

Coupling of σ -acetylide ligands at Group 4 metallocene complexes to yield methylenecyclopropene-type frameworks

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Abstract

Treatment of a variety of bis(alkynyl)metallocenes $\text{Cp}_2\text{M}(-\text{C}\equiv\text{C}-\text{R})_2$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{R} = \text{CH}_3, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, \text{cyclo-C}_6\text{H}_{11}$) with tris(pentafluorophenyl)borane yields the metallocene($\mu\text{-RC}_6\text{F}_5$)borate betaines **3**. These seem to be in an endothermic equilibrium with their methylenecyclopropene derived isomers—by means of an intramolecular alkyne insertion reaction—which are very effectively trapped by the reaction with *tert*-butylisocyanide to yield the complexes **6** that exhibit a methylenecyclopropene derived σ -ligand framework. The zirconocene compounds **6a** ($\text{R} = \text{CH}_3$), **6c** ($\text{R} = n\text{-C}_3\text{H}_7$), **6d** ($\text{R} = n\text{-C}_4\text{H}_9$), and **6e** ($\text{R} = \text{cyclo-C}_6\text{H}_{11}$) were characterized by X-ray crystal structure analyses. The hydrolysis of **6a**, **6c** and **6d** gave the respective metal free systems **7** that exhibit a pronounced cyclopropenylium–borate–betaine character. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Acetylide coupling; Methylenecyclopropenes; d^0 -Isonitrile complexes; Alkyne insertion; Zirconocene complexes

1. Introduction

Carbon-rich ligand systems are often constructed by acetylide coupling reactions in the coordination sphere of transition metal complex fragments [1]. Such coupling may initially lead to the formation of elongated carbon chains; cyclic frameworks containing an array of quaternary carbon centers may be formed consecutively [2,3]. We have recently found and described first examples of such reactions resulting in the formation of three-membered rings [4–6]. Treatment of bis(σ -propynyl)zirconocene (**1a**) [7] with the strong organometallic Lewis acid tris(pentafluorophenyl)borane [8], led to the formation of the linear acetylide coupling product (**3a**) [9]. We have assumed that a σ -propynyl group is transferred from zirconium to boron followed by alkyne insertion at the stage of the intermediate ion

pair (or betaine-type coordination product) **2a** to yield **3a**. Subsequent treatment of **3a** with excess *tert*-butylisocyanide resulted in the formation of the organometallic methylenecyclopropene derivative **6a**, that was isolated in a good yield and characterized by X-ray diffraction, as it was recently described in a preliminary communication by us [4]. It must be assumed that the linear acetylide coupling product **3a** is in equilibrium with its isomer **4a**. The formation of **4a** from **3a** results from an intramolecular insertion of the π -alkyne moiety of the hexadiyne ligand into the metal- sp^2 -carbon σ -bond at the zirconium moiety. The formation of **4a** is, of course, very endothermic, but apparently the subsequent isocyanide insertion reaction very efficiently removes the thermodynamically unfavorable isomer **4a** from this equilibrium to eventually yield the stabilized product **6a** (via **5a**, see Scheme 1).

Similarly, **4a** was trapped from the $\text{3a} \rightleftharpoons \text{4a}$ equilibrium by treatment with the bulky 2,6-dimethylphenylisocyanide [9] and also by treatment with benzonitrile [5], but only reactions starting from

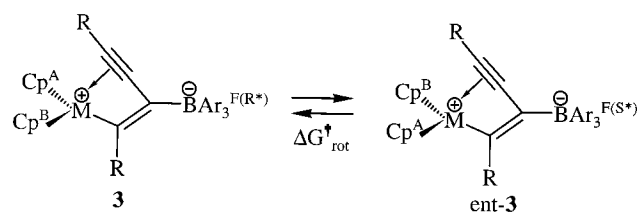
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bis(propynyl)ZrCp₂ had been described so far. We have extended this study to the use of other bis(acetylide) Group 4 metallocene complexes as starting materials for this sequence of CC-coupling steps. This has resulted in a more complete structural and spectroscopic characterization of the unusually structured organometallic methylenecyclopropene derivatives **6** and the interesting organic hydrolysis products derived from them. A variety of typical examples is described in this article.

2. Results and discussion

The general procedure that was followed in the preparation of the methylenecyclopropene compounds **6** is illustrated for the example **6c**. The corresponding starting material **1c** was prepared by reacting zirconocene dichloride with two molar equivalents of 1-lithio-1-pentyne. The resulting bis(1-pentyne)zirconocene starting material (**1c**) was then treated with B(C₆F₅)₃ in a 1:1 ratio in toluene solution. The reagents were combined at –78°C and then the mixture was allowed to warm to room temperature (r.t.) and stirred for 3 h to ensure that the addition and coupling reaction goes to completion. Conventional workup then gave the Cp₂Zr(μ-4,6-decadiyne)B(C₆F₅)₃ betaine complex **3c** in 85% yield as an orange colored solid.

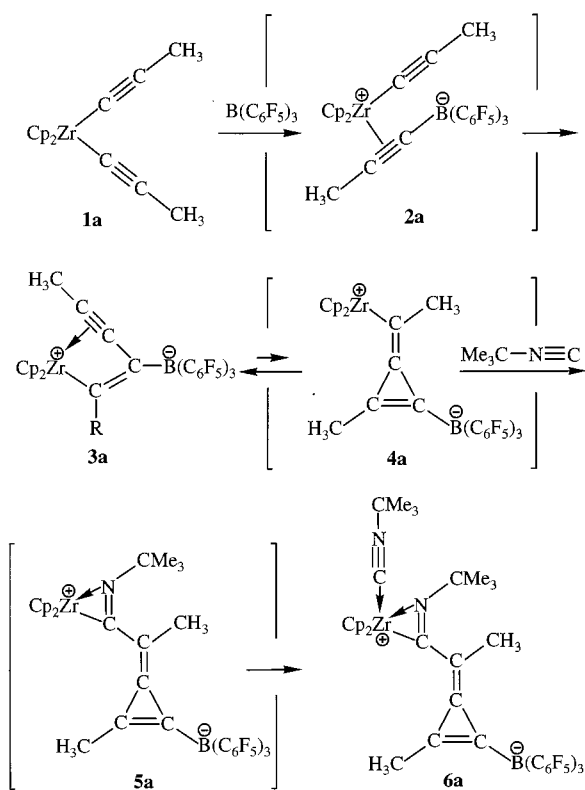


Complex **3c** shows a ¹³C-NMR signal of the sp²-carbon center of the bridging ligand that is σ-bonded to zirconium at δ 245.0 ppm [10]. The NMR resonances of the π-complexed alkyne moiety appear at δ 107.5 and 106.4 ppm [11]. Below a Cp-coalescence temperature of 323 K complex **3c** exhibits diastereotopic sets of ¹H- and ¹³C-NMR Cp-resonances (δ 5.63, 5.36/113.03, 111.9 in benzene-d₆). The apparent chirality of **3c** originates from a hindered rotation of the (sp²-C)–B(C₆F₅)₃ unit. The rotation barrier associated with the borate propeller-type geometry was derived at Δ*G*_{rot}[‡] = 15.0 ± 0.4 kcal mol^{–1} from the dynamic NMR behavior of complex **3c**. This seems to be a typical feature of the substituted Cp₂M(μ-RC₄R)B(C₆F₅)₃-type complexes [9].

