

Dynamic features of the zirconocene–boron–betaine complexes obtained by treatment of bis(alkynyl) zirconocenes with the tris(pentafluorophenyl) borane Lewis-acid¹

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Abstract

Bis(propynyl)zirconocene (**6a**) reacts with tris(pentafluorophenyl)borane to yield the carbon–carbon coupled $Cp_2M(\mu-RCA)B(C_6F_5)_3$ betaine product **4a** ($M = Zr$, $R = CH_3$). A variety of differently substituted analogs was prepared ($M = Zr$, $R = n$ -butyl, phenyl, cyclohexyl; $M = Ti$, $R = CH_3$; $M = Hf$, $R = CH_3$, phenyl, $SiMe_3$). These complexes **4** are chiral due to the presence of a rather stable propeller-like $R-B(aryl)_3$ conformation. The activation barrier of the intramolecular enantiomerization process of many examples of this series of complexes was determined by dynamic ¹H NMR spectroscopy, with ΔG^\ddagger values ranging from ca. 13 to 16 kcal mol⁻¹, depending on the substitution pattern. Complex **4a** reacts with 2,6-dimethylphenylisocyanide to yield the methylenecyclopropene derivative **1** that was characterized by X-ray diffraction.

Keywords: Betaine; Boron; Early transition metals; Zirconium–boron–betaine; Conformational chirality; Metallocenes

1. Prologue and introduction

The chemistry of ionic organic and organometallic systems is often dominated by charge effects [1–4]. Kinetic lability towards nucleophiles or ion pairing features may mask other interesting per se properties of such charged species. A possible way to suppress dominating reaction pathways resulting from strong Coulomb interaction is to covalently bind a balanced anionic counterpart to the cationic framework in such a way that the principal features of the underlying cation system is in its essential part preserved in the resulting overall neutral dipolar molecule (for recent examples in metallocene chemistry see e.g. Ref. [4]).

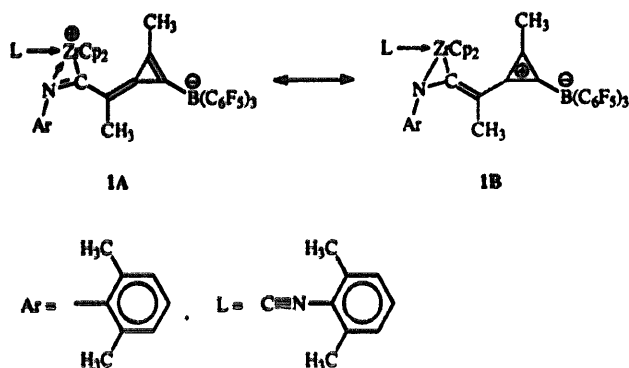
We have tried to use this general concept to synthesize Group 4 metallocene cation complexes that bear their anion covalently bonded with them [5]. Such Group 4 metallocene–boron–betaines may be of great interest since it is possible to introduce analogs of highly reactive organic π -systems between the Cp_2M and BAR_3 ends of these organometallic dipoles and study them in a stable molecular environment [6] (for related examples see Ref. [7]).

Complex **1** represents a typical example. Formally, it contains an iminoacyl-substituted methylenecyclopropene moiety bridging between a $Cp_2Zr(L)$ unit ($L = 2,4$ -dimethylphenylisocyanide) and a tris(pentafluorophenyl)borane unit. The connecting organic system possesses a fully conjugated π -system. Its central σ -framework is completely planar. One could formally describe this compound by a chemical formula (resonance form **1A**) that exhibits a positive charge at the metal center and a negative charge at boron. However, there is substantial evidence for this compound, as well as a number of recently described related systems in this

¹ Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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series, that a pronounced contribution of the resonance form **1B** has to be taken into account; this has the positive charge placed in the three-membered ring, and thus would constitute some cyclopropenylum–betaine character (for a closely related non-organometallic example see Ref. [8]) to the dipolar complex **1**. This evidence comes from the X-ray crystal structure analysis of **1** (see Fig. 1) that clearly indicates an about equal contribution of both the resonance hybrid structures **1A** and **1B** to adequately describe the observed overall bonding situation.



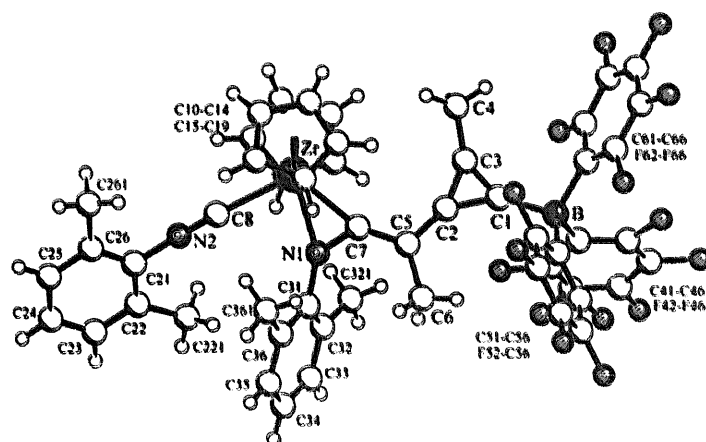
In complex **1** the C1–B bond length is 1.604(11) Å. The adjacent C1–C3 bond inside the three-membered ring is short (1.328(10) Å), but the distal three-membered ring bond is also short at 1.379(10) Å (the C–C bond length inside the three-membered ring of the

triphenylcyclopropenylum cation is almost identical to this value at 1.378 Å [9]). The C2–C5 bond is 1.382(10) Å, the adjacent C5–C7 bond is only slightly longer at 1.408(9) Å. We conclude that the organic bridging π -ligand in the very stable metallocene-(π -organyl)–boron–betaine complex exhibits some unusual bonding features that bear some resemblance with a partial alkenylcyclopropenylum-type system.

The formation of **1** and the explanation of the observed reaction pattern is rather straightforward. Obviously, the direct precursor of the ligand-stabilized system **1** is the unstable donor ligand free (η^2 -iminoacyl)zirconocene species **2** [10], whose precursor obviously is **3**. In our reaction, this is generated from **4a**, which was isolated and fully characterized (see below and the preliminary communication in Ref. [11]).

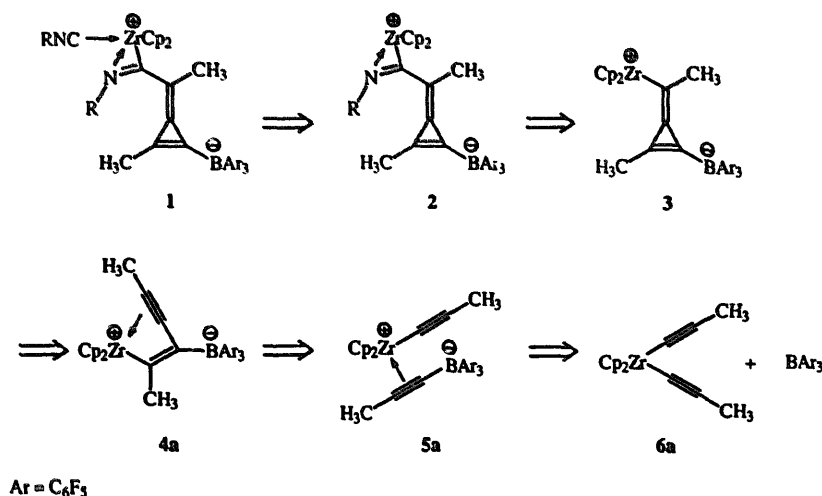
Apparently, the open-chain betaine complex **4a** is in an equilibrium with the thermodynamically less favored (but much more reactive) cyclic species **3**, that is preferentially trapped by the added isonitrile reagent. The **4a** → **3a** rearrangement can simply be regarded as an intramolecular alkyne insertion into an adjacent zirconium to carbon σ -bond. Complex **4a**, in turn, is formed by a similar reaction. It is obtained by treatment of the bis(alkynyl)zirconocene complex **6a** with B(C₆F₅)₃. In this case σ -ligand transfer (to give **5a**) followed by alkyne insertion into the Zr–C σ -bond straightforwardly explains the reaction course taken (Scheme 1).

