

Five-Membered Zirconacycloallenoids: Synthesis and Characterization of Members of a Unique Class of Internally Metal-Stabilized Bent Allenoid Compounds

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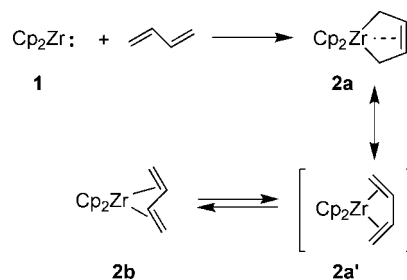
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Abstract: Treatment of the bis-acetylide zirconocene complexes $(\text{RCp})_2\text{Zr}(\text{C}\equiv\text{C}-\text{SiMe}_3)_2$ (**8a**, $\text{R} = \text{CH}_3$; **8b**, $\text{R} = \text{tert-butyl}$) with $\text{HB}(\text{C}_6\text{F}_5)_2$ results in the formation of the five-membered organometallic zirconacycloallenoid products (**9a**, **9b**). Both were characterized by X-ray diffraction, and the special bonding features of **9a** were studied by DFT calculation. The overall reaction was followed by NMR experiments at variable temperature. Starting from **8a** the reaction proceeds by alkynyl abstraction to give a zwitterionic $[(\text{MeCp})_2\text{ZrC}\equiv\text{C}-\text{SiMe}_3]^+[\eta\text{-Ar}^{\text{F}}_2\text{B}(\text{H})\text{C}\equiv\text{C}-\text{SiMe}_3]^-$ intermediate (**12a**), single crystals of which were obtained at -30°C for characterization by X-ray diffraction, followed by a 1,1-hydroboration/ σ -ligand coupling sequence to give the new five-membered zirconacycloallenoid product **9a**.

Introduction

The group 4 bent metallocenes Cp_2M ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) exhibit a unique set of three-valence molecular orbitals that are all located in the major $\text{Cp}-\text{M}-\text{Cp}$ bisecting symmetry plane.^{1,2} Bonding of unsaturated ligands at the front side of the bent metallocene wedge in the formal $\text{M}^{(+2)}$ oxidation state results in strong metal-to-ligand backbonding, giving rise to the formation of complexes with a high metal–carbon σ -bond character.^{3,4} (Butadiene)zirconocene (**2**) is a typical example.⁵ Its “s-cis-diene” metallocene isomer (**2a**) is largely an envelope-shaped zirconacyclopentene, with a small internal $\text{C}2-\text{C}3$ π -olefin metal coordination component which varies in strength, depending on the substituents present at the $\text{C}2/\text{C}3$ -positions

Scheme 1



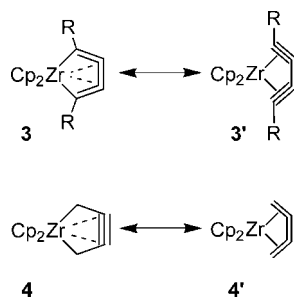
of the 1,3-diene ligand system.⁶ The mesomeric valence structure (**2a'**) plays no significant role for the description of the properties of (s-cis-butadiene)zirconocene (see Scheme 1). The appearance of the stable “s-trans-butadiene” zirconocene isomer (**2b**) is another consequence of the unique in-plane arrangement of the set of the three Cp_2Zr valence orbitals. In **2b** all four carbons of the distorted s-trans-C₄H₆ conformer are bonded to the metal center; actually, the internal carbon atoms $\text{C}2/\text{C}3$ are found to be closer to Zr than $\text{C}1/\text{C}4$.^{5–7}

The unique stereoelectronic features of Cp_2Zr : (**1**) and its group 4 metal congeners were used for the formation of a variety of metallacyclic systems that contain strongly distorted carbon-based π -systems. Typical examples include the metallacyclo-

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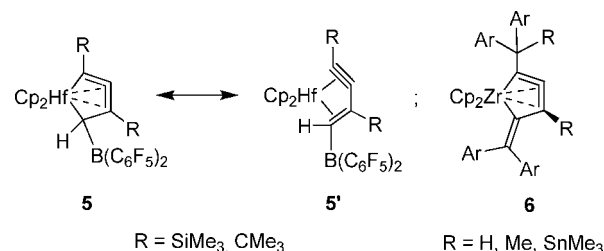
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Scheme 2



pentatrienes (**3**), described by U. Rosenthal^{8–10} in many variations, or the formal metallacyclopentynes derivatives (**4**), first introduced by N. Suzuki et al. (see Scheme 2).^{11,12} The reported examples of these classes of compounds feature metallacyclic structures containing pairs of metal-to-carbon σ -bonds, and they show strongly bent geometries at the internal formally two-coordinate sp-carbon centers, a situation that would not be stable in the related carbocyclic systems.^{13,14} However, the complexes **3** and **4** are remarkably persistent. They can be isolated and kept at room temperature, and they do not undergo