Complex **3c** was then treated at 0°C with excess *tert*-butylisocyanide. Two molar equivalents of the isonitrile reagent were taken up. One R–N≡C molecule was inserted to form an η²-iminoacyl functional group at zirconium [12], the other was just added as such to serve as a stabilizing donor ligand at the electron-deficient bent metallocene moiety inside the resulting dipolar product **6c**. The most noteworthy feature of **6c** is that it contains a highly unsaturated three-membered ring framework, resulting from a subsequent CC-coupling of the two initially introduced σ-alkynyl moieties, that is connecting the formally positively charged Cp₂Zr(L) end of the overall dipolar structure of **6c** with its negative borate counterpart.

Single crystals of **6c** were obtained by the diffusion method (gaseous pentane into a toluene/THF solution of **6c**) and allowed to determine its molecular geometry by an X-ray crystal structure analysis.

The crystal complex **6c** exhibits a close to planar σ-ligand framework that ranges from the η²-iminoacyl nitrogen center (and its substituent) all the way to the boron atom bonded to the carbon atom C₁ of the newly formed three-membered ring system. In principle this ligand system comprises two coplanar π-systems, namely the η²-iminoacyl moiety coordinated to zirconium and the methylenecyclopropene unit bonded to boron. Their torsional angle, as determined by θ(N1–C7–C4–C3), amounts to 177.0(6)/171.9(5)° in complex **6c** (values are given for the two independent molecules in the crystal). The sequence of short and long C–C bonds in the C1–C4 unit is as expected for a methylenecyclopropene moiety: the C1–C2 bond is short (1.339(7)/1.337(6) Å), whereas the adjacent C1–C3 (1.447(7)/1.427(6) Å) and C2–C3 (1.393(7)/1.388(6)



Scheme 1.

Table 1
Selected spectroscopic features of the complexes **6**

Compound	M	R	Yield(%)	$\delta^{11}\text{B}$	δC1	C2	C3	C4	C7	$\tilde{\nu}(\text{RN}\equiv\text{C})$	$\tilde{\nu}_{\text{mcp}}^{\text{f}}$
6a	Zr	CH ₃	Quant.	^d	169.0 ^c	152.3	158.2	84.5	204.0	2195	1809
6b	Ti	CH ₃	71	−18.7 ^a	^e	152.6 ^c	145.5	80.4	195.8	2183	1814
6c	Zr	<i>n</i> -C ₃ H ₇	81	−18.6 ^a	^e	152.6 ^a	154.9	91.1	202.8	2196	1803
6d	Zr	<i>n</i> -C ₄ H ₉	82	−18.7 ^b	^e	152.7 ^a	154.6	90.9	202.7	2195	1797
6e	Zr	<i>c</i> -C ₆ H ₁₁	94	−18.2 ^a	^e	145.4 ^a	152.5	91.6	215.2	2193	1796
6f	Hf	CH ₃	87	−18.4 ^b	^e	147.1 ^b	158.8	85.9	211.7	2200	1814

^a In CDCl₃.

^b In *d*₆-benzene.

^c In *d*₈-THF.

^d Not determined.

^e Not located.

^f Methylene-cyclopropene IR-band (cm^{−1}), in KBr.

Å) bonds are markedly longer. As expected, the C3–C4 linkage is again shorter at 1.370(7)/1.380(6) Å. This is a tendency similar to that found in the parent hydrocarbon methylenecyclopropene (bond lengths, from microwave spectroscopy/quantumchemical calculations, inside the three-membered ring are ca. 1.32 and 1.44 Å, and 1.33 Å for the *exo*-methylene C–C distance [13]), but we must note a slight bond lengths equalizing effect in the organometallic system with the C–C single and C=C double bond differences in **6c** being slightly smaller than observed for methylenecyclopropene itself. This may indicate some tendency of **6c** towards a cyclopropenylium–borate–betaine participation, but the significance of such a resonance form is not very pronounced for **6c** (and its relatives **6a–f**, see Table 2). The *n*-propyl substituents, attached at carbons C2 and C4, are arranged in *trans*-positions relative to each other at the central planar C1–C4 framework. This is what is expected from the alkyne insertion mechanism (see Scheme 1) postulated for the formation of the complexes **6** from **3**.

The N1–C2 bond of the η^2 -iminoacyl moiety of **6c** is in the C=N double bond range at 1.299(6)/1.293(5) Å [12]. From Fig. 1 it is evident that all three available coordination sites at the front of the bent metallocene wedge are occupied in complex **6c** [14]. Thus, a *tert*-butylisocyanide is attached at a lateral Cp₂Zr-coordination site coplanar with the η^2 -iminoacyl group. Of the two geometric isomers possible for such an arrangement only the *N*-inside η^2 -imino-acyl ligand orientation is found here [15].

Within the dipolar metallocene–borate–betaine framework the zirconocene unit in **6c** should exhibit a pronounced d⁰-Group 4 metallocene cation character. Therefore, the coordination of the Me₃C–N≡C ligand is not expected to profit from any pronounced back-bonding properties of the Cp₂Zr-unit [16]. The Cp₂Zr←C≡N–CMe₃ subunit in complex **6c** should behave as a typical donor-ligand L→(d⁰)–M-type complex [17], whose bonding features are dominated by the

σ -donor/ σ -acceptor properties of the ligand/metal complex pair and by electrostatic contributions [18]. This is supported by the structural features of this unit in **6c**.

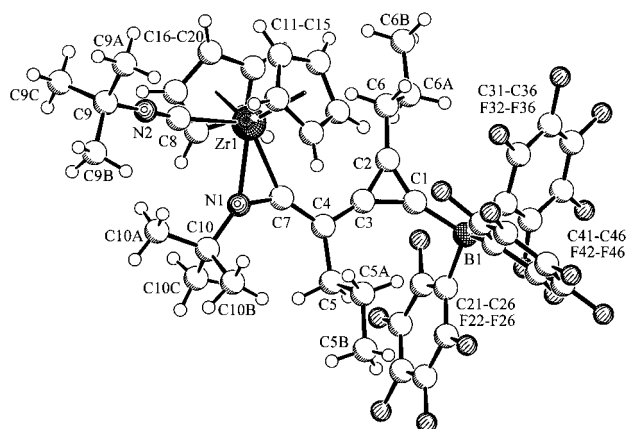


Fig. 1. A view of the molecular structure of **6c**. Selected bond lengths (Å) and angles (°) of the two independent molecules: B1–C1 1.611(8), B2–C51 1.616(7), C1–C2 1.339(7), C51–C52 1.337(6), C1–C3 1.447(7), C51–C53 1.427(6), C2–C3 1.393(7), C52–C53 1.388(6), C2–C6 1.485(8), C52–C56 1.485(6), C3–C4 1.370(7), C53–C54 1.380(6), C4–C5 1.525(7), C54–C55 1.516(6), C4–C7 1.424(6), C54–C57 1.419(6), C7–N1 1.299(6), C57–N51 1.293(5), N1–C10 1.474(6), N51–C60 1.490(6), C7–Zr1 2.226(5), C57–Zr2 2.217(4), N1–Zr1 2.192(4), N51–Zr2 2.178(4), Zr1–C8 2.345(6), Zr2–C58 2.350(5), C8–N2 1.154(6), C58–N52 1.154(6), N2–C9 1.468(7), N52–C59 1.466(6); B1–C1–C2 152.8(5), B2–C51–C52 149.7(4), B1–C1–C3 147.4(5), B2–C51–C53 150.0(4), C2–C1–C3 59.9(4), C52–C51–C53 60.2(3), C1–C2–C3 64.0(4), C51–C52–C53 63.1(3), C1–C2–C6 147.3(5), C51–C52–C56 147.0(4), C6–C2–C3 148.7(5), C56–C52–C53 149.8(4), C1–C3–C2 56.2(4), C51–C53–C52 56.7(3), C2–C3–C4 155.8(5), C52–C53–C54 157.1(4), C3–C4–C5 115.8(4), C53–C54–C55 116.0(4), C3–C4–C7 118.3(4), C53–C54–C57 117.3(4), C5–C4–C7 125.2(4), C55–C54–C57 126.5(4), C4–C7–N1 139.1(5), C54–C57–N51 140.1(4), C4–C7–Zr1 148.7(4), C54–C57–Zr2 148.6(3), N1–C7–Zr1 71.5(3), N51–C57–Zr2 71.2(3), C7–N1–C10 134.5(4), C57–N51–C60 133.2(4), C7–N1–Zr1 74.3(3), C57–N51–Zr2 74.5(3), C7–Zr1–N1 34.2(2), C57–Zr2–N51 34.2(1), C7–Zr1–C8 120.0(2), C57–Zr2–C58 121.4(2), N1–Zr1–C8 86.2(2), N51–Zr2–C58 87.4(2), Zr1–C8–N2 172.5(5), Zr2–C58–N52 172.4(4), C8–N2–C9 176.6(6), C58–N52–C59 176.3(5).