In some respects, the key intermediates in this reaction sequence are the zirconium–boron–betaine complexes **4**. It has turned out that these systems exhibit a dynamic behavior. We have now prepared a variety of differently substituted systems **4** from differently substi-



Zr–C8 2.349(9), C8–N2 1.148(9), Zr–N1 2.173(6), Zr–C7 2.202(8), N1–C7 1.289(8), C7–C5 1.408(9), C5–C2 1.382(10), C2–C1 1.423(10), C2–C3 1.379(10), C1–C3 1.328(10), C1–B 1.604(11), Zr–C8–N 175.4(7), N1–Zr–C7 34.3(2), Zr–N1–C7 74.1(5), Zr–C7–N1 71.6(5), N1–C7–C5 129.5(7), C7–C5–C2 117.7(7), C5–C2–C1 148.5(8), C5–C2–C3 154.9(8), B–C1–C2 151.4(8), B–C1–C3 148.1(8), C1–C2–C3 56.5(5), C2–C3–C1 63.4(6), C3–C1–C2 60.1(6).

Fig. 1. A view of the molecular structure of **1** with atom numbering scheme and selected bond lengths (Å) and angles (deg).

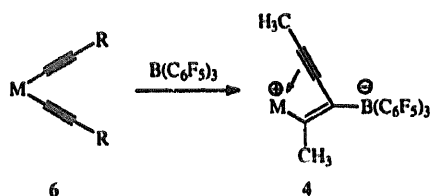


Scheme 1. Retrosynthetic pathway of the formation of complex 1.

tuted precursors **6** to gain insight into the nature of this unexpected dynamic behavior.

2. Results and discussion

The metallocene [(μ -1,4-bis(hydrocarbyl)butadiyne)borato-betaine] complexes **4** were, in this study, all prepared by stoichiometric treatment of the respective bis(alkynyl)metallocene precursors [12] with tris(pentafluorophenyl)borane. Five zirconium complexes (**4a–4e**) were prepared containing methyl-, *n*-butyl-, phenyl-, or cyclohexyl-substituents at the bridging organic ligand. Usually, the parent Cp₂Zr moiety was used, only in one case (**4b**) did we employ the related bis(η^5 -methylcyclopentadienyl)zirconium unit. In addition, we prepared a corresponding titanocene (μ -R-C₄-R)B(C₆F₅)₃ betaine complex (**4f**, with R = CH₃) and three related hafnocene systems (**4g–4i**, with R = CH₃, Ph, and SiMe₃).



- M = Cp₂Zr, R = CH₃ (**a**), *n*-C₄H₉ (**c**), Ph (**d**), cyclohexyl (**e**);
 M = (MeCp)₂Zr, R = CH₃ (**b**);
 M = Cp₂Ti, R = CH₃ (**f**);
 M = Cp₂Hf, R = CH₃ (**g**), Ph (**h**), SiMe₃ (**i**).

The reactions between the bis(alkynyl)metallocenes (**6a–6i**) with tris(pentafluorophenyl)borane were all car-

ried out analogously. As a typical example, a solid sample of bis(propynyl)zirconocene (**6a**) was mixed with solid B(C₆F₅)₃ at -78°C . Addition of toluene at low temperature and work-up after several hours of stirring under ambient conditions resulted in an amorphous solid of **4a**·toluene (ca. 90% isolated). The zirconocenec(μ -hexadiyne)borato-betaine complex **4a** does not exhibit any typical IR band in the $\tilde{\nu}(\text{C}\equiv\text{C})$ range (contrary to the starting material **6a**). The ¹³C NMR resonances of the internally coordinated $-\text{C}\equiv\text{C}-\text{R}$ triple bond are observed at δ 108.5 and 105.0. The ¹³C NMR signal of the α -alkenyl carbon center of the bridging hydrocarbyl ligand that is bonded to zirconium appears at a typically high δ value (255.2) [13], the corresponding β -carbon signal was not observed, probably because of extensive line broadening due to the neighboring boron atom. Surprisingly, complex **4a** is chiral and exhibits temperature-dependent dynamic NMR spectra. The ¹H NMR spectrum (200 MHz) of **4a** in [D₈]toluene at 300 K shows methyl singlets at δ 2.20 and 1.09 and a very broad cyclopentadienyl resonance centered at δ 5.3. Decreasing the monitoring temperature rapidly leads to a splitting into two Cp-singlets of equal intensity that are observed at δ 5.39 and 5.11 in the limiting low temperature ¹H NMR spectrum at 273 K. A Gibbs activation energy of $\Delta G^\ddagger(292\text{K}) = 14.3 \pm 0.5 \text{ kcal mol}^{-1}$ was estimated (using the method described in Ref. [14]) for the intramolecular enantiomerization process of complex **4a** at the Cp-coalescence temperature.

It turns out that the ¹⁹F NMR spectrum of complex **4a** (Fig. 2) is also dynamic. At 303 K the ¹⁹F NMR resonances (at 564 MHz) of most of the B(C₆F₅)₃ fluorine atoms are broad (see Fig. 2); lowering the monitoring temperature rapidly leads to sharpening and splitting of the signals. At 233 K a set of nicely separated ¹⁹F NMR resonances is observed; this indicates that all 15 fluorine substituents in the betaine complex **4a** are

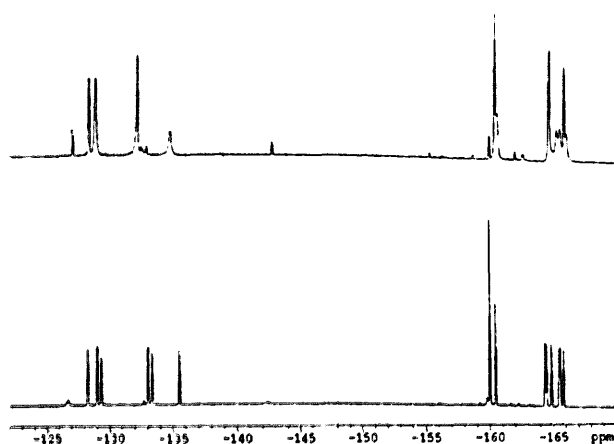


Fig. 2. ^{19}F NMR spectra (564 MHz, CD_2Cl_2) of **4a** at 303 K (top) and 233 K (bottom).

chemically inequivalent. We have observed six C_6F_5 *o*-F signals at δ -128.3, -129.0, -129.3, -133.1, -133.3, -133.5, two overlapping (δ -160.0) and a single *p*- C_6F_5 resonance (-160.4) and six *m*- C_6F_5 signals at δ -164.4, -164.5, -164.9, -165.5 (two closely adjacent signals), and -165.8.

It appears that complex **4a** exhibits a dynamic process in the course of which the diastereotopic faces of the μ -hexadiyne ligand become equilibrated. The bridging hydrocarbyl ligand itself remains unaffected by this process — its methyl groups do not become equilibrated; only the diastereotopic cyclopentadienyl ligands exchange their respective chemical environments during this process. This 'top \rightleftharpoons bottom' exchange remains the essential topological feature of this dynamic process. This rearrangement is not accompanied by a possibly related 'left \rightleftharpoons right' equilibration. This has become evident by following the NMR dynamics of the related bis(methylcyclopentadienyl)Zr(μ -MeC₄Me)B(C_6F_5)₃ betaine complex **4b**. This was prepared analogously by treatment of $(\text{MeCp})_2\text{Zr}(-\text{C}\equiv\text{C}-\text{Me}_3)_2$ (**6b**) with $\text{B}(\text{C}_6\text{F}_5)_3$ in an equimolar ratio. Complex **4b** also shows temperature dependent dynamic ^{19}F NMR spectra. Also, at low temperature a set of 15 separated fluorine resonances are observed: six *o*-F signals at low field, accompanied by three *p*-F- and six *m*-F-resonances at subsequently lower δ values (see Section 4).

The ^1H NMR spectrum of **4b** (200 MHz, CD_2Cl_2) shows two hexadiyne-methyl singlets at δ 2.30 and 2.08 that are not changed with temperature in addition to the two MeCp methyl singlets. These are located at δ 2.09 and 1.89 at 235 K, but rapidly broaden upon raising the temperature of the NMR probe. Eventually they undergo coalescence and then show a single sharp resonance at high temperature. From these dynamic ^1H NMR spectra a Gibbs-activation energy of $\Delta G^\ddagger(269\text{K}) = 13.3\text{ kcal mol}^{-1}$ was calculated [14]. We have also recorded the variable-temperature ^1H NMR spectra of

Table 1

Gibbs activation energies ($\Delta G^\ddagger(T_c)$) of the intramolecular enantiomerization process of complexes $[\text{M}(\mu\text{-RC}_4\text{R})\text{B}(\text{C}_6\text{F}_5)_3]$ **4**

	[M]	R	ΔG^\ddagger^a (kcal mol^{-1})	T_c (K)
4a	Cp_2Zr	CH_3	14.3	292
4b	$(\text{MeCp})_2\text{Zr}$	CH_3	13.3	269
4c	Cp_2Zr	<i>n</i> -C ₄ H ₉	15.0	323
4e	Cp_2Zr	cyclohexyl	16.4	332
4f	Cp_2Ti	CH_3	13.2	272
4g	Cp_2Hf	CH_3	13.8	282

^a Determined by dynamic ^1H NMR spectroscopy from the Cp-coalescence (**4b**: Cp-CH₃ coalescence), ΔG^\ddagger values $\pm 0.5\text{ kcal mol}^{-1}$.