Scheme 3



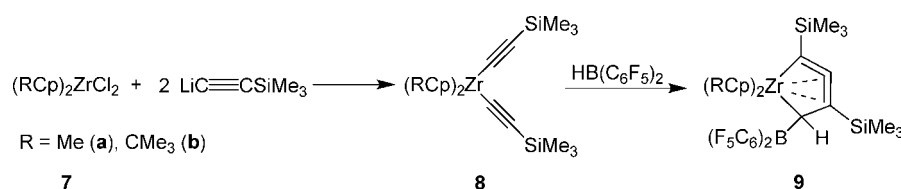
reactions¹⁵ that are typical for bent cumulenes or bent alkynes.^{16,17} The unusual stability of these metallacyclic systems is probably due to a unique supplementary in-plane interaction of the bent Cp_2M unit with the central unsaturated CC moiety making use of the remaining metallocene acceptor orbital in the σ -ligand plane.¹⁸ The mesomeric π -complex forms (**3'**, **4'**) may play a minor role for the formal description of these compounds.

It was tempting to use these unique bonding features of a group 4 metallocene to generate corresponding five-membered ring structures which contain an internally metal-stabilized bent allene moiety, the parent five-membered carbocyclic allene analogues of which would be highly unstable and reactive.¹⁴ We recently isolated first examples of such five-membered metallacycloalleneoid compounds. The hafnacycles **5** were isolated and characterized by X-ray diffraction, spectroscopically and by a DFT analysis.¹⁹ They are of a high persistence similar to that of the Rosenthal (**3**) and Suzuki (**4**) compounds, and show similar bonding features, including a marked interaction of the internal carbon centers C2/C3 with the group 4 metal atom in the σ -plane. The formal π -complex mesomeric structure (**5'**) may play some role, but not a major one. Suzuki et al.

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Scheme 4



shortly thereafter described the similarly structured systems (**6**) that were obtained by a very different synthetic route²⁰ (Scheme 3).

We have now found that our synthesis can be extended to the zirconacycloalleneoid analogues of **5**. We here describe the synthesis and characterization of a pair of representative examples of this unique class of compounds, including their X-ray crystal structure analyses, and we have gained a picture of the mechanistic pathway of their formation by characterizing an important intermediate and products from competing reaction alternatives.

Results and Discussion

Synthesis and Characterization of the New Zirconacycloalleneoids. We started our synthesis with the preparation of the bis(trimethylsilyl)ethynylzirconocene complexes **8a** and **8b**. These compounds were prepared by treatment of the precursors (methyl-Cp)₂ZrCl₂ (**7a**) and (*tert*-butyl-Cp)₂ZrCl₂ (**7b**), respectively, with lithium trimethylsilylacetylide.²¹ We chose these more bulky zirconocene derivatives in favor of the parent system, since treatment of Cp₂ZrCl₂ with the alkynyllithium salt in our hands met with difficulties, invariably leading to the formation of the known very stable (Cp₂Zr)₂(μ-C≡C-SiMe₃)₂ product instead.^{17d,22} In the more bulky methyl-Cp and *tert*-butyl-Cp-substituted systems the required mononuclear metallocene bis-acetylide products were obtained in 44% (**8a**, after crystallization from pentane) and 59% yield (**8b**), respectively. Complex **8a** shows a ¹H NMR AA'BB' C₅H₄ pattern at δ 6.16/5.61 and a corresponding CpCH₃ methyl proton NMR resonance at δ 2.29 (s, 6H). The Si(CH₃)₃ signal is at δ ¹H 0.22 (²J_{Si,H} = 6.8 Hz), with a corresponding ²⁹Si NMR feature at δ −24.1 (*d*₆-benzene, 298 K). Complex **8a** shows an IR acetylene stretching band at $\tilde{\nu}$ = 2035 cm^{−1}.