The N2–C8 bond length (1.154(6)/1.154(6) Å) is only slightly longer than that of free *tert*-butylisocyanide (1.145 Å). In **6c** the Zr–C8 bond length is 2.345(6)/2.350(5) Å. This might be compared with [Cp₃Zr←C≡N–CMe₃]⁺ (Zr–C 2.313(3) Å, C–N 1.145(4) Å) [17f–h].

Coordination of *tert*-butylisocyanide to e.g. Cp₃Zr⁺ results in a slight shifting of the IR(C≡N–) stretching band to higher wavenumbers (from 2140 cm⁻¹ in the free isonitrile to 2209 cm⁻¹ in the tris(cyclopentadienyl)Zr–L⁺ complex) [17f–h]. For **6c** a similar effect is observed [$\tilde{\nu}(\text{C}\equiv\text{N}^-) = 2196 \text{ cm}^{-1}$], although it is marginally smaller in magnitude.

The ¹³C-NMR resonance of the κ -C-isonitrile ligand of **6c** is observed at δ 149.6 ppm. The η^2 -iminoacyl carbon NMR resonance is located at a typical value of δ 202.8 [12]. The ¹³C-NMR resonances of the methylenecyclopropene unit of **6c** are found at δ 152.6 (C2), 154.9 (C3) and 91.4 (C4). The C1 carbon resonance was not located for **6c**, probably because of extensive line broadening due to the adjacent boron nucleus. Only for **6a** was the respective C1 ¹³C-NMR signal located at δ 169.0, and for the analogous (MeCp)₂Zr complex **6a'** (δ 170.1 ppm).

The reactions between the Cp₂M(μ-R-C₄R)B(C₆F₅)₃ betaines **3b** (M = Ti), **3a**, **3d**, **3e** (M = Zr) and **3f** (M = Hf) with *tert*-butylisocyanide proceed analogously. In each case two molar equivalents of Me₃C–N≡C are used, and the initial isonitrile insertion reaction very effectively serves to consume the otherwise undetected respective C4-metallated methylenecyclopropene isomers **4** to eventually give high yields of the corresponding products **6** (see Table 1). The X-ray crystal structure analysis of **6a** is very similar to that of **6c**, that was described above (see Table 2). In addition, single crystals suited for the X-ray diffraction analysis were obtained from the bis-*n*-butyl and bis-cyclohexyl-substituted complexes **6d** and **6e** (see Table 2 and Figs. 2 and 3). The X-ray crystal structure analysis of **6d** is of good quality, whereas some disorder problems at the κ -C-*tert*-butylisocyanide ligand remained for **6e**. Therefore, we do not discuss the structural parameters of **6e** in detail.

The structural frameworks and the characteristic structural parameters of the complexes **6a**, **6c** and **6d** are very similar (see Table 2). However, in **6d** some steric influence of the increasingly bulky substituents attached at the methylenecyclopropene framework carbon centers C2 and C4 begin to become structurally relevant. The methyl and *n*-propyl substituted systems **6a** and **6c** both have almost completely planar frameworks with the torsional angles $\theta(\text{N1}–\text{C7}–\text{C4}–\text{C3})$ being 178.9(4)° and 177.0(6)/171.9(5)°, respectively. An increased steric substituent effect has changed this situation for the first time in **6d**; here the η^2 -iminoacyl and the methylenecyclopropene planes are rotated substan-

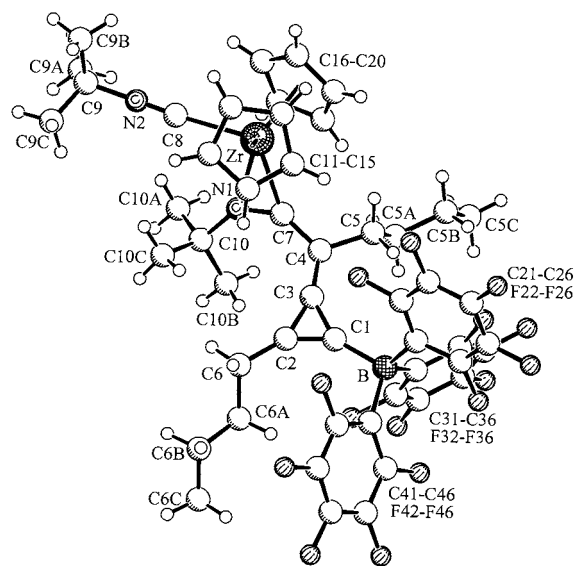


Fig. 2. A projection of the molecular structure of complex **6d**. Selected bond lengths (Å) and angles (°): B–C1 1.609(5), C1–C2 1.328(5), C1–C3 1.432(4), C2–C3 1.417(5), C2–C6 1.474(5), C3–C4 1.353(4), C4–C5 1.523(4), C4–C7 1.430(4), C7–N1 1.277(4), N1–C10 1.482(4), C7–Zr 2.219(3), N1–Zr 2.197(3), Zr–C8 2.351(3), C8–N2 1.137(4), N2–C9 1.457(4); B–C1–C2 150.6(3), B–C1–C3 147.4(3), C2–C1–C3 61.7(2), C1–C2–C3 62.8(2), C1–C2–C6 145.9(4), C6–C2–C3 151.2(3), C1–C3–C2 55.6(2), C2–C3–C4 159.0(3), C3–C4–C5 117.7(3), C3–C4–C7 124.7(3), C5–C4–C7 116.7(3), C4–C7–N1 142.1(3), C4–C7–Zr 144.6(2), N1–C7–Zr 72.3(2), C7–N1–C10 135.7(3), C7–N1–Zr 74.1(2), C7–Zr–N1 33.6(1), C7–Zr–C8 118.2(1), N1–Zr–C8 84.6(1), Zr–C8–N2 175.1(3), C8–N2–C9 176.7(4).

tially: in complex **6d** the N1–C7–C4–C3 torsional angle amounts to $-38.6(7)^\circ$. In the even more sterically congested bis-cyclohexyl-substituted complex **6e** the same rotational angle is even increased to $> 50^\circ$ (see Table 2). In both cases, the remaining structural parameters and also the characteristic spectroscopic features (see Table 1) remain largely unaffected by this torsional interruption of the conjugation of the iminoacyl substituent with the central methylenecyclopropene moiety. This structural and spectroscopic C7–C4 torsional invariance indicates that the contribution of the cyclopropenylium–borate–betaine mesomeric form is not of great importance for the description of the ground state properties of the complexes **6**.

