics 14 (1995) 4617.
[74] M. Bochmann, S.J. Lancaster, O.B. Robinson, J. Chem. Soc., Chem. Commun. (1995) 2081.
[75] H. Braunschweig, T. Wagner, Chem. Ber. 127 (1994) 1613.
[76] S. Braun, H. Kalinowski, S. Berger, 100 and More Basic NMR Experiments, VCH, Weinheim, 1996.
[77] G. Erker, K. Kropp, J.L. Atwood, W.E. Hunter, Organometallics 2 (1983) 1555.
[78] P. Czisch, G. Erker, J. Organomet. Chem. 253 (1983) C9.
[79] P. Czisch, G. Erker, H.-G. Korth, R. Sustmann, Organometallics 3 (1984) 945.
[80] I. Hyla-Kryspin, R. Gleiter, C. Krüger, R. Zwettler, G. Erker, Organometallics 9 (1990) 517.
[81] G. Erker, R. Zwettler, C. Krüger, I. Hyla-Kryspin, R. Gleiter, Organometallics 9 (1990) 524.
[82] Y. Raoult, R. Choukroun, D. Gervais, G. Erker, J. Organomet. Chem. 399 (1990) C1.
[83] G. Erker, Nachr. Chem. Tech. Lab. 40 (1992) 1099.
[84] M. Albrecht, G. Erker, C. Krüger, Synlett (1993) 441.
[85] A.D. Horton, J. de With, A.J. van der Linden, H. van de Weg, Organometallics 15 (1996) 2672.
[86] G. Erker, U. Dorf, Angew. Chem. 95 (1983) 800; Angew. Chem. Int. Ed. Engl. 22 (1983) 777.
[87] G. Erker, Angew. Chem. 101 (1989) 411; Angew. Chem. Int. Ed. Engl. 28 (1989) 397.
[88] G. Erker, F. Sosna, P. Betz, S. Werner, C. Krüger, J. Am. Chem. Soc. 113 (1991) 564.
[89] G. Erker, R. Pfaff, C. Krüger, S. Werner, Organometallics 10 (1991) 3559.
[90] G. Erker, R. Pfaff, C. Krüger, M. Nolte, R. Goddard, Chem. Ber. 125 (1992) 1669.
[91] G. Erker, R. Pfaff, Organometallics 12 (1993) 1921.

[92] G. Erker, R. Pfaff, D. Kowalski, E.-U. Würthwein, C. Krüger, R. Goddard, J. Org. Chem. 58 (1993) 6771.
[93] M. Berlekamp, G. Erker, B. Schönecker, R. Krieg, A.L. Rheingold, Chem. Ber. 126 (1993) 2119.
[94] G. Erker, M. Berlekamp, L. López, M. Grehl, B. Schönecker, R. Krieg, Synthesis (1994) 212.
[95] L. López, M. Berlekamp, D. Kowalski, G. Erker, Angew. Chem. 106 (1994) 1168; Angew. Chem. Int. Ed. Engl. 33 (1994) 1114.
[96] Z. Wu, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 117 (1995) 5867.
[97] C.P. Casey, S.L. Hallenbeck, D.W. Pollock, C.R. Landis, J. Am. Chem. Soc. 117 (1995) 9770.
[98] A.D. Horton, A.G. Orpen, Organometallics 11 (1992) 8.
[99] G. Erker, K. Engel, U. Dorf, J.L. Atwood, W.E. Hunter, Angew. Chem. 94 (1982) 915; Angew. Chem. Int. Ed. Engl. 21 (1982) 914.
[100] U. Dorf, K. Engel, G. Erker, Angew. Chem. 94 (1982) 916; Angew. Chem. Int. Ed. Engl. 21 (1982) 914.
[101] K. Engel, Doctoral Thesis, Univ. Bochum, 1983.
[102] H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.
[103] M. Aulbach, F. Küber, Chemie Unserer Zeit 28 (1994) 197.
[104] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. 107 (1995) 1255; Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.
[105] M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255.
[106] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.
[107] D. Schinzer, Ed., Selectivities in Lewis Acid Promoted Reactions, NATO ASI Ser. C 289 (1989).
[108] S. Thiele, G. Erker, Chem. Ber. 130 (1997) 201.
[109] R. Waymouth, P. Pino, J. Am. Chem. Soc. 112 (1990) 4911.
[110] P. Pino, P. Cioni, J. Wei, J. Am. Chem. Soc. 109 (1987) 6189.
[111] P. Pino, P. Cioni, M. Galimberti, J. Wei, N. Piccolrovazzi, in: W. Kaminsky, H. Sinn (Eds.), Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer, New York, 1980, p. 269.
[112] W.E. Piers, J.E. Bercaw, J. Am. Chem. Soc. 112 (1990) 9406.
[113] C.M. Haar, C.L. Stern, T.J. Marks, Organometallics 15 (1996) 1765.
[114] T.J. Marks, M.R. Gagne, J. Am. Chem. Soc. 111 (1989) 4108.
[115] J.R. Young, J.R. Stille, Organometallics 9 (1990) 3022.
[116] N.S. Barta, B.A. Kirk, J.R. Stille, J. Am. Chem. Soc. 116 (1994) 8912.
[117] N.S. Barta, B.A. Kirk, J.R. Stille, J. Organomet. Chem. 487 (1995) 47.
[118] W.E. Piers, P.J. Shapiro, E.E. Bunel, E. Bercaw, Synlett (1990) 74.
[119] G.A. Molander, J.O. Hobert, J. Am. Chem. Soc. 114 (1992) 3123.
[120] J. Christoffers, R.G. Bergman, J. Am. Chem. Soc. 118 (1996) 4715.