4b at 600 MHz. In combination with the dynamic ^1H NMR 200 MHz spectrum in [*D*₈]toluene, this has revealed that the C₅H₄CH₃ methine resonances are changing from an eight signal pattern at low temperature (233 K: δ 6.13, 6.11, 6.09, 6.07, 5.83, 5.80, 5.75, 5.67) to a four signal pattern above the coalescence point. Thus, the in-plane asymmetry of the bridging CH₃C₄CH₃ ligand remains unaffected in the course of the rearrangement process; apparently there is no rotation about the Zr-C σ -bond taking place on the NMR time scale. Also, any process that would require the formation of a C_{2v} (instead of C_s) symmetric intermediate (or its dynamic rapidly equilibrating symmetry analog) is not compatible with the observed symmetry properties of the dynamic process as it is revealed by the appearance of the temperature dependent NMR spectra of complexes **4a** and **4b**.

The activation barrier of the dynamic process shows a measurable substituent dependence. Attaching *n*-butyl or cyclohexyl groups instead of the methyl groups to the ends of the μ -butadiyne ligand results in gradually increased ΔG^\ddagger values of the internal enantiomerization process (see Table 1). The corresponding zirconocene-borate-betaine complex **4c** exhibits $\Delta G^\ddagger_{\text{enant}}(323\text{K}) = 15.0 \pm 0.5\text{ kcal mol}^{-1}$. This complex also shows 15 clearly distinguished ^{19}F NMR signals at low temperature (see Fig. 3). The cyclohexyl-substituted complex **4e** has an even higher enantiomerization barrier at $\Delta G^\ddagger(332\text{K}) = 16.4\text{ kcal mol}^{-1}$.

The corresponding phenyl-substituted zirconocene betaine system (**4d**) was also generated, but this turned

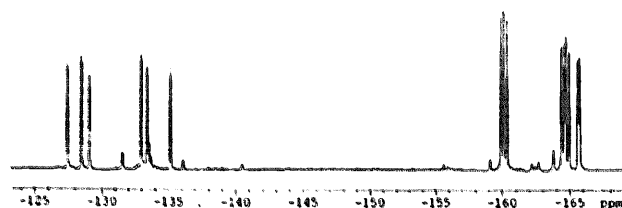


Fig. 3. ^{19}F NMR spectrum (564 MHz, CD_2Cl_2) of complex **4c** at 233 K.

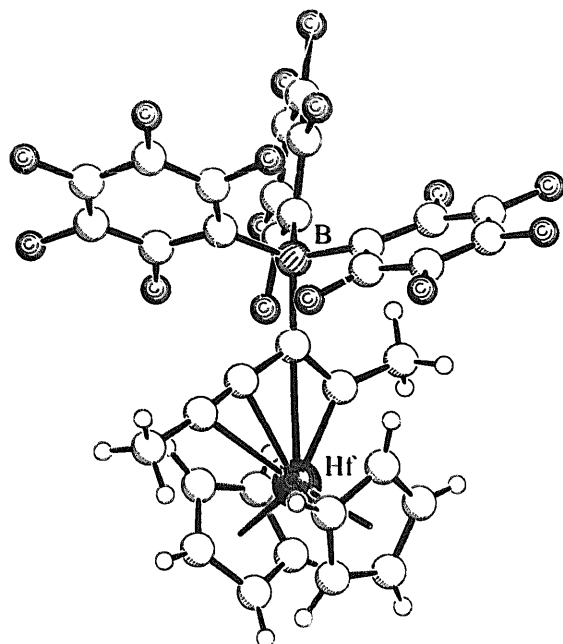


Fig. 4. A projection of the molecular structure of complex 4g in the crystal.

out to be rather unstable and so a reliable ΔG^\ddagger value could not be obtained. Bis(propynyl)titanocene (6f) reacted cleanly with $B(C_6F_5)_3$ to give 4f. The enantiomerization barrier is smaller than that of the analogous zirconium complex (4f: $\Delta G^\ddagger(272\text{ K}) = 13.2 \pm 0.5\text{ kcal mol}^{-1}$; 4a: $\Delta G^\ddagger(292\text{ K}) = 14.3\text{ kcal mol}^{-1}$).

Hafnium to carbon σ -bonds are slightly stronger and shorter than their corresponding Zr-C analogs [15]. Therefore, it is expected that hafnocene complexes attain a position intermediate between their corresponding titanocene and zirconocene congeners. In this case, the $Ti < Hf < Zr$ series is also followed by the order of the $\Delta G_{\text{enanti}}^\ddagger$ values. The hafnocene complex 4g was prepared in the usual way and its enantiomerization barrier determined as $\Delta G^\ddagger(282\text{ K}) = 13.8\text{ kcal mol}^{-1}$. Again, the corresponding phenyl-substituted metallocene-betaine system 4h turned out to be too sensitive for a reliable quantitative analysis of its dynamic behavior. In the trimethylsilyl-substituted analog (4i) the Cp-signals were unfortunately isochronous (or very close to isochronous) under all conditions investigated. Therefore, its $\Delta G_{\text{enanti}}^\ddagger$ value could not be determined.

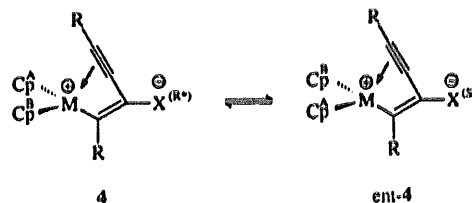
The dynamic process observed of the Group 4 metallocene(μ -butadiyne)borate-betaine complexes 4 requires the presence of a molecular element of chirality that is reversibly inverted in the course of the observed thermally induced equilibration process. The fact that all 15 fluorine atoms of each of the complexes 4 are observed to be chemically inequivalent, points to the chirality information being located at the triarylborate-end of the betaine. The presence of 15 different fluorine substituents requires that all three C_6F_5 groups are

diastereotopic and that there is a stereochemical differentiation between the *ortho*- and *meta*-fluorine pairs at each C_6F_5 -ring. Thus the $B(C_6F_5)_3$ moiety must have attained a chiral conformation within the $R-B(C_6F_5)_3$ unit. We propose that the $-B(C_6F_5)_3$ building block inside the complexes 4 attains a chiral propeller-like orientation of the three $-C_6F_5$ substituents. Inside the overall framework of the complexes 4 this would be sufficient to make the metallocene Cp-ligand systems diastereotopic, provided the molecule is looked at in the kinetic regime where the stereochemically essential rotations about the B-C σ -bonds are sufficiently slow on the NMR time scale.

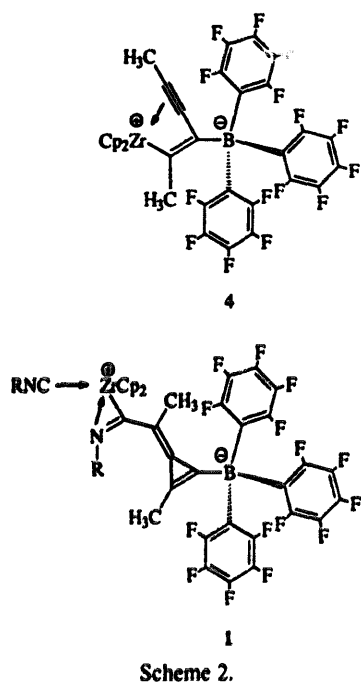
This explanation of the dynamic features of the complexes 4 is supported by the results of a preliminary X-ray crystal structure analysis of the hafnocene(μ -hexadiyne)borate-betaine complex 4g. Owing to problems caused by crystal twinning the quality of the X-ray crystal structure analysis is below the usual standard, so details of the structure will not be discussed. It is, however, sufficient to provide an outline of the overall structural framework of the complexes 4. They exhibit a planar $R-C_4-R$ carbon framework that is located in the main plane of the bent metallocene wedge that bisects the Cp-M-Cp angle, and it shows that the $-B(C_6F_5)_3$ unit attains a chiral distorted three-bladed propeller-like conformation (see Fig. 4).