The products **6a**, **6c**, and **6d** were hydrolyzed by treatment with excess methanol in toluene solution at slightly elevated temperature. The newly formed carbon–boron linkage remained intact. Details of the chemical and structural features of the zirconium-free product **7a** thus obtained by hydrolysis of **6a** had been reported by us previously [19]. We had shown that a ca. 85:15 mixture of the stereoisomers *Z*-**7a** and *E*-**7a** was formed (Scheme 2). The ratio varied slightly with the solvent polarity. Their interconversion barrier was determined by dynamic NMR spectroscopy. The obtained

Table 2
A compilation of selected structural parameters of the complexes **6**

Compound	M	R	C1–C2 (Å)	C2–C3	C3–C1	C3–C4	C4–C7	θ^a	N1–C7	N2–C8
6a^b	Zr	CH ₃	1.341(5)	1.403(5)	1.422(4)	1.376(4)	1.412(4)	178.9(4)	1.293(4)	1.152(5)
6c^c	Zr	<i>n</i> -C ₃ H ₇	1.339(7), 1.337(6)	1.393(7), 1.388(6)	1.447(7), 1.427(6)	1.370(7), 1.380(6)	1.424(6), 1.419(6)	177.0(6), 171.9(5)	1.299(6), 1.293(5)	1.154(6), 1.154(6)
6d	Zr	<i>n</i> -C ₄ H ₉	1.328(5)	1.417(5)	1.432(4)	1.353(4)	1.430(4)	–38.6(7)	1.277(4)	1.137(4)
6e^d	Zr	<i>c</i> -C ₆ H ₁₁	1.341(10)	1.421(10)	1.474(10)	1.357(11)	1.430(10)	53.4(12)	1.260(9)	1.158(10)

^a Torsional angle N1–C7–C4–C3.

^b The structure of **6a** was previously reported (see Ref. [4]), but a better data set was obtained in this study.

^c Two independent molecules in the crystal.

^d The *tert*-butyl group of the Me₃C–N=C ligand in **6e** is disordered (ratio 0.57(3):0.43(3)).

value ($\Delta G_{\text{isom.}}^\ddagger \approx 17 \text{ kcal mol}^{-1}$) is very low for the required rotation around the C3–C4 bond of **7a**. This indicates that the double bond character of the C3–C4 linkage is largely reduced, and that the properties of this product—in contrast to its organometallic precursor **6a**—are probably correctly to be described by a large contribution of a cyclopropenylium–borate–betaine type resonance form. The structural parameters of *Z*-**7a**, that were determined by X-ray diffraction, are in accord with this interpretation: C1–C2 1.353(6) Å, C2–C3 1.378(6) Å, C1–C3 1.407(6) Å, C3–C4 1.391(6) Å, C4–C7 1.376(6) Å [19].

The hydrolysis reactions of **6c** and **6d**, that were carried out in the course of this study, furnished similar results. In each case a mixture of two isomers, namely *E*-/*Z*-**7c** and -**7d** were formed in good yield. The absolute assignment remains unclear, but tentatively we assign the major isomer the *Z*-**7** structure, in accord with the arguments presented in our previous study [19]. Again, the *E*-/*Z*-**7c,d** product ratio seems to be slightly dependent on the solvent polarity. An *E*-/*Z*-**7c** ratio of 86:14 was found in CDCl₃, the *E*-/*Z* ratio is 90:10 for **7d** in this solvent.

This study shows that methylenecyclopropene derived carbon-rich frameworks can be very easily prepared stoichiometrically by a consecutive 2-fold alkyne-insertion reaction into zirconium carbon σ -bonds under the influence of the strong organometallic Lewis acid tris(pentafluorophenyl)borane. The second, intramolecular, insertion requires a subsequent exothermic trapping reaction, here isonitrile insertion, to remove it effectively from a thermodynamically unfavorable equilibrium situation. In the product, the B(C₆F₅)₃ group is found attached to the three-membered ring of the resulting carbon framework. In the hydrolysis products (**7**) this leads to the unique situation, that overall neutral cyclopropenylium cation-type systems, that bear their own counteranion covalently bonded with them, are formed. We have begun to explore the chemistry of such systems in order to find out if there is a specific cyclopropenylium chemistry that is not dominated by ionic or charge effects.

3. Experimental

Reactions with organometallic substrates or reagents 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. For additional general information including a list of the instrumentation used for physical characterization of the compounds employed and obtained see Refs. [9] and [19]. Formation and properties of the complexes **3**, except **3c**, were previously described [9]. Complex **6a** was described in a previous preliminary communication [4]. Some of its spectroscopic features are listed below for comparison. An X-ray crystal structure analysis of **6a** of slightly better quality was obtained in the meantime. Details of the preparation of the hydrolysis product **7a**, including its X-ray crystal structure analysis were described by us previously [19]. Data sets were collected with Enraf-Nonius CAD4 and MACH3 diffractometers. Programs used: data reduction MOLEN, structure solution SHELXS-86, structure refinement SHELXL-97, graphics SCHAKAL-92. Tris(pentafluorophenyl)borane was prepared according to a literature procedure [8].

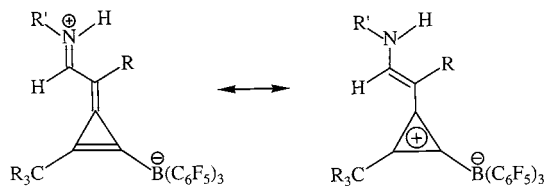
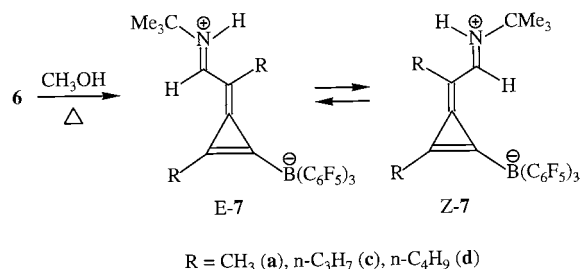
3.1. Reaction of bis(1-pentynyl)zirconocene with tris(pentafluorophenyl)borane: formation of **3c**

A total of 2.00 g (5.62 mmol) of bis(pentynyl)zirconocene was dissolved in 10 ml of toluene and cooled to -78°C . During 1 h a solution of 2.88 g (5.62 mmol) of B(C₆F₅)₃ in 8 ml of toluene was added dropwise with stirring. The mixture was stirred for 30 min at -78°C , then allowed to warm to r.t. and stirred for another 3h. Solvent was removed in vacuo and the residue washed twice with pentane to yield 4.16 g (85%) of **3c** as a pale orange colored solid, m.p. 138°C (dec.). ¹H-NMR (benzene-*d*₆): δ = 5.63 (s, 5H, Cp); 5.36 (s, 5H, Cp); 1.25 (m, 4H, CH₂); 0.90 (m, 4H, CH₂); 0.54 (t, 6H, CH₃). ¹³C-NMR (benzene-*d*₆): δ = 245.0 (Zr–C=); 148.7 (¹J_{CF} = 233 Hz); 139.5 (¹J_{CF} = 234 Hz); 137.5 (o,p,m-C of B(C₆F₅)₃); ¹J_{CF} = 243 Hz); 113.0 (Cp); 111.9

(Cp); 107.5; 106.4 (C≡C); 44.1, 24.7, 24.6, 21.8 (CH₂); 14.7 (CH₃); 12.8 (CH₃); [B–C= and *ipso*-C of B(C₆F₅)₃ not located]. IR (KBr): $\tilde{\nu}$ = 3120; 2963; 2934; 2873; 1644; 1515; 1462; 1379; 1275; 1089; 1017; 977; 812; 771; 761; 735; 686; 679; 674; 669; 665 cm⁻¹. UV–vis (dichloromethane): λ_{\max} = 230 (ϵ = 15190); 237 (sh, ϵ = 12070); 258 (ϵ = 5440); 325 (ϵ = 1280). B(C₆F₅)₃ rotational barrier: $\Delta G_{\text{rot}}^{\ddagger}$ = 15.0 kcal mol⁻¹ (T_c = 323 K, $\Delta\nu$ = 51 Hz; toluene-d₈).