We then reacted the (MeCp)₂Zr(C≡CSiMe₃)₂ complex **8a** with a stoichiometric amount of HB(C₆F₅)₂²³ in toluene. The reaction was completed by keeping the mixture for 5 h at 60 °C. After workup, the new metallacyclic product **9a** (see Scheme 4) was isolated as an orange-red solid in 26% yield. Single crystals of complex **9a** were obtained from a pentane solution at −30 °C. The compound was characterized by an X-ray crystal structure analysis. In the crystal complex **9a** features isolated molecular entities. The bent metallocene unit [Cp(centroid)–Zr–Cp(centroid) angle: 126.9°] shows a conformation that has the methyl substituents in an anti-arrangement oriented toward the narrow back side of the bent metallocene wedge. The five-membered metallacyclic framework at the front side has all four carbon atoms C1 to C4 within bonding distance to the zirconium atom (see Figure 1 and Table 1). The Zr–C1 (2.520(4) Å) and Zr–C2 (2.568(4) Å) bond lengths of **9a** are in about the same range as are the Zr–C(Cp) distances (2.497(5) Å to 2.547(5) Å). The Zr–C3 (2.347(4) Å) and Zr–C4 (2.380(4) Å) bonds are shorter. Consequently, the five-membered metallacycle of **9a** exhibits small internal bond angles at C1 (Zr–C1–C2 74.9(2)°) and C4 (Zr–C4–C3 72.9(3)°) and the “σ-ligand angle” at Zr is rather large [C1–Zr–C4 = 86.5(1)°]. The C1–C2 bond (1.478(6) Å) is just within the typical C(sp³)–C(sp²) range. The adjacent C2–C3 bond (1.379(6) Å) is within the C=C double bond range, whereas the C3–C4 bond is markedly shorter (1.276(6) Å). The C1–B bond (1.474(6) Å) is very short. It is probably one of the shortest C–B(C₆F₅)₂ linkages reported to date.^{24,25} The C1–C2–C3 angle is 112.4(4)°. The angle at C3 amounts to C2–C3–C4 = 158.4(5)°, which is ca. 20° below a linear allene arrangement. The metallacyclic framework of complex **9a** is nonplanar. It shows an allenoid distortion along the bent C2–C3–C4 unit characterized by torsion angles of 50.9(3)° (C1–C2⋯C4–Zr) and 63.4(5)° (Si11–C2⋯C4–Si41), respectively.

The metallacyclic framework of **9a** contains two chirality elements. There is the chiral carbon center C1, bearing four different substituents in a distorted pseudotetrahedral arrangement. Due to its marked torsion angle the C2 to C4 allenoid subunit contains an element of axial chirality.²⁶ Therefore, complex **9a** should potentially form two diastereoisomers. In the crystal, we have observed only one, namely *syn*-**9a** which

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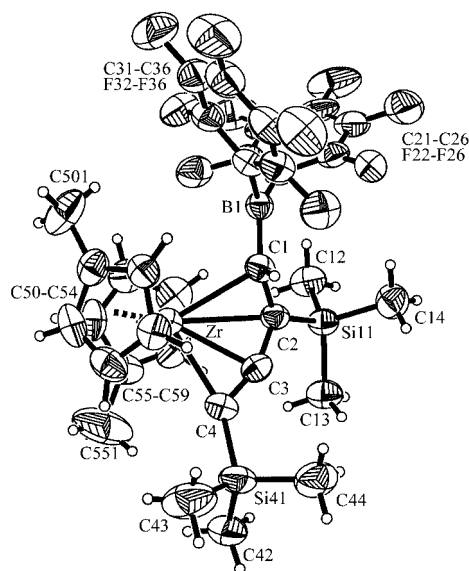


Figure 1. Molecular structure of complex *syn-9a*.

Table 1. Selected Experimental (X-ray) and DFT Calculated Structural Data^a of the Complexes **9** (M = Zr) and **5** (M = Hf, R = SiMe₃)^b

	<i>syn-9a</i> (X-ray)	<i>syn-9a</i> (DFT) ^c	<i>anti-9a</i> (DFT) ^c	<i>syn-9b</i> (X-ray)	<i>anti-5</i> (X-ray)
Zr–C1	2.520(4)	2.457	2.505	2.499(2)	2.494(3)
Zr–C2	2.568(4)	2.523	2.496	2.526(2)	2.513(3)
Zr–C3	2.347(4)	2.337	2.325	2.335(2)	2.314(3)
Zr–C4	2.380(4)	2.383	2.366	2.412(2)	2.340(3)
C1–C2	1.478(6)	1.468	1.470	1.476(3)	1.490(4)
C2–C3	1.379(6)	1.372	1.361	1.383(3)	1.356(4)
C3–C4	1.276(6)	1.280	1.285	1.269(3)	1.276(4)
B–C1	1.474(6)	1.488	1.499	1.482(3)	1.474(4)
Zr–C1–C2	74.9(2)	75.3	72.6	73.9(1)	73.4(2)
C1–C2–C3	112.4(4)	114.8	121.4	115.4(2)	119.2(3)
C2–C3–C4	158.4(5)	157.0	155.3	158.7(2)	156.4(3)
C3–C4–Zr	72.9(3)	72.3	72.4	71.1(1)	73.0(2)
C1–Zr–C4	86.5(1)	88.8	91.8	88.4(1)	91.3(1)
C1–C2...C4–Zr	50.9(3)	47.3	42.7	–48.8(1)	43.5(3)

^a Bond lengths in Å, angles in deg; single crystals of **9a** and **9b** were obtained from pentane at –30°C. ^b From ref 19. ^c For details see the section DFT Calculations.

is characterized by a *syn*-arrangement of the C2–Si11 and C1–B1 vectors relative to a mean central ring plane (see Figure 2). This is in contrast to the Hf analogue **5**, of which we had previously observed the corresponding *anti-5* structural arrangement in the crystal.