3. Conclusions

The dynamic equilibration typically observed of the complexes 4 in solution can thus be explained as being due to a conformational inversion of a three-bladed propeller-like conformation of the $-B(C_6F_5)_3$ unit inside the metallocene(μ -hydrocarbyl)borate structure [16].



The observed variation of the enantiomerization barrier from the substituents at the bridging μ -butadiyne-derived ligand and of the nature of the attached metallocene unit (see Table 1) clearly indicates that some steric interaction of the $-C_6F_5$ groups at boron with the extended planar μ - $R-C_4-R$ system is determining the height of this barrier. This is further supported by the



observation that the related metallocene(μ -iminoacyl-methylenecyclopropene)-borate-betaine complexes (such as 1), mentioned and discussed in Section 1, up to now have in no case shown a similar behavior. Although these systems also contain chiral $R-B(C_6F_5)_3$ conformations in the solid state, we have not been able to freeze out their enantiomerization process on the NMR time scale so far. It thus appears that the increased steric interaction with the laterally extended conjugated planar C_4 -framework (and its terminal substituents) provides an essential feature for generating a rather large kinetic barrier of the $-B(aryl)_3$ propeller inversion process at the $R-B(C_6F_5)_3$ building block of the metallocene-borate-betaine complexes 4 (see Scheme 2).

4. 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. Instrumentation used for physical characterization: NMR, Bruker AC 200 P (1H 200.1 MHz, ^{13}C 50.3 MHz), Bruker ARX 300 (1H 300.1 MHz, ^{13}C 75.5 MHz), Bruker AM 360 (1H 360.1 MHz, ^{13}C 90.6 MHz), Varian unity plus (1H 600 MHz, ^{13}C 150 MHz, ^{19}F 564 MHz) spectrometer; IR, Nicolet 5 DXC FT IR spectrometer; elemental analyses, Foss-Heraeus CHNO-Rapid; melting points, DSC 910, DuPont; X-ray crystal structure analyses, Enraf-Nonius MACH 3 diffractometer, SHELX 86, SHELX 93, SCHAKAL. The bis(alkynyl)metallocene complexes (6) were prepared according to literature procedures [12]. Previously described reagents 6 were only characterized spectroscopically. $B(C_6F_5)_3$ was prepared as described in the literature [17]. It was freshly recrystallized from pentane prior to use. ^{19}F NMR chemical shifts were determined by external calibration using the room temperature $C_6H_5CF_3$ resonance ($\delta = -64$ ppm); the listed values are relative to the $CFCl_3$ standard ($\delta = 0$ ppm).

4.1. Preparation of the bis(alkynyl)metallocene complexes 6: general procedure

One equivalent of the metallocenedichloride was mixed with two equivalents of the respective alkynyllithium compound. Tetrahydrofuran was added at $0^\circ C$. After stirring for 2 h at this temperature the solvent was evaporated in vacuo and replaced by dichloromethane. The lithium chloride was removed by filtration, the solvent evaporated in vacuo, the residue stirred with pentane and the resulting solid product collected by filtration.

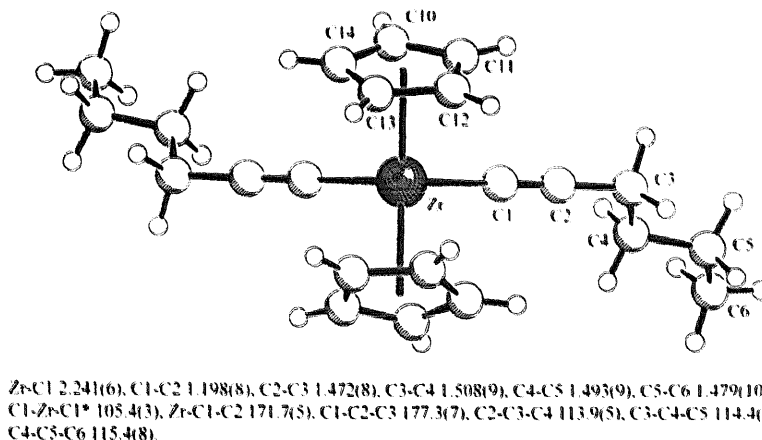


Fig. 5. A view of the molecular structure of 6c with selected bond lengths (\AA) and angles (deg).

4.1.1. Bis(propynyl)zirconocene (6a)

Treatment of 0.80 g (17.4 mmol) of propynyllithium with 2.52 g (8.60 mmol) of zirconocene dichloride in 50 ml of tetrahydrofuran gave 2.00 g (78%) of 6a. ^1H NMR (C_6D_6): $\delta = 6.12$ (s, 10H, Cp), 1.78 (s, 6H, CH_3).

4.1.2. Bis(η^5 -methylcyclopentadienyl)bis(propynyl)zirconocene (6b)

Treatment of 2.40 g (52.2 mmol) of propynyllithium with 8.38 g (26.2 mmol) of $(\text{MeCp})_2\text{ZrCl}_2$ in 80 ml tetrahydrofuran yielded to 4.68 g (55%) of 6b. ^1H NMR (C_6D_6): $\delta = 6.17$ (pt, 4H, Cp), 5.75 (pt, 4H, Cp), 2.30 (s, 6H, Cp- CH_3), 1.76 (s, 6H, CH_3).

4.1.3. Bis(hexynyl)zirconocene (6c)

Reaction of 3.56 g (40.5 mmol) of hexynyllithium with 5.90 g (20.2 mmol) zirconocene dichloride in 80 ml of tetrahydrofuran gave 4.52 g (58%) of 6c as orange needles. ^1H NMR (C_6D_6): $\delta = 6.14$ (s, 10H, Cp), 2.24 (m, 4H, CH_2), 1.44 (m, 8H, CH_2), 0.84 (m, 6H, CH_3). IR (KBr): $\tilde{\nu} = 3087, 2953, 2948, 2929, 2866, 2080, 1840, 1730, 1641, 1438, 1360, 1319, 1311, 1299, 1244, 1103, 1015, 947, 902, 799, 737, 612, 522, 429\text{ cm}^{-1}$. Anal. Found: C, 67.52; H, 7.39. $\text{C}_{22}\text{H}_{28}\text{Zr}$ (383.66). Calc.: C, 68.89; H, 7.31%.

X-ray crystal structure analysis of 6c (see Fig. 5). Needles were obtained by cooling a pentane solution down to -20°C . $\text{C}_{22}\text{H}_{28}\text{Zr}$ (383.66), crystal size $0.80 \times 0.25 \times 0.10\text{ mm}$, $T = 223\text{ K}$, $\lambda = 0.71073\text{ \AA}$, orthorhombic, space group $P2_12_12$ (No. 18), cell parameters $a = 7.535(1)\text{ \AA}$, $b = 20.104(5)\text{ \AA}$, $c = 6.461(1)\text{ \AA}$, $V = 978.7(3)\text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc.}} = 1.302\text{ g cm}^{-3}$, $\mu = 5.6\text{ cm}^{-1}$, 1191 collected reflections, 1190 independent and 1076 observed reflections, full matrix least squares refinement on F^2 , $R = 0.039$, $wR^2 = 0.107$. Further information about the X-ray structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405298, the names of the authors, and the journal citation.

4.1.4. Bis(phenylethynyl)zirconocene (6d)

Treatment of 7.58 g (70.1 mmol) of phenylethynyllithium with 10.2 g (34.8 mmol) of zirconocene dichloride in 100 ml of tetrahydrofuran gave 8.87 g (60%) of the dark brown product 6d. ^1H NMR (C_6D_6): $\delta = 7.50$ (m, 4H, Ph), 7.00 (m, 6H, Ph), 6.14 (s, 10H, Cp).

4.1.5. Bis(cyclohexylethynyl)zirconocene (6e)

1.70 g (14.6 mmol) of cyclohexylethynyllithium was treated with 2.13 g (7.30 mmol) of zirconocene dichloride to yield 1.17 g (37%) of 6e. ^1H NMR (C_6D_6): $\delta = 6.14$ (s, 10H, Cp), 1.70 (m, 22H, cyclohexyl). ^{13}C NMR (C_6D_6): $\delta = 110.8$ (Cp), 33.8, 31.3, 26.5, 25.1 (cyclohexyl), quaternary carbons not observed.