3.2. Treatment of **3a** with *tert*-butylisocyanide: preparation of **6a**

tert-Butylisocyanide (0.2 ml, 154 mg, 1.86 mmol) was added at 0°C to a suspension of 2.00 g (2.21 mmol) of the zirconocene-(μ -hexadiyne)-borate–betaine complex **3a** in 30 ml of toluene. The resulting clear yellowish solution was stirred for 1 h at ambient temperature and then kept overnight at –30°C. The precipitated solid was recovered by filtration, washed with a little toluene and dried in vacuo. Yield of **6a**: quantitative, m.p. 59°C, the solid contains one equivalent of toluene. ¹H-NMR (benzene-d₆): δ = 5.26 (s, 10H, Cp); 2.38 (s, 3H, CH₃-5); 2.33 (s, 3H, CH₃-6); 0.95 (s, 9H); 0.75 (s, 9H, *tert*-butyl). ¹³C-NMR (THF-d₈): δ = 204.0 (C7); 169.0 (C1; ¹J_{CB} = 63.7 Hz); 158.2 (C3); 152.3 (C2); 149.1 (¹J_{CF} = 233 Hz); 139.73 (¹J_{CF} = 246 Hz); 137.7



Scheme 2.

(*o,p,m* of B(C₆F₅)₃, ¹J_{CF} = 251 Hz); 147.0 (C8); 106.2 (Cp); 84.5 (C4); 60.0; 57.5; 31.6; 29.3 (*t*-butyl); 23.4 (C5); 12.0 (C6); [toluene: 138.4, 129.6, 128.8, 126.0 (Ar); 21.4 (CH₃)]; [*ipso*-C of B(C₆F₅)₃ not observed]. IR (KBr): $\tilde{\nu}$ = 3152; 2986, 2932, 2873; 2195 (C≡N); 1809 (methylene-cyclopropene); 1642; 1580 (C=N); 1513; 1495; 1465; 1374; 1277; 1188; 1092; 1045; 1013; 978; 893; 801; 731; 686 cm⁻¹. UV–vis (dichloromethane): λ_{\max} = 231 (ϵ = 12290); 317 (ϵ = 9780). Anal. Calc. for C₄₄H₃₄BN₂F₁₅Zr·C₇H₈ (1069.92) C, 57.25; H, 3.96; N, 2.62; Found: C, 56.93; H, 4.07; N, 2.90%.

X-ray crystal structure analysis of **6a**: Single crystals from toluene. Formula C₄₄H₃₄N₂BF₁₅Zr·3C₇H₈, M = 1154.16, colourless crystal, 0.40 × 0.40 × 0.20 mm, a = 13.399(2), b = 14.789(1), c = 17.266(1) Å, α = 65.42(1), β = 73.02(1), γ = 89.98(1)°, V = 2946.7(5) Å³, $\rho_{\text{calc.}}$ = 1.413 g cm⁻³, $F(000)$ = 1284 e, μ = 23.10 cm⁻¹, empirical absorption correction via ψ -scan data (0.785 ≤ C ≤ 0.999), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 12503 reflections collected ($\pm h$, $+k$, $\pm l$), $[(\sin \theta)/\lambda]$ = 0.62 Å⁻¹, 12 014 independent and 9220 observed reflections [$I > 2\sigma(I)$], 768 refined parameters, R = 0.057, wR^2 = 0.144, max. residual electron density 1.12 (–1.47) e Å⁻³, three solvent molecules (toluene) in the asymmetric unit, hydrogens calculated and refined as riding atoms.

3.3. Preparation of **6b**

A sample of 500 mg (581 μ mol) of the titanocene–boron–betaine complex **3b** was suspended in 15 ml of toluene and cooled to –20°C. *tert*-Butylisocyanide (0.2 ml, 154 mg, 1.86 mmol) was added and the mixture allowed to slowly warm to r.t. with stirring. After 2 h volatiles were removed in vacuo and the residue stirred with 5 ml of pentane. The solid was collected by

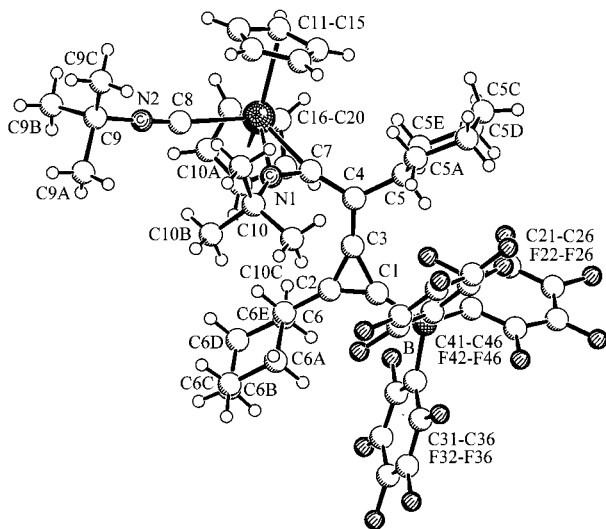


Fig. 3. A view of the molecular geometry of complex **6e**. B–C1 1.610(11), C1–C2 1.341(10), C1–C3 1.474(10), C2–C3 1.421(10), C2–C6 1.491(11), C3–C4 1.357(10), C4–C5 1.530(11), C4–C7 1.430(11), C7–N1 1.260(9), N1–C10 1.500(10), C7–Zr 2.235(8), N1–Zr 2.206(6), Zr–C8 2.351(9), C8–N2 1.158(10), N2–C9 1.483(12); B–C1–C2 151.6(7), B–C1–C3 144.8(7), C2–C1–C3 60.4(5), C1–C2–C3 64.4(6), C1–C2–C6 148.6(8), C6–C2–C3 146.8(8), C1–C3–C2 55.2(5), C2–C3–C4 154.3(7), C3–C4–C5 118.0(8), C3–C4–C7 118.9(6), C5–C4–C7 122.8(8), C4–C7–N1 133.3(7), C4–C7–Zr 153.4(6), N1–C7–Zr 72.3(5), C7–N1–C10 136.2(7), C7–N1–Zr 74.8(5), C7–Zr–N1 33.0(2), C7–Zr–C8 115.3(3), N1–Zr–C8 82.4(3), Zr–C8–N2 173.5(7), C8–N2–C9 174.6(10).