In solution we have observed the presence of the pair of *anti*/*syn*-diastereoisomers of complex **9a** by NMR. At ambient conditions the isomers *anti-9* and *syn-9* rapidly equilibrate by means of a “ring-flip” of the nonplanar five-membered metalacyclic ring structure (see Scheme 5), a process that topologically corresponds to an inversion of the configuration of the axially chiral allenoid subunit,¹⁹ giving rise to averaged NMR spectra. Lowering the monitoring temperature eventually leads to decoalescence, and at 213 K we have observed the separate NMR resonances of the ca. 3:1 mixture of diastereoisomers in solution. An absolute assignment of the *syn*/*anti*-isomers was not done for the structures in solution, but the results of our DFT calculations (see below) renders the *anti-9a* isomer by 0.9 kcal/mol more stable than *syn-9a*.

The major **9a** diastereomer features a 9H:9H intensity pair of –SiMe₃ ¹H NMR signals at δ 0.08 and –0.05 (with

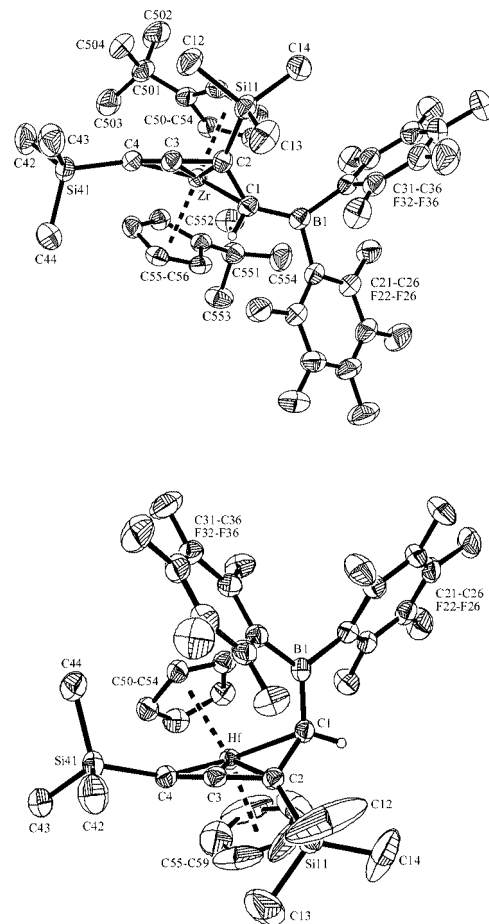


Figure 2. Comparison of the molecular structures of complexes *syn-9b* (top) and *anti-5* (R = SiMe₃, bottom) in the crystal.

corresponding ²⁹Si resonances at δ –2.4 and –6.5). The MeCp ligands are in different environments. Each gives rise to a set of four C₅H₄CH₃ ¹H NMR resonances (Cp^A: δ 5.51, 5.40, 5.17, 4.41; Cp^B: δ 5.37, 5.07, 4.86, 4.55; ¹H NMR Cp–CH₃ signals at δ 1.76 and δ 1.34). The C1–H ¹H NMR resonance was found at δ 2.08 (¹³C: 88.3). The ¹³C NMR signals of the terminal allenoid carbon atoms of the major **9a** isomer were located at δ 95.0 (C2) and δ 116.9 (C4). The central =C= allenoid carbon atom exhibits a ¹³C NMR resonance at δ 138.8. The ¹⁹F NMR spectrum at 223 K showed two sets of resonances for the diastereotopic C₆F₅ groups at the boron atom. One consists of five signals each with an integral of one fluorine [δ –126.4 (o), –127.4 (o), –155.2 (p), –161.7 (m), –162.0 (m)] according to a hindered rotation around the B–C_{ipso}(C₆F₅) vector. In contrast, rotational equilibration of the other C₆F₅ group caused a broadened AA′BB′M spin system [–130.0 (br, 2F, o), –154.0 (1F, p), –161.1 (very br, without integral value)].

The minor-**9a** isomer shows similar NMR features (for details, see Table 2 and the Experimental Section). It is noteworthy that the C1–H ¹H NMR signal of the minor-**9a** isomer is found at a much larger δ value (3.88, ¹³C: δ 73.0) than in major-**9a**. The ¹³C NMR signals of the allenoid moiety of minor-**9a** were monitored at δ 93.2 (C2), δ 141.4 (C3), and δ 129.7 (C4). The ¹⁹F NMR spectrum shows two AA′BB′M spin systems [δ –123.2 (br, 2F, o), –153.4 (1F, p), –162.7 (2F, m) (C₆F₅); –127.7 (br, 2F, o), –154.0 (1F, p), –162.4 (2F, m) (C₆F₅)], indicating free rotation of both C₆F₅ groups.