4.1.6. Bis(propynyl)titanocene (6f)

The reaction of 2.15 g (46.7 mmol) of propynyllithium with 5.82 g (23.4 mmol) of titanocene dichloride in 80 ml of tetrahydrofuran gave 5.11 g (86%) of 6f. ^1H NMR (CDCl_3): $\delta = 6.31$ (s, 10H, Cp), 1.90 (s, 6H, CH_3).

4.1.7. Bispropynylhafnocene (6g)

Treatment of 2.67 g (58.0 mmol) of propynyllithium with 11.0 g (29.0 mmol) of hafnocene dichloride in 50 ml of tetrahydrofuran yielded 10.2 g (89%) of 6g. ^1H NMR (C_6D_6): $\delta = 6.04$ (s, 10H, Cp), 1.72 (s, 6H, CH_3).

4.1.8. Bis(phenylethynyl)hafnocene (6h)

1.08 g (10.0 mmol) of phenylethynyllithium was reacted with 1.89 g (5.00 mmol) of hafnocene dichloride in 80 ml of tetrahydrofuran to yield 1.80 g (70%) of the pale yellow colored product 6h. ^1H NMR (C_6D_6): $\delta = 7.50$ (m, 4H, Ph), 7.00 (m, 6H, Ph), 6.08 (s, 10H, Cp).

4.1.9. Bis(trimethylsilylethynyl)hafnocene (6i)

1.10 g (10.5 mmol) of trimethylsilylethynyllithium was treated with 2.00 g (5.77 mmol) of hafnocene dichloride in 100 ml of tetrahydrofuran to yield 2.00 g (80%) of 6i. ^1H NMR (C_6D_6): $\delta = 5.99$ (s, 10H, Cp), 0.23 (s, 18H, CH_3).

4.2. Preparation of metallocene-boron-betaines 4: general procedure

The respective bis(alkynyl)metallocene (6) and tris(pentafluorophenyl)borane were mixed as solids in a 1:1 molar ratio. Toluene was added at -78°C and the mixture was stirred vigorously at that temperature. After 2 h the cooling bath was removed and the reaction mixture was allowed to warm to room temperature with stirring. The resulting precipitate was isolated by filtration and washed twice with a small amount of toluene.

4.2.1. [Bis(η^5 -cyclopentadienyl)zirconium(IV)]-hex-2-ene-4-yne-2-yl-3-[tris(pentafluorophenyl)]borate (4a)

Treatment of 3.00 g (10.0 mmol) of bis(propynyl)zirconocene (6a) with 5.12 g (10.0 mmol) of tris(pentafluorophenyl)borane in 15 ml of toluene yielded 8.01 g (88%) of the orange colored product 4a, m.p. 74°C (dec., DSC). ^1H NMR (C_6D_6): $\delta = 5.32$ (br s, 10H, Cp), 2.26 (s, 3H, CH_3), 1.04 (s, 3H, CH_3); (toluene: 7.08 (m, 5H, Ph), 2.11 (s, 3H, CH_3)). ^{13}C NMR (CD_2Cl_2): $\delta = 255.2, 151.2$ (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 232\text{ Hz}$), 142.0 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 242\text{ Hz}$), 140.1 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 240\text{ Hz}$), 116.3 (Cp), $108.5, 105.0, 29.7, 10.7$; (toluene: $141.4, 132.4, 131.6, 128.7$ (Ph), 24.5 (CH_3)). ^{19}F NMR (CD_2Cl_2): $\delta = -124.6, -125.6, -131.5, -134.0$ (*o*- C_6F_5), -159.6 (*p*- C_6F_5), $-164.7, -165.2$ (*m*- C_6F_5). IR (KBr): $\tilde{\nu} = 3120, 2970, 2929, 2142, 1644, 1516, 1461, 1376, 1276, 1092, 1018, 977$,

815, 761, 694 cm^{-1} . Anal. Found: C, 52.23; H, 2.59. $\text{C}_{34}\text{H}_{16}\text{BF}_{15}\text{Zr} \cdot 0.5\text{C}_7\text{H}_8$ (857.7). Calc.: C, 52.52; H, 2.35%.

4.2.2. [Bis(η^5 -methylcyclopentadienyl)zirconium(IV)]-hex-2-ene-4-yne-2-yl-3-[tris(pentafluorophenyl)]borate (4b)

Treatment of 1.50 g (4.58 mmol) of bis(η^5 -methylcyclopentadienyl)bis(propynyl)zirconocene **6b** with 2.34 g (4.58 mmol) of tris(pentafluorophenyl)borane in 60 ml of toluene yielded 2.32 g (60%) of the yellow colored betaine **4b**, m.p. 150°C (dec., DSC). ^1H NMR (C_6D_6): $\delta = 5.23$ (br m, 8H, Cp), 2.23 (s, 3H, CH_3), 1.39 (br s, 6H, Cp- CH_3), 1.09 (s, 3H, CH_3). ^{13}C NMR (CDCl_3): $\delta = 244.1$, 147.9 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 246$ Hz), 138.9 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 279$ Hz), 136.7 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 245$ Hz), 112.6, 112.5, 111.3 (Cp), 105.7, 102.1, 14.7 (Cp- CH_3), 7.49 (CH_3), 0.97 (CH_3) (*ipso*-C of C_6F_5 not found). ^{19}F NMR (CD_2Cl_2 , 213 K): $\delta = -133.0$, -133.5, -134.7, -138.1, -138.6, -140.2 (*o*- C_6F_5), -165.2, -165.3, -165.7 (*p*- C_6F_5), -169.5, -169.7, -170.0, -170.8, -170.9, -171.0 (*m*- C_6F_5). ^{19}F NMR (CD_2Cl_2 , 303 K): $\delta = -133.3$, -134.0 (br s), -137.4, -139.5 (br s) (*o*- C_6F_5), -166.1, -166.3 (*p*- C_6F_5), -170.3, -171.0 (br s), -171.6 (*m*- C_6F_5). IR (KBr): $\tilde{\nu} = 2964$, 2933, 2919, 2128, 1644, 1599, 1516, 1461, 1378, 1275, 1090, 1035, 976, 867, 815, 755, 733, 693, 674, 615 cm^{-1} .

4.2.3. [Bis(η^5 -cyclopentadienyl)zirconium(IV)]-dodec-5-ene-7-yne-5-yl-6-[tris(pentafluorophenyl)]borate (4c)

Treatment of 1.50 g (3.91 mmol) of bis(hexynyl)zirconocene **6c** with 2.00 g (3.91 mmol) of tris(pentafluorophenyl)borane in 20 ml of toluene yielded 2.61 g (74%) of the product **4c**, m.p. 152°C (dec., DSC). ^1H NMR (C_6D_6): $\delta = 5.63$ (s, 5H, Cp), 5.36 (s, 5H, Cp), 1.34–1.15 (m, 4H, CH_2), 1.05–0.80 (m, 8H, CH_2), 0.80–0.65 (m, 6H, CH_3). ^{13}C NMR (C_6D_6): $\delta = 244.9$, 148.6 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 238$ Hz), 139.4 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 248$ Hz), 137.3 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 248$ Hz), 113.0 (Cp), 112.0 (Cp), 106.9, 105.2, 41.6, 33.5, 30.4, 23.4, 22.5, 21.8, 13.7, 13.3 (*ipso*-C of C_6F_5 not found). ^{19}F NMR (CD_2Cl_2): $\delta = -133.1$, -133.9, -134.6, -138.3, -138.7, -140.4 (*o*- C_6F_5), -165.6, -165.8, -166.0 (*p*- C_6F_5), -170.0, -170.2, -170.4, -170.6, -171.1, -171.4 (*m*- C_6F_5). IR (KBr): $\tilde{\nu} = 3120$, 2963, 2956, 2936, 2872, 2104, 1731, 1721, 1645, 1517, 1462, 1378, 1273, 1091, 1019, 977, 867, 812, 758, 695, 673, 608, 587, 577, 555, 472, 431, 423 cm^{-1} . Anal. Found: C, 53.19; H, 3.49. $\text{C}_{38}\text{H}_{28}\text{BF}_{15}\text{Zr}$ (871.6). Calc.: C, 53.63; H, 3.13%.