filtration, washed with toluene and pentane to give 385 mg (71%) of **6b** as a beige colored solid, m.p. 176°C. ¹H-NMR (benzene-d₆): δ = 4.99 (s, 10H, Cp); 2.28 (s, 3H); 2.24 (s, 3H, CH₃); 0.95 (s, 9H); 0.81 (s, 9H, *tert*-butyl). ¹³C-NMR (THF-d₈, 90.6 MHz): δ = 195.8 (C7); 152.6 (C2); 149.1 (¹J_{CF} = 239 Hz); 139.7 (¹J_{CF} = 247 Hz); 137.6 (¹J_{CF} = 250 Hz); 118.3 (o,p,m, *ipso*-C of B(C₆F₅)₃); 145.5 (C3); 134.5 (C8); 106.2 (Cp); 80.8 (C4); 60.1; 51.2; 30.8; 29.4 (*tert*-butyl); 22.5 (C5); 12.0 (C6); [toluene: 134.5, 132.2, 119.3, 116.4 (Ar); 19.2 (CH₃)]; [C1 not observed]. ¹¹B-NMR (chloroform-d): δ = -18.7. ¹⁹F-NMR (chloroform-d, 282.4 MHz): δ = -133.2; -161.2; -165.8 (o,p,m-B(C₆F₅)₃). IR (KBr): $\tilde{\nu}$ = 3124; 2984, 2977; 2183 (C≡N), 1814 (methylenecyclopropene); 1642; 1606 (C=N); 1514; 1463; 1373; 1330; 1274; 1250; 1233; 1190; 1137; 1091; 1019; 897; 893; 877; 809; 768; 684; 574 cm⁻¹. Anal. Calc. for C₄₄H₃₄BN₂F₁₅Ti (934.45) C, 56.55; H, 3.64; N, 2.99; Found: C, 56.91; H, 4.07; N, 2.86%.

3.4. Preparation of **6c**

A sample of the zirconocene-(μ-decadiyne)borate-betaine complex **3c** (2.00 g, 2.31 mmol) was suspended in 15 ml of toluene and at 0°C charged with 2 ml of *tert*-butylisocyanide. After stirring the mixture overnight at r.t. volatiles were removed in vacuo and the residue washed twice with pentane (10 ml each) to give 1.91 g (81%) of solid **6c**, m.p. 155°C (dec.). ¹H-NMR (benzene-d₆): δ = 5.35 (s, 10H, Cp); 2.85 (m, 2H, CH₂); 2.68 (m, 2H, CH₂); 1.21 (m, 4H, CH₂); 1.02 (s, 9H, *t*-Bu); 0.90 (m, 6H, CH₃); 0.83 (s, 9H, *t*-Bu). ¹³C-NMR (chloroform-d, 90.6 MHz): δ = 202.8 (C7); 154.9 (C3); 152.6 (C2); 149.6 (C8); 148.3 (¹J_{CF} = 244 Hz); 138.9 (¹J_{CF} = 233 Hz); 136.8 (¹J_{CF} = 245 Hz); 121.0 (o,p,m *ipso*-C of B(C₆F₅)₃); 105.3 (Cp); 91.1 (C4); 59.1; 57.5 (CMe₃); 38.3 (C5); 30.8; 29.9 (C(CH₃)₃); 28.9 (C6); 25.7; 20.7 (CH₂); 14.8; 13.6 (CH₃); [C1 not observed]. ¹¹B-NMR (chloroform-d): δ = -18.6. ¹⁹F-NMR (chloroform-d, 282.4 MHz): δ = -132.5; -161.5; -166.00 (o,p,m-B(C₆F₅)₃). IR (KBr): $\tilde{\nu}$ = 3125; 2963, 2932, 2874, 2852; 2196 (C≡N); 1803 (methylenecyclopropene); 1642; 1581; 1513; 1462; 1375; 1262; 1188; 1089; 1016; 977; 801 cm⁻¹. UV-vis (dichloromethane): λ_{max} = 233 (ε = 18800); 285 (ε = 8720); 328 (ε = 6000). Anal. Calc. for C₄₈H₄₂BN₂F₁₅Zr (1033.88) C, 55.76; H, 4.09; N, 2.71; Found C, 56.69; H, 4.48; N, 2.33%.

X-ray crystal structure analysis of **6c**: crystals from toluene/THF solution by the diffusion method (pentane). Formula C₄₈H₄₂BN₂F₁₅Zr·C₇H₈, *M* = 1126.00, light yellow crystal, 0.50 × 0.30 × 0.20 mm, *a* = 14.249(2), *b* = 17.948(1), *c* = 20.565(1) Å, α = 87.15(1), β = 82.38(1), γ = 89.09(1)°, *V* = 5206.2(9) Å³, ρ_{calc.} = 1.437 g cm⁻³, *F*(000) = 2296 e, μ = 3.04 cm⁻¹, empirical absorption correction via ψ-scan data

(0.979 ≤ *C* ≤ 0.999), *Z* = 4, triclinic, space group *P* $\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223 K, ω/2θ scans, 18 970 reflections collected (±*h*, -*k*, ±*l*), [(sin θ)/λ] = 0.59 Å⁻¹, 18 333 independent and 10 248 observed reflections [*I* ≥ 2σ(*I*)], 1244 refined parameters, *R* = 0.057, *wR*² = 0.149, max. residual electron density 0.96 (-0.70) e Å⁻³, two solvent molecules (toluene) in the asymmetric unit refined with constraints and one common isotropic displacement parameter, hydrogens calculated and refined as riding atoms.

3.5. Preparation of **6d**

A sample of 310 mg (346 μmol) of **3d** was suspended in 20 ml of toluene. At 0°C 139 mg (0.18 ml) of *tert*-butylisocyanide was added and the mixture stirred overnight at r.t. Solvent was evaporated in vacuo and the oily residue solidified by treatment with 5 ml of pentane to yield 300 mg (82%) of **6d**, m.p. 120°C (dec.). ¹H-NMR (chloroform-d, 360.1 MHz): δ = 5.60 (s, 10H, Cp); 2.79 (m, 2H, CH₂-5); 2.30 (m, 2H, CH₂-6); 1.67 (s, 9H, *t*-Bu); 1.35 (br m, 4H, CH₂-); 1.20 (s, 9H, *t*-Bu); 0.86 (m, 4H, CH₂-); 0.69 (m, 6H, CH₃-); ¹³C-NMR (chloroform-d, 90.6 MHz): δ = 202.7 (C7); 154.6 (C3); 152.7 (C2); 149.7 (C8); 148.3 (¹J_{CF} = 259 Hz); 138.9 (¹J_{CF} = 244 Hz); 136.7 (¹J_{CF} = 231 Hz); 121.5 (o,p,m, *ipso*-C of B(C₆F₅)₃); 105.3 (Cp); 90.9 (C4); 59.1; 57.5 (CMe₃); 36.3 (C5); 35.2 (C6); 30.3; 29.7 (C(CH₃)₃); 29.5; 28.8; 23.2; 22.8 (CH₂); 14.0; 13.6 (CH₃); [C1 not observed]. ¹¹B-NMR (benzene-d₆): δ = -18.7. ¹⁹F-NMR (chloroform-d, 282.4 MHz): δ = -132.5; -161.6; -165.8 (o,p,m-B(C₆F₅)₃). IR (KBr): $\tilde{\nu}$ = 3124; 2962, 2934, 2873; 2195 (C≡N); 1797 (methylenecyclopropene); 1642; 1617 (C=N); 1576; 1514; 1464; 1419; 1375; 1365; 1276; 1262; 1196; 1187; 1091; 1049; 1021; 979; 894; 801; 771; 763; 751; 686; 669; 450; 407; 402 cm⁻¹. UV-vis (dichloromethane): λ_{max} = 225 (ε = 9390); 261 (ε = 14110); 293 (ε = 15980); 314 (sh, ε = 14580); 331 (ε = 13650). Anal. Calc. for C₅₀H₄₆BN₂F₁₅Zr (1061.94) C, 56.87; H, 3.79; N, 2.65; Found C, 56.21; H, 4.35; N, 2.45%.