The ¹¹B and ¹⁹F NMR spectra measured at higher temperature correspond to averaged values of the equilibrating diastereoi-

Scheme 5

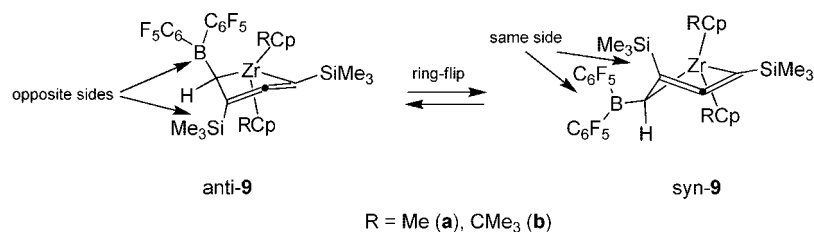


Table 2. Selected NMR Data of the Major and Minor Diastereoisomers of the Metallaallenoid Complexes **9a**, **9b** and **5**

	M		δ ¹ H1	δ ¹³ C1	δ ¹³ C2	δ ¹³ C3	δ ¹³ C4
9a^a	Zr	major	2.08	88.3	95.0	138.8	116.9
		minor	3.88	73.0	93.2	141.4	129.7
9b^b	Zr	major	2.03	86.9	99.2	140.9	119.4
		minor	4.13	72.0	94.4	145.0	130.6
5^{c,d}	Hf	major	2.36	84.8	93.7	136.2	114.4
		minor	3.65	66.1	88.7	141.5	127.1

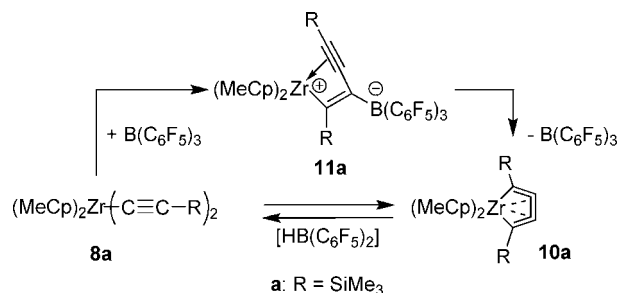
^a *d*₈-Toluene at 213 K. ^b *d*₈-Toluene at 223 K. ^c R = SiMe₃; see Scheme 3 from ref 19. ^d *d*₈-Toluene at 233 K.

somers of **9a**. We find a broad ¹¹B NMR signal at δ 41²⁷ (27 °C) and a 1:1 set of ¹⁹F NMR signals of the pair of C₆F₅ substituents at δ -126.2 (ortho), δ -155.9 (para), and δ -163.1 (meta)/ δ -129.5 (ortho), δ -155.3 (para), and δ -162.9 (meta) (80 °C) with a rather small p/m chemical shift separation.²⁸ In contrast to its precursor **8a** there is no IR (C≡C) stretching band observed in **9a**.

Compound **9b** shows similar NMR spectra (see Table 2). It also features two diastereoisomers in a 3:1 molar ratio that were characterized from the mixture at 223 K. Single crystals of complex **9b** were obtained from pentane at low temperature. The X-ray crystal structure analysis has revealed the presence of a single isomer in the solid state (syn-**9b**). Its structural parameters are similar to those of syn-**9a** (see Figure 2 and Table 1).

Mechanistic Studies. This qualitative mechanistic investigation was carried out by performing the reaction of **8a** with HB(C₆F₅)₂ in *d*₈-toluene under varying reaction conditions that allowed in situ observation and characterization of the products by NMR. We started by mixing **8a** with a stoichiometric amount of the HB(C₆F₅)₂ reagent in *d*₈-toluene at -78 °C. With just a little shaking to ensure some mixing of the reagents the reaction mixture was allowed to slowly warm to -30 °C and kept at this temperature during the NMR measurements. Under these conditions the HB(C₆F₅)₂ reagent did not completely dissolve, so we assume that the observed reaction was basically catalytic in borane. We observed the formation of the 1,4-bis(trimethylsilyl)-substituted zirconacyclocumulene product (**10a**)⁸ under these special conditions. The C_{2v}-symmetric product (**10a**)

Scheme 6



featured a single set of MeCp NMR resonances, a single set of -SiMe₃ signals and the very typical ¹³C NMR features of the C1/C4 (δ 184.5) and C2/C3 (δ 137.4) ring carbon atoms. We had previously shown that some zirconocene bis-acetylide complexes can very effectively be catalytically transformed into their metallacumulene isomers by B(C₆F₅)₃.²⁹ We had shown that these reactions proceeded via the zwitterionic systems (**11**) (that were isolated under stoichiometric conditions and unambiguously characterized spectroscopically and by X-ray crystal structure analyses of some examples^{28c,30}). We assume that treatment of **8a** with a catalytic amount of HB(C₆F₅)₂ here proceeds analogously (see Scheme 6). The formation of **10a** is probably reversible.