4.2.4. [Bis(η^5 -cyclopentadienyl)zirconium(IV)]-1,4-diphenyl-but-1-ene-3-yne-1-yl-2-[tris(pentafluorophenyl)]borate (4d)

Treatment of 200 mg (0.47 mmol) of bis(phenylethynyl)zirconocene with 242 mg (0.47 mmol) of

tris(pentafluorophenyl)borane in 10 ml of toluene yielded 380 mg (79%) of the brown betaine **4d**, m.p. 5°C (dec.). ^1H NMR (C_6D_6): $\delta = 8.02$ (br s, 5H, Ph), 7.31 (br s, 5H, Ph), 5.27 (br s, 10H, Cp). ^{13}C NMR (C_7D_8): $\delta = 244.8$, 148.5 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 260$ Hz), 146.2, 139.5 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 236$ Hz), 137.4 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 240$ Hz), 131.5, 131.3, 129.7, 129.2, 125.9, 122.3 (Ph), 119.5, 114.4 (Cp), 111.7, 102.9 (*ipso*-C of C_6F_5 not found). IR (KBr): $\tilde{\nu} = 3113$, 3054, 3027, 2964, 1646, 1594, 1519, 1466, 1383, 126, 1091, 1022, 978, 817, 736, 697, 472 cm^{-1} .

4.2.5. [Bis(η^5 -cyclopentadienyl)zirconium(IV)]-1,4-bis-cyclohexyl-but-1-ene-3-yne-1-yl-2-[tris(pentafluorophenyl)]borate (4e)

Treatment of 600 mg (1.38 mmol) of bis(cyclohexylethynyl)zirconocene **6e** with 760 mg (1.38 mmol) of tris(pentafluorophenyl)borane in 20 ml of toluene yielded 990 mg (68%) of the orange colored betaine **4e**, m.p. 133°C (DSC). ^1H NMR (C_6D_6): $\delta = 5.69$ (s, 5H, Cp), 5.44 (s, 5H, Cp), 1.8–1.2 (m, 22H, cyclohexyl); (toluene: 7.1–7.0 (m, 5H, Ph), 2.11 (s, 3H, CH_3)). ^{13}C NMR (CDCl_3): $\delta = 243.8$, 148.0 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 238.4$ Hz), 138.8 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 235$ Hz), 136.8 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 242$ Hz), 112.7 (Cp), 111.8 (Cp), 109.8, 109.1, 50.6, 35.5, 34.4, 33.4, 32.7, 31.9, 26.2, 26.0 (cyclohexyl); (toluene: 129.0, 128.2, 125.3, 115.9 (Ph), 24.8 (CH_3)). IR (KBr): $\tilde{\nu} = 3123$, 2935, 2857, 2100, 1642, 1513, 1462, 1371, 1280, 1085, 1015, 978, 814 cm^{-1} . Anal. Found: C, 56.47; H, 3.64. $\text{C}_{44}\text{H}_{32}\text{BF}_{15}\text{Zr}$ (947.8). Calc.: C, 57.41; H, 3.63%.

4.2.6. [Bis(η^5 -cyclopentadienyl)titanium(IV)]-hex-2-ene-4-yne-2-yl-3-[tris(pentafluorophenyl)]borate (4f)

Treatment of 1.50 g (5.90 mmol) of bis(propynyl)titanocene (**6f**) with 3.00 g (5.90 mmol) of tris(pentafluorophenyl)borane in 60 ml of toluene yielded 4.00 g (5.22 mmol, 88%) of the violet colored betaine **4f**, m.p. 74°C (dec., DSC). ^1H NMR (C_6D_6): $\delta = 5.24$ (br s, 10H, Cp), 1.99 (s, 3H, CH_3), 0.79 (s, 3H, CH_3); (toluene: 7.14–6.95 (m, 5H, Ph), 2.10 (s, 3H, CH_3)). ^{13}C NMR (CD_2Cl_2): $\delta = 262.7$, 152.7 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 232$ Hz), 143.0 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 240$ Hz), 139.9 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 240$ Hz), 119.6 (Cp), 104.9, 99.6, 24.5, 10.1; (toluene: 141.4, 132.4, 131.6, 128.7 (Ph), 24.5 (CH_3)). IR (KBr): $\tilde{\nu} = 3131$, 3033, 2967, 2921, 2144, 1643, 1517, 1462, 1377, 1278, 1093, 1020, 979, 871, 827, 786, 733, 698, 672, 470 cm^{-1} . Anal. Found: C, 57.10; H, 2.72. $\text{C}_{34}\text{H}_{16}\text{BF}_{15}\text{Ti} \cdot \text{C}_7\text{H}_8$ (860.3). Calc.: C, 57.24; H, 2.81%.

4.2.7. [Bis(η^5 -cyclopentadienyl)hafnium(IV)]-hex-2-ene-4-yne-2-yl-3-[tris(pentafluorophenyl)]borate (4g)

Treatment of 2.00 g (5.1 mmol) of bis(propynyl)hafnocene **6g** with 2.60 g (5.1 mmol) of tris(pentafluorophenyl)borane in 15 ml of toluene yielded

3.90 g (77%) of the yellow betaine **6g**, m.p. 78 °C (dec., DSC). $^1\text{H NMR}$ (C_6D_6): $\delta = 5.27$ (br s, 10H, Cp), 2.34 (s, 3H, CH_3), 1.00 (s, 3H, CH_3); (toluene: 7.08 (m, 5H, Ph), 2.11 (s, 3H, CH_3)). $^{13}\text{C NMR}$ (CDCl_3): $\delta = 251.4$, 147.9 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 235$ Hz), 138.7 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 254$ Hz), 136.6 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 245$ Hz), 111.7 (Cp), 107.3, 96.4, 26.9 (CH_3), 21.4 (CH_3); (toluene: 129.0, 128.2, 125.3, 114.1 (Ph), 7.78 (CH_3), *ipso*-C of C_6F_5 not found). IR (KBr): $\tilde{\nu} = 3118$, 2967, 2927, 1646, 1517, 1463, 1381, 1279, 1094, 1017, 980, 806, 772, 697 cm^{-1} . Anal. Found: C, 48.15; H, 2.37. $\text{C}_{34}\text{H}_{16}\text{BF}_{15}\text{Hf} \cdot \text{C}_7\text{H}_8$ (990.9). Calc.: C, 49.70; H, 2.44%.

X-ray structure analysis of **4g**: $\text{C}_{40}\text{H}_{22}\text{BF}_{15}\text{Hf}$ (976.88), crystal size $0.7 \times 0.5 \times 0.4$ mm, $T = 223$ K, $\lambda = 0.71073$ Å, monoclinic, space group $P2_1/n$ (No. 14), cell parameters $a = 13.242(6)$ Å, $b = 16.493(7)$ Å, $c = 16.865(4)$ Å, $\beta = 106.24(2)^\circ$, $V = 3536(2)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.835$ g cm^{-3} , $\mu = 30.6$ cm^{-1} , 7458 collected reflections, 7148 independent and 4635 observed reflections, full matrix least squares refinement on F^2 , $R = 0.096$, $wR^2 = 0.231$. Selected bond lengths (Å) and angles (deg): Hf–C2 2.65(2), Hf–C3 2.33(2), Hf–C4 2.63(2), Hf–C5 2.15(2), C1–C2 1.49(3), C2–C3 1.20(2), C3–C4 1.45(2), C4–C5 1.35(2), C4–B 1.66(2), C5–C6 1.49(2); C1–C2–C3 174(2), C2–C3–C4 176(2), C3–C4–C5 117(2), C3–C4–B 114(1), C5–C4–B 129(2), C4–C5–C6 124(2). Further information about the X-ray structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405297, the names of the authors, and the journal citation.

4.2.8. [Bis(η^5 -cyclopentadienyl)hafnium(IV)]-1,4-diphenyl-but-1-ene-3-yne-1-yl-2-[tris(pentafluorophenyl)]borate (**4h**)

Treatment of 100 mg (0.20 mmol) of bis(phenylethynyl)hafnocene **6h** with 100 mg (0.20 mmol) of tris(pentafluorophenyl)borane in 10 ml of toluene yielded 130 mg (65%) of the brown colored betaine **6h**, m.p. 5 °C (dec.). $^1\text{H NMR}$ (C_6D_6): $\delta = 8.10$ (br s, 5H, Ph), 7.30 (br s, 5H, Ph), 5.26 (br s, 10H, Cp); (toluene: 7.08 (m, 5H, Ph), 2.11 (CH_3)). IR (KBr): $\tilde{\nu} = 3117$, 3056, 3031, 2961, 2927, 2859, 1643, 1525, 1472, 1387, 1268, 1084, 1025, 979, 827, 761, 702 cm^{-1} . Anal. Found: C, 54.31; H, 2.80. $\text{C}_{44}\text{H}_{20}\text{BF}_{15}\text{Hf} \cdot \text{C}_7\text{H}_8$ (1115.1). Calc.: C, 54.94; H, 2.53%.