X-ray crystal structure analysis of **6d**: single crystals were obtained from toluene/THF by the diffusion method (pentane diffusion through the gasphase). Formula C₅₀H₄₆BN₂F₁₅Zr·C₅H₁₂, *M* = 1134.06, colourless crystal, 0.80 × 0.50 × 0.50 mm, *a* = 12.894(1), *b* = 15.091(1), *c* = 15.595(2) Å, α = 102.89(1), β = 105.41(1), γ = 104.67(1)°, *V* = 2689.4(4) Å³, ρ_{calc.} = 1.400 g cm⁻³, *F*(000) = 1164 e, μ = 2.94 cm⁻¹, empirical absorption correction via ψ-scan data (0.924 ≤ *C* ≤ 0.999), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223 K, ω/2θ scans, 11 350 reflections collected (±*h*, +*k*, ±*l*), [(sin θ)/λ] = 0.62 Å⁻¹, 10 920 independent and 7655 observed reflections [*I* ≥ 2σ(*I*)], 644 refined parameters, *R* = 0.049, *wR*² = 0.135, max. residual electron density 0.78 (-0.49) e Å⁻³, one solvent molecule

(pentane) in the asymmetric unit refined isotropic displacement parameters, hydrogens calculated and refined as riding atoms.

3.6. Preparation of **6e**

A sample of complex **3e** (400 mg, 422 μmol) was suspended in toluene. *tert*-Butylisocyanide (0.5 ml) was added at 0°C. The resulting clear solution was kept for 1 h at r.t. Volatiles were then removed in vacuo and the residue washed twice with pentane (5 ml each) to yield 405 mg (94%) of **6e** as a yellow solid, m.p. 110°C (dec.). ¹H-NMR (chloroform-d, 360.1 MHz): δ = 5.65 (s, 10H, Cp); 2.58 (m, 1H, CH); 2.45 (m, 1H, CH); 1.71 (s, 9H, *t*-Bu); 1.62 (m, 10H, cHex); 1.19 (s, 9H, *t*-Bu); 1.11 (m, 10H, cHex). ¹³C-NMR (chloroform-d, 90.6 MHz): δ = 215.2 (C7); 152.5 (C3); 148.2 (¹J_{CF} = 242 Hz); 138.6 (¹J_{CF} = 246 Hz); 136.60 (¹J_{CF} = 237 Hz); 123.0 (br s, o,p,m, *ipso*-C of B(C₆F₅)₃); 145.4 (C2); 137.7 (C8); 106.2 (Cp); 91.6 (C4); 60.2; 59.5 (CMe₃); 44.4 (C5); 37.4 (C6); 33.4; 30.0 (CH₂); 29.8; 29.4 (C(CH₃)₃); 26.7; 26.2; 25.79, 25.75 (CH₂); [C1 not observed]. ¹¹B-NMR (chloroform-d): δ = -18.2. ¹⁹F-NMR (benzene-d₆, 282.4 MHz): δ = -131.2; -162.1; -166.5 (o,p,m-B(C₆F₅)₃). IR (KBr): $\tilde{\nu}$ = 3125; 2929, 2852; 2193 (C≡N); 1796 (methylenecyclopropene); 1643; 1598 (C=N); 1513; 1462; 1391; 1263; 1275; 1193; 1088; 1013; 978; 805 cm⁻¹. UV-vis (dichloromethane): λ_{max} = 231 (ϵ = 5890); 281 (ϵ = 2620); 335 (ϵ = 1670). Anal. Calc. for C₅₄H₅₀BN₂F₁₅Zr (1114.01) C, 58.22; H, 4.52; N, 2.51; Found C, 57.12; H, 4.61; N, 2.59%.

X-ray crystal structure analysis of **6e**: single crystals were obtained from dichloromethane/THF by the diffusion method (pentane diffusion through the gas phase). Formula C₅₄H₅₀BN₂F₁₅Zr, *M* = 1113.99, yellow crystal, 0.50 × 0.20 × 0.10 mm, *a* = 19.621(9), *b* = 14.055(5), *c* = 18.468(2) Å, β = 95.78(2)°, *V* = 5067(3) Å³, $\rho_{\text{calc.}}$ = 1.460 g cm⁻³, *F*(000) = 2272 e, μ = 3.11 cm⁻¹, empirical absorption correction via ψ -scan data (0.881 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group *P*2₁/*c* (No. 14), λ = 0.71073 Å, *T* = 223 K, $\omega/2\theta$ scans, 9195 reflections collected (+*h*, +*k*, ±*l*), [(sin θ)/ λ] = 0.59 Å⁻¹, 8919 independent and 4549 observed reflections [*I* ≥ 2 σ (*I*)], 689 refined parameters, *R* = 0.072, *wR*² = 0.206, max. residual electron density 0.79 (-1.10) e Å⁻³, disorder in the *tert*-butyl group at C9 (ratio 0.57:0.43(3)), hydrogens calculated and refined as riding atoms.

3.7. Preparation of **6f**

Hafnocene-(μ -hexadiyne)-borate-betaine **3f** (750 mg, 762 μmol) was suspended in 15 ml of toluene and charged with 0.7 ml (0.56 g, 6.65 mmol) of *tert*-butylisocyanide at 0°C. After the usual workup complex **6f** was obtained as an off-white solid (705 mg,

87%), m.p. 177°C (dec.) that was only characterized spectroscopically. ¹H-NMR (CDCl₃): δ 6.29 (s, 10H, Cp); 2.46 (s, 3H); 1.96 (s, 3H, CH₃); 1.68 (s, 9H); 1.21 (s, 9H, *tert*-butyl). ¹³C-NMR (benzene-d₆): δ 211.7 (C7); 158.8 (C3); 152.4 (¹J_{CF} = 247 Hz); 139.4 (¹J_{CF} = 232 Hz); 137.5 (¹J_{CF} = 249 Hz, o,p,m-B(C₆F₅)₃); 149.0 (C8); 147.1 (C2); 105.2 (Cp); 85.9 (C4); 60.2; 57.9; 31.5; 29.3 (*tert*-butyl); 23.8; 12.2 (CH₃); (C1 not observed). ¹¹B-NMR (benzene-d₆): δ -18.4. IR (KBr): $\tilde{\nu}$ = 3111; 2936; 2871; 2200 (C≡N); 1814 (methylenecyclopropene); 1653; 1578; 1514; 1462; 1394; 1375; 1366; 1274; 1263; 1192; 1091; 1016; 977; 805 cm⁻¹. UV-vis (dichloromethane): λ_{max} = 232 nm (ϵ = 8090); 250 (ϵ = 8220); 291 (ϵ = 5840); 323 (ϵ = 6730).