After the NMR sample was ejected, vigorously shaken at room temperature for seconds, and injected into the spectrometer (-40 °C) again, the clear solution contained mostly the new zwitterionic complex **12a**, which actually seems to be a direct intermediate on the pathway of the formation of the five-membered zirconacyclopentadiene product **9a** (see Scheme 7). Complex **12a** was the major product observed at -40 °C. It was characterized spectroscopically and by X-ray diffraction. Single crystals of this temperature-sensitive intermediate were grown from an undisturbed biphasic mixture of a toluene solution containing in situ-generated **12a** carefully topped with pentane. At -30 °C single crystals of **12a** were grown in the interphase region during 12 h. Complex **12a** was probably formed by abstraction of one trimethylsilylacetylide anion unit from the metallocene-bis(acetylide) complex **8a** by the HB(C₆F₅)₂ Lewis acid. A zwitterionic compound is formed in which the respective alkynylborate anion has remained coordinated to the residual alkynylzirconocene cation. Such product types were proposed as intermediates in a variety of transformations of geminal bis(acetylide) compounds of d-block metals, as well as of main group metals by boranes.³¹⁻³⁴ In some way the structure of compound **12a** represents a connecting link

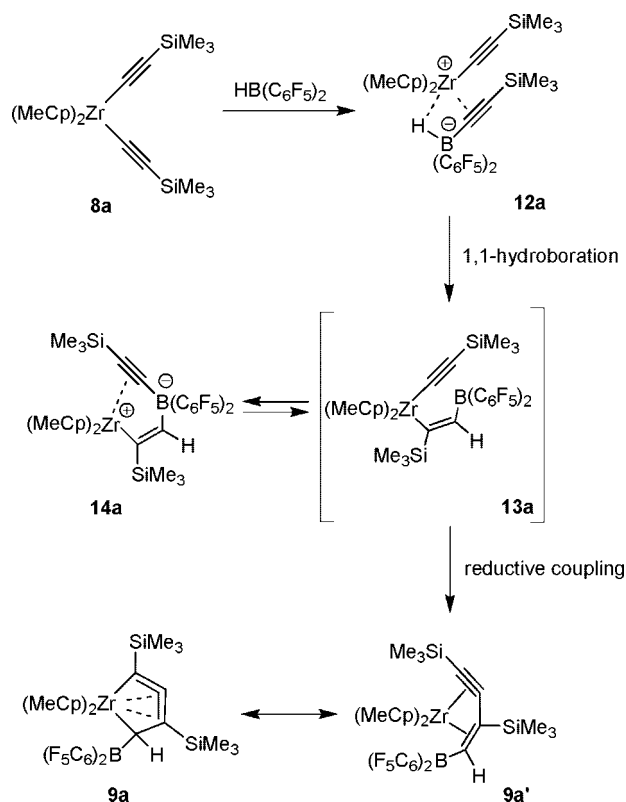
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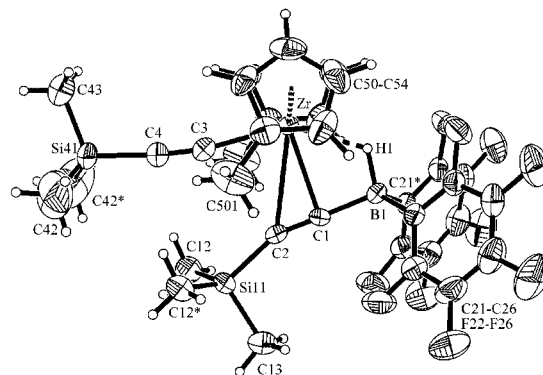
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Scheme 7



between the respective chemistry of the main group metals and the transition-metal series.

The structure of complex **12a** contains some truly remarkable features (see Figure 3 and Table 3). The Cp-ligands are found in an eclipsed conformation with both (Cp)C–CH₃ vectors oriented to the open front side of the bent metallocene wedge.³⁵ A single trimethylsilyl-substituted ethynyl ligand has remained σ -bonded to the Zr metal center. Its metal–carbon distance (Zr–C3, see Table 3) is in the typical Zr–C σ -bond range.^{22,36} The C3–C4 bond is short and typical of a C≡C triple bond. The σ -ligand framework is close to linear.