4.2.9. [Bis(η^5 -cyclopentadienyl)hafnium(IV)]-1,4-bis(trimethylsilyl)-but-1-ene-3-yne-1-yl-2-[tris(pentafluorophenyl)]borate (**4i**)

Treatment of 200 mg (0.40 mmol) of bis(trimethylsilyl)hafnocene **6i** with 204 mg (0.40 mmol) of tris(pentafluorophenyl)borane in 10 ml of toluene yielded 370 mg (92%) of the orange colored betaine **4i**, m.p.

20 °C (dec.). $^1\text{H NMR}$ (C_6D_6): $\delta = 5.86$ (s, 10H, Cp), 0.08 (s, 18H, CH_3). $^{13}\text{C NMR}$ (C_7D_8 , 243 K): $\delta = 173.6$, 148.7 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 242$ Hz), 140.4 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 240$ Hz), 137.6 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 246$ Hz), 118.5 (*ipso*-C of C_6F_5), 118.2, 112.9 (Cp), 101.7, 1.4 (CH_3), -0.50 (CH_3). IR (KBr): $\tilde{\nu} = 3131$, 2960, 2908, 1980, 1651, 1525, 1473, 1387, 1262, 1091, 992, 847, 828, 762, 690 cm^{-1} . Anal. Found: C, 44.53; H, 2.75. $\text{C}_{38}\text{H}_{28}\text{BF}_{15}\text{HfSi}_2$ (1015.1). Calc.: C, 44.96; H, 2.78%.

4.3. Preparation of the 2,6-dimethylphenylisocyanide insertion product (**1**)

1.50 g (1.65 mmol) of **4a** was suspended in 15 ml of toluene. After addition of 1.09 mg (8.31 mmol) of 2,6-dimethylphenylisocyanide at -20°C the mixture was stirred for 1 h at room temperature and then the precipitate isolated by filtration and washed twice with toluene to give 1.78 g (93%) of the pale yellow product **1**, m.p. 192 °C (dec., DSC). $^1\text{H NMR}$ (CDCl_3): $\delta = 7.12$ – 7.08 (m, 2H, Ph), 6.81–6.78 (m, 4H, Ph), 5.92 (s, 10H, Cp), 2.61 (s, 3H, CH_3), 2.08 (s, 6H, Ph- CH_3), 1.89 (s, 6H, Ph- CH_3), 1.14 (s, 3H, CH_3); (toluene: 7.40–7.15 (m, 5H, Ph), 2.08 (s, 3H, CH_3)). $^{13}\text{C NMR}$ ($\text{THF-}d_6$): $\delta = 201.9$, 160.8, 149.0, 148.5 (d, *o*- C_6F_5 , $^1J_{\text{CF}} = 238$ Hz), 147.9, 139.2 (d, *p*- C_6F_5 , $^1J_{\text{CF}} = 246$ Hz), 137.1 (d, *m*- C_6F_5 , $^1J_{\text{CF}} = 248$ Hz), 136.2, 131.5, 131.2, 129.1, 124.8, 124.6 (Ph), 106.6 (Cp), 89.8, 18.8, 17.6 (Ph- CH_3), 16.0, 11.5, 122.0 (br s, *ipso*-C of C_6F_5); (toluene: 129.4, 128.5, 128.3, 125.4 (Ph), 20.9 (CH_3)). $^{19}\text{F NMR}$ (CDCl_3): $\delta = -133.2$ (*o*- C_6F_5), -161.1 (*p*- C_6F_5), -165.7 (*m*- C_6F_5). IR (KBr): $\tilde{\nu} = 3068$, 3031, 3024, 2957, 2923, 2863, 2173, 1816, 1643, 1558, 1513, 1461, 1380, 1317, 1277, 1154, 1091, 1053, 1049, 1019, 1011, 976, 896, 868, 800, 769, 732, 686, 616, 572, 466 cm^{-1} . Anal. Found: C, 58.32; H, 3.31; N, 2.61. $\text{C}_{52}\text{H}_{34}\text{BF}_{15}\text{N}_2\text{Zr}$ (1073.8). Calc.: C, 58.16; H, 3.19; N, 2.61%.

4.3.1. X-ray crystal structure analysis of **1**

Single crystals were obtained by slow diffusion of pentane into a toluene solution of **1**. $\text{C}_{52}\text{H}_{34}\text{BF}_{15}\text{N}_2\text{Zr}$ (1073.8), crystal size $0.25 \times 0.20 \times 0.10$ mm, $T = 223$ K, $\lambda = 0.71073$ Å, monoclinic, space group $P2_1/n$ (No. 14), cell parameters $a = 8.871(1)$ Å, $b = 25.913(3)$ Å, $c = 20.256(3)$ Å, $\beta = 101.37(1)^\circ$, $V = 4564.9(10)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.562$ g cm^{-3} , $\mu = 3.42$ cm^{-1} , 6420 collected reflections, 5969 independent and 2617 observed reflections, full matrix least squares refinement on F^2 , $R = 0.054$, $wR^2 = 0.089$, programs used: SHELX86, SHELX93, SCHAKAL. Further information about the X-ray structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405299, the names of the authors, and the journal citation.