3.8. Hydrolysis reaction of **6c**: preparation of **7c**

Methanol (5 ml) was added to a suspension of 500 mg (484 μmol) of **6c** in 5 ml of toluene. The mixture was carefully warmed with a heat-gun until all solids were dissolved. The mixture was stirred overnight at r.t. and then the volatiles were removed in vacuo. The residue was stirred up with pentane. The solid was dissolved in 5 ml of toluene, filtered through silica gel and evaporated to dryness. Treatment with pentane (8 ml) overnight gave 181 mg (51%) of **7c**, m.p. 136°C, mixture of *E*-/*Z*-**7c** (86:14 in CDCl₃). Major isomer: ¹H-NMR (chloroform-d, 360.1 MHz): δ = 7.32 (d, 1H, H-7; ³J_{HH} = 15.4 Hz); 5.38 (d, 1H, NH; ³J_{HH} = 15.4 Hz); 2.76 (t, 2H, H-5; ³J_{HH} = 7.6 Hz); 2.17 (t, 2H, H-6; ³J_{HH} = 7.4 Hz); 1.64 (m, 2H); 1.47 (m, 2H, CH₂); 1.17 (s, 9H, *t*-Bu); 0.88 (t, 6H, CH₃). ¹³C-NMR (chloroform-d, 90.6 MHz): δ = 174.7 (q, C1; ¹J_{CB} = 55.8 Hz); 165.3 (C3); 158.4 (C2); 155.2 (C7); 147.9 (¹J_{CF} = 237 Hz); 139.2 (¹J_{CF} = 249 Hz); 136.9 (¹J_{CF} = 241 Hz); 119 (m, o,p,m, *ipso*-C of B(C₆F₅)₃); 92.4 (C4); 53.9; 29.5 (*t*-Bu); 28.8 (C5); 27.8 (C6); 21.6; 20.1 (CH₂); 13.9; 13.6 (CH₃). Minor isomer: ¹H-NMR (chloroform-d, 360.1 MHz): δ = 7.4 (d, 1H, H-7; ³J_{HH} = 15.5 Hz); 5.38 (d, 1H, NH; ³J_{HH} = 15.5 Hz); 2.84 (t, 2H, H-5; ³J_{HH} = 7.5 Hz); 1.99 (t, 2H, H-6; ³J_{HH} = 7.5 Hz); 1.36 (s, 9H, *t*-Bu); 0.72 (t, 6H, CH₃); [CH₂ signal under major isomer]. ¹³C-NMR (chloroform-d, 90.6 MHz): δ = 174.7 (q, C1; ¹J_{CB} = 55.8 Hz); 166.7 (C3); 159.3 (C2); 153.9 (C7); 147.9 (¹J_{CF} = 237 Hz); 139.2 (¹J_{CF} = 249 Hz); 136.9 (¹J_{CF} = 241 Hz); 119 (m, o,p,m, *ipso*-C of B(C₆F₅)₃); 94.4 (C4); 53.9; 30.0 (*t*-Bu); 28.9 (C5); 27.7 (C6); 21.4; 20.1 (CH₂); 13.8; 13.6 (CH₃). Major isomer: ¹¹B-NMR (benzene-d₆): δ = -18.3. ¹⁹F-NMR (benzene-d₆, 282.4 MHz): δ = -132.7; -158.7; -164.2 (o,p,m-B(C₆F₅)₃) (only one isomer was obtained in benzene). IR (KBr): $\tilde{\nu}$ = 3405 (NH); 2966, 2937, 2877; 1814; 1643; 1615; 1515; 1464; 1375; 1329; 1238; 1198; 1094; 983; 804 cm⁻¹. UV-vis (dichloromethane): λ_{max} = 229 (ϵ = 13770); 263 (ϵ = 7900); 307 (ϵ = 38330). MS (EI): *m/z* = 731 ([*M*⁺], 16%); 716 (18%); 647 (9%);

646 (32%); 632 (16%); 564 (6%); 277 (5%); 181 (5%); 106 (4%); 58 (10%); 57 (100%). HRMS: (C₃₃H₂₅BNF₁₅): Calc. 731.1847. Found 731.1861.

3.9. Hydrolysis of **6d**: preparation of **7d**

A sample of 589 mg (555 μmol) of **6d** was treated with 5 ml of methanol in toluene as described above. Volatiles were removed in vacuo after 12 h at ambient temperature to give an oil. This was treated with pentane and the product was dissolved in 5 ml of toluene and filtered. Removal of the toluene solvent in vacuo gave an orange colored oil. Treatment with pentane gave **7d** as a solid, yield 205 mg (49%), m.p. 104°C (*Z*-/*E*-isomer mixture 90:10 in CDCl₃, single isomer detected in benzene-d₆). Major isomer: ¹H-NMR (chloroform-d, 360.1 MHz): δ = 7.21 (d, 1H, H-7; ³J_{HH} = 15.5 Hz); 5.26 (d, 1H, NH; ³J_{HH} = 15 Hz); 2.89 (t, 2H, CH₂-6; ³J_{HH} = 8 Hz); 2.08 (t, 2H, CH₂-5; ³J_{HH} = 8 Hz); 1.49 (m, 4H, CH₂); 1.16 (m, 4H, CH₂); 1.07 (s, 9H, *t*-Bu); 0.82 (t, 3H, CH₃; ³J_{HH} = 7 Hz); 0.76 (t, 3H, CH₃; ³J_{HH} = 7 Hz). ¹³C-NMR (chloroform-d, 90.6 MHz): δ = 174.2 (q, C1; ¹J_{CB} = 59 Hz); 165.2 (C3); 158.6 (C2); 155.1 (C7); 149.4 (¹J_{CF} = 242 Hz); 139.3 (¹J_{CF} = 250 Hz); 136.9 (¹J_{CF} = 242 Hz); 119.5 (br s, o,p,m, *ipso*-C of B(C₆F₅)₃); 92.8 (C4); 53.9 (CMe₃); 30.6 (C5); 29.5 (C(CH₃)₃); 28.6 (C6); 26.6; 25.7; 22.5; 22.4 (CH₂); 13.9; 13.4 (CH₃). Minor isomer: ¹H-NMR (chloroform-d, 360.1 MHz): δ = 7.44 (d, 1H, H-7; ³J_{HH} = 15.5 Hz); 5.26 (d, 1H, NH; ³J_{HH} = 15 Hz); 2.87 (m, 2H, CH₂-5); 2.01 (m, 2H, CH₂-6); 1.27 (s, 9H, *t*-Bu); [remaining signals under major isomer]. ¹³C-NMR (chloroform-d, 90.6 MHz): δ = 174.2 (q, C1; ¹J_{CB} = 59 Hz); 165.4 (C3); 159.2 (C2); 153.8 (C7); 92.8 (C4); 53.9 (CMe₃); 30.3 (C5); 30.0 (C(CH₃)₃); 28.6 (C6); 26.7; 25.5; 22.5; 22.4 (CH₂); 13.9; 13.4 (CH₃). B(C₆F₅)₃ signals like major isomer. ¹¹B-NMR (chloroform-d): δ = -18.5 (br s, *w*_{1/2} = 25 Hz). ¹⁹F-NMR (chloroform-d, 282.4 MHz): δ = -132.9; -159.8; -164.9 (o,p,m-B(C₆F₅)₃). IR (KBr): ν̄ = 3405 (NH); 2963, 2936, 2877; 1816; 1643; 1615; 1515; 1464; 1375; 1094; 983; 804 cm⁻¹. MS (EI): *m/z* = 760 ([*M*⁺] + H, 6%); 759 ([*M*⁺], 20%); 744 ([*M*⁺] - CH₃, 24%); 702 (20%); 660 (41%); 646 (18%); 604 (8%); 168 (4%); 58 (32%); 57 (100%). UV-vis (dichloromethane): λ_{max} = 231 (ε = 9060); 263 (ε = 5620); 307 (ε = 23580). HRMS: C₃₅H₂₉BNF₁₅: Calc. 759.2160. Found: 759.2141.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 102136, 102137, 102138, 102139. Copies of the data can be

obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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