Figure 3. Molecular structure of complex **12a**.Table 3. Comparison of Experimental (X-ray) and DFT-Calculated Structural Parameters of the Zwitterionic Complex **12a**^a

	12a (X-ray)	12a (DFT) ^b
Zr–C1	2.513(5)	2.458
Zr–C2	2.841(5)	2.793
C1–C2	1.209(7)	1.235
B1–C1	1.594(7)	1.569
B1–C1–C2	178.7(5)	178.7
C1–C2–Si11	157.8(4)	158.9
Zr–C3	2.266(5)	2.251
C3–C4	1.208(7)	1.235
Zr–C3–C4	170.8(5)	171.4
C3–C4–Si41	174.5(5)	174.5
(B1–H)	1.19(5)	1.260
(Zr–H)	2.12(5)	2.163
(Zr–H–B1)	118(3)	109.0

^a Bond lengths in Å, angles in deg. ^b For details see the section DFT Calculations.

The remaining coordination sites of the bent metallocene in the central major plane are used for binding the newly formed $[(\text{C}_6\text{F}_5)_2\text{B}(\text{H})\text{--C}\equiv\text{C--SiMe}_3]^+$ borate ligand. Its bonding features are quite unusual. It seems that the anionic ligand is coordinated to the zirconium center in the formally cationic $[(\text{MeCp})_2\text{Zr--C}\equiv\text{C--SiMe}_3]^+$ moiety predominantly through the acetylene carbon atom C1. The Zr–C1 distance is in the same range as the Zr–C(CpMe) linkage.³⁷ The Zr–C2 distance is much larger ($\Delta d \text{ Zr--C1/C2} \approx 0.33 \text{ Å}$). The C1–C2 bond length is very short: it is in the typical undisturbed acetylene C≡C range. It seems that the [B]-acetylene-[Si] unit is very unsymmetrically coordinated to Zr in a polarized Zr–(η^2 -CC) coordination mode. The ligand is close to linear at C1, but markedly bent at C2. We note that the hydride at boron lies in the bent metallocene σ -ligand plane and is oriented toward zirconium. This lets us assume that the coordination of the formally anionic

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H[B]–C≡C–[Si] ligand to the formally cationic [Zr]–C≡C–[Si] unit is supported by [B]–H anion coordination to the metal.^{23b,c,38}

The ¹H NMR spectrum of complex **12a** shows an ABCD pattern of signals of the pair of η^5 -C₅H₄–CH₃ ligands at Zr and a single methyl singlet at δ 1.87 (in *d*₈-toluene at –50 °C), indicating overall C_s-symmetry in solution as expected. The B–H proton gives rise to a broad 1:1:1:1 quartet³⁹ at δ –0.65 with a corresponding ¹¹B NMR B–H doublet at δ –27 (¹J_{BH} = 60 Hz).⁴⁰ Unfortunately, only the ¹³C NMR signals of the acetylene carbon centers adjacent to silicon could be located. The acetylide ≡C–SiMe₃ ¹³C NMR resonance occurs at δ 137.1; the adjacent –SiMe₃ group features typical NMR signals of a trimethylsilyl substituent at an acetylene (¹H: δ 0.17, ²⁹Si: δ –25.4).⁴¹ The η^2 -coordinated 1-boryl-2-silyl-acetylene features a ≡C–SiMe₃ ¹³C NMR carbon signal at a markedly smaller δ value (δ 111.9). The adjacent –SiMe₃ group seems to experience the bending at that carbon center toward an olefin-like situation. It features a markedly shifted ²⁹Si NMR resonance of δ –9.7 (¹H NMR Si(CH₃)₃ singlet at δ 0.40).^{19,21c,41}

In the NMR experiment, warming the *d*₈-toluene solution to >0 °C results in a rapid disappearance of the typical NMR signals of the intermediate **12a**. This reactive intermediate is consumed with concomitant formation of complex **14a**, admixed with some final product **9a**. The relative amount of the latter is slowly increasing with time under these conditions. We assume that complex **12a** undergoes a thermally induced 1,1-hydroboration reaction at temperatures >0 °C to form the new intermediate **13a** (see Scheme 7). This is not directly observed. However, it apparently can be stabilized in an equilibrium situation by means of an intramolecular transfer of the remaining σ -C≡C–SiMe₃ ligand from zirconium to the adjacent strongly electrophilic boron center to form its borate isomer **14a**.

Complex **14a** features a typical metal- σ -alkenyl ¹³C NMR resonance of carbon atom C1 at δ 201.5.⁴² The adjacent C2–H carbon resonance was located at δ 112.3. The corresponding C2–H ¹H NMR resonance shows up at δ 8.21 as a broad signal due to the presence of the neighboring ³/₂ nuclear spin boron center. The ¹¹B NMR resonance of complex **14a** itself is at δ –25. The ¹⁹F NMR signals of the C₆F₅ substituents at boron [δ –133.5 (o), –158.0 (p), –163.8 (m)] show the small δ (m/p) separation that is typical of a four coordinate borate situation. We have observed two ²⁹Si NMR signals at δ –3.2 (Si1) and δ –10.0 (Si5) for the pair of –SiMe₃ substituents in **14a**. Again, we have only located the acetylide β -≡C–SiMe₃ ¹³C NMR signal (δ 105.8) of the remaining [B]–C≡C–SiMe₃ group. Complex **14a** is apparently in an endothermic equilibrium with the (not observed) intermediate **13a**. It seems that via this pathway it is eventually converted to the final product, the zirconacycloallenoid **9a**, at temperatures >0 °C under conditions of thermodynamic control.