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References

- [1] G.A. Olah and P.v.R. Schleyer, *Carbonium Ions*, Vols. I–V, Wiley, New York (1968–1976). G.A. Olah, *Angew. Chem.*, 107 (1995) 1519; *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 1393 and references cited therein.
- [2] R.F. Jordan, *Adv. Organomet. Chem.*, 32 (1991) 325 and references cited therein. X. Yang, C.L. Stern and T. Marks, *J. Am. Chem. Soc.*, 116 (1994) 10015.
- [3] G. Erker and D. Röttger, *Angew. Chem.*, 105 (1993) 1691; *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 1623. D. Röttger, G. Erker, M. Grehl and R. Fröhlich, *Organometallics*, 13 (1994) 3897. D. Röttger, G. Erker, R. Fröhlich, M. Grehl, S.J. Silverio, I. Hyla-Kryspin and R. Gleiter, *J. Am. Chem. Soc.*, 117 (1995) 10503. D. Röttger, G. Erker and R. Fröhlich, *Chem. Ber.*, 128 (1995) 1045. D. Röttger, S. Schmuck and G. Erker, *J. Organomet. Chem.*, 508 (1996) 263. D. Röttger, J. Pflug, G. Erker, S. Kotila and R. Fröhlich, *Organometallics*, 15 (1996) 1265.
- [4] G.G. Hlatky, H. Turner and R.R. Eckman, *J. Am. Chem. Soc.*, 111 (1989) 2728. M. Bochmann, G. Karger and A.J. Jaggar, *J. Chem. Soc. Chem. Commun.*, (1990) 1038. A.D. Horton and J.H.G. Frijns, *Angew. Chem.*, 103 (1991) 1181; *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 1152. D.M. Amorose, R.A. Lee and J.L. Petersen, *Organometallics*, 10 (1991) 2191. X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc.*, 113 (1991) 3623. C. Sishta, R.M. Hathorn and T.J. Marks, *J. Am. Chem. Soc.*, 114 (1992) 1112. X. Yang, C.L. Stern and T.J. Marks, *Angew. Chem.*, 104 (1992) 1406; *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 1375. G.G. Hlatky, R.R. Eckman and H.W. Turner, *Organometallics*, 11 (1992) 1413. C.J. Schaverien, *Organometallics*, 11 (1992) 3476. M. Bochmann, *Angew. Chem.*, 104 (1992) 1206; *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 1181. C. Pellecchia, A. Immirzi, A. Grassi and A. Zambelli, *Organometallics*, 12 (1993) 4473. C. Pellecchia, A. Grassi and A. Immirzi, *J. Am. Chem. Soc.*, 115 (1993) 1160. J.J. Eisch, S.I. Pombrik and G.-X. Zheng, *Organometallics*, 12 (1993) 3856. D.J. Gillis, M.J. Tudoret and M.C. Baird, *J. Am. Chem. Soc.*, 115 (1993) 2543. K. Mashima, S. Fujikawa and A. Nakamura, *J. Am. Chem. Soc.*, 115 (1993) 10990. A.R. Siedle, R.A. Newmark, W.M. Lamanna and J.C. Huffman, *Organometallics*, 12 (1993) 1491. F. Calderazzo, G. Pampaloni, L. Rocchi and U. Englert, *J. Am. Chem. Soc.*, 116 (1994) 2592. J.L. Kiplinger, T.G. Richmond and C.E. Osterberg, *Chem. Rev.*, 94 (1994) 373. K. Mashima, S. Fujikawa, H. Urata, E. Tanaka and A. Nakamura, *J. Chem. Soc. Chem. Commun.*, (1994) 1623. H. Braunschweig and T. Wagner, *Chem. Ber.*, 127 (1994) 1613. R.E.v.H. Spence and W.E. Piers, *Organometallics*, 14 (1995) 4617. M. Bochmann, S.J. Lancaster and O.B. Robinson, *J. Chem. Soc. Chem. Commun.*, (1995) 2081. K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka and A. Nakamura, *Organometallics*, 14 (1995) 2633. D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck and C.L. Stern, *Organometallics*, 14 (1995) 3132. F. Barsan and M.C. Baird, *J. Chem. Soc. Chem. Commun.*, (1995) 1065. L. Jia, X. Yang, A. Ishihara and T.J. Marks, *Organometallics*, 14 (1995) 3135.
- [5] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich and S. Kotila, *Angew. Chem.*, 107 (1995) 1867; *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 1755. J. Ruwwe, G. Erker and R. Fröhlich, *Angew. Chem.*, 108 (1996) 108; *Angew. Chem. Int. Ed. Engl.*, 35 (1996) 80. D. Röttger, G. Erker, R. Fröhlich and S. Kotila, *J. Organomet. Chem.*, 518 (1996) 17. B. Temme, J. Karl and G. Erker, *Chem. Eur. J.*, 2 (1996) 919. G. Erker, M. Albrecht, S. Werner and C. Krüger, *Z. Naturforsch. Teil B.*, 45 (1990) 1205. G. Erker, M. Albrecht and C. Psiorz, *Z. Naturforsch. Teil B.*, 46 (1991) 1571. G. Erker, R. Noe, C. Krüger and S. Werner, *Organometallics*, 11 (1992) 4174. G. Erker, R. Noe and D. Wingbermühle, *Chem. Ber.*, 127 (1994) 805.
- [6] B. Temme, G. Erker, R. Fröhlich and M. Grehl, *J. Chem. Soc., Chem. Commun.*, (1994) 1713.
- [7] G. Erker, W. Frömberg, C. Krüger and E. Raabe, *J. Am. Chem. Soc.*, 110 (1988) 2400. G. Erker, W. Frömberg, J.L. Atwood and W.E. Hunter, *Angew. Chem.*, 96 (1984) 72; *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 68.
- [8] G. Erker, W. Ahlers and R. Fröhlich, *J. Am. Chem. Soc.*, 117 (1995) 5853.
- [9] M. Sundaralingam and L.H. Jensen, *J. Am. Chem. Soc.*, 88 (1966) 198.
- [10] R.D. Adams and D.F. Chodosh, *Inorg. Chem.*, 17 (1978) 41. F.H. Elsner and T.D. Tilley, *J. Organomet. Chem.*, 358 (1988) 169. L.D. Durfee and I.P. Rothwell, *Chem. Rev.*, 88 (1988) 1059. G. Erker, R. Zwitterler and C. Krüger, *Chem. Ber.*, 122 (1989) 1377. R.F. Jordan and D.F. Taylor, *J. Am. Chem. Soc.*, 111 (1989) 778. R.F. Jordan, D.F. Taylor and N.C. Baenziger, *Organometallics*, 9 (1990) 1546. A.S. Guram and R.F. Jordan, *Organometallics*, 9 (1990) 2116; 2190. S.M. Beshouri, D.E. Chebi, P.E. Fanwick, I.P. Rothwell and J.C. Huffman, *Organometallics*, 9 (1990) 2375. A.S. Guram, D.C. Swenson and R.F. Jordan, *J. Am. Chem. Soc.*, 114 (1992) 8991. F.R. Lemke, D.J. Szakla and R.M. Bullock, *Organometallics*, 11 (1992) 876. A.S. Guram and R.F. Jordan, *J. Org. Chem.*, 58 (1993) 5595. P.G. Cozzi, T. Carofiglio, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 12 (1993) 2845. A.S. Guram, Z. Guo and R.F. Jordan, *J. Am. Chem. Soc.*, 115 (1993) 4902. *Organometallics*, 10 (1991) 3470. Z. Guo, D.C. Swenson, A.S. Guram and R.F. Jordan, *Organometallics*, 13 (1994) 766 and references cited therein.
- [11] B. Temme, G. Erker, R. Fröhlich and M. Grehl, *Angew. Chem.*, 106 (1994) 1570; *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 1480.
- [12] G. Erker, W. Frömberg, R. Mynott, B. Gabor and C. Krüger, *Angew. Chem.*, 98 (1986) 456; *Angew. Chem. Int. Ed. Engl.*, 25 (1986) 463. P.N.V.P. Kumar and E.D. Jemmis, *J. Am. Chem. Soc.*, 110 (1988) 125. G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund and C. Krüger, *Organometallics*, 8 (1989) 911. G.L. Wood, C.B. Knobler and M.F. Hawthorne, *Inorg. Chem.*, 28 (1989) 382. H. Lang and L. Zsolnai, *J. Organomet. Chem.*, 406 (1991) C5. H. Lang, M. Herres, L. Zsolnai and W. Imhof, *J. Organomet. Chem.*, 409 (1991) C7. H. Lang and W. Imhof, *Chem. Ber.*, 125 (1992) 1307. U. Rosenthal and H. Görls, *J. Organomet. Chem.*, 439 (1992) C36. J.R. Berenguer, L.R. Falvello, J. Forniés, E. Laliude and M. Tomás, *Organometallics*, 12 (1993) 6. G. Erker, M. Albrecht, C. Krüger, M. Nolte and S. Werner, *Organometallics*, 12 (1993) 4979.
- [13] G. Erker, K. Kropp, J.L. Atwood and W.E. Hunter, *Organometallics*, 2 (1983) 1555. P. Czisch and G. Erker, *J. Organomet. Chem.*, 253 (1983) C9. P. Czisch, G. Erker, H.-G. Korth and R. Sustmann, *Organometallics*, 3 (1984) 945. I. Hyla-Kryspin, R. Gleiter, C. Krüger, R. Zwitterler and G. Erker, *Organometallics*, 9 (1990) 517. G. Erker, R. Zwitterler, C. Krüger, I. Hyla-Kryspin and R. Gleiter, *Organometallics*, 9 (1990) 524. Y. Raoult, R. Choukroun, D. Gervais and G. Erker, *J. Organomet. Chem.*, 399 (1990) C1. G. Erker, *Comments Inorg.*

- Chem.*, 13 (1992) 111. G. Erker, *Nachr. Chem. Tech. Lab.*, 40 (1992) 1099. M. Albrecht, G. Erker and C. Krüger, *Synlett*, (1993) 441.
- [14] M.L.H. Green, L.-L. Wong and A. Sella, *Organometallics*, 11 (1992) 2660.
- [15] J.A. Connor, *Topics Curr. Chem.*, 71 (1977) 71. J.K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978, pp. 237–245. W.E. Hunter, J.L. Atwood, G. Fachinetti and C. Floriani, *J. Organomet. Chem.*, 204 (1981) 67. W.E. Hunter, D.C. Hrcir, R. Vann Bynum, R.A. Penttila and J.L. Atwood, *Organometallics*, 2 (1983) 750 and references cited therein. G. Erker, C. Krüger and G. Müller, *Adv. Organomet. Chem.*, 24 (1985) 1. C. Krüger, G. Müller, G. Erker, U. Dorf and K. Engel, *Organometallics*, 3 (1985) 215. A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard and D.G. Watson, *J. Chem. Soc. Dalton Trans.*, (1989) S1.
- [16] J.F. Blount, P. Finocchiaro, D. Gust and K. Mislow, *J. Am. Chem. Soc.*, 95 (1973) 7019. W.D. Hounshell, L.D. Iroff, D.J. Iverson, R.J. Wroczynski and K. Mislow, *Isr. J. Chem.*, 20 (1980) 65. U. Berg, T. Liljefors, C. Roussel and J. Sandström, *Acc. Chem. Res.*, 18 (1985) 80. E.L. Eliel and S.H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994, pp. 1156–1163 and references cited therein.
- [17] A.G. Massey and A.J. Park, *J. Organomet. Chem.*, 2 (1964) 245.