DFT Calculations. In order to understand the electronic structures of the key compounds **9a** and **12a** in more detail, calculations based on Kohn–Sham density functional theory (DFT⁴³) have been carried out using the TURBOMOLE quantum chemical program system.⁴⁴ Starting from the X-ray structures we first have performed full, unconstrained structural optimizations. Large triple- ζ Gaussian AO basis sets (def2-TZVP⁴⁵), which yield almost converged results for the investigated properties, and the RI integral approximation⁴⁶ have been employed. As density functionals the almost nonempirical GGA (PBE⁴⁷) and meta-GGA (TPSS⁴⁸) constructions from the Perdew group have been used. In recent benchmark studies⁴⁹ it has once again been shown that these semilocal approaches are superior for transition-metal systems than common hybrid functionals like B3LYP (similar conclusions have been drawn for transition-metal thermodynamics, see e.g. refs. 50). Because the PBE and TPSS results are rather similar, we will discuss in the following only the latter. In all DFT treatments we use the now well-established correction for long-range London dispersion effects (DFT-D method⁵¹) that are more or less absent in all standard density functionals. Intramolecular dispersion effects are of particular importance for large molecules when bulky substituents (SiMe₃ and C₆F₅ in our case) spatially come close together

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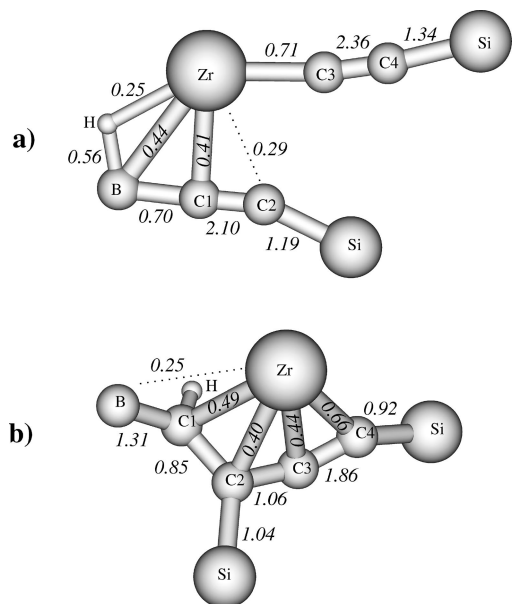


Figure 4. Computed (TPSS-D/def2-TZVP) structures (only Zr–BH–C1–C4–Si fragment shown) of *syn*-**9a** (b) and **12a** (a) with Wiberg bond orders. The bond orders of *anti*-**9a** (not shown) deviate only slightly (<0.1) from the values of *syn*-**9a**.

(for a recent example see e.g. ref 52). The final theoretical level discussed in the following is dubbed TPSS-D/def2-TZVP.

A comparison of theoretical and experimental key structural data for **9a** and **12a** is given in Tables 1 and 3. The agreement can in general be regarded as excellent. Most deviations for bond lengths are on the order of 0.01–0.03 Å, which approximately is the experimental uncertainty and also the estimated effect of crystal-packing that is not considered in the calculations. A similar accuracy of the computations is found for bending angles. Note that also the more sensitive torsion angles in the cycloalleneoid substructure of **9a** are described very accurately at our theoretical level [C1–C2⋯C4–Zr: 50.9(3)° (X-ray, found) vs 47.3 (DFT, calcd.)]. All in all this clearly demonstrates that the in part rather complicated electronic structures (in particular that of **9a**) are described correctly, which is a prerequisite for the following analysis of the bonding situations. This is performed with the help of Wiberg bond orders (WBO⁵³) that provide a good measure of the covalent bond order for two interacting atoms (see Figure 4). We also transformed the canonical KS-molecular orbitals to a localized basis (LMO) according to the algorithm of Pipek and Mezey.⁵⁴ The resulting LMO are typically localized only on one or two atomic centers for lone-pairs and conventional 2e–2c covalent bonds, respectively. Unusual bonding situations, multicenter bonding, and other delocalization effects are clearly reflected in the spatial extent of these LMO. This and their AO composition are used in the following for analysis. Note that the localization procedure does not introduce any theoretical “artifacts” because it leaves the KS-determinant (and all derivable properties) unchanged.

First, we want to discuss the intermediate **12a** that features an agostic H–Zr interaction (X-ray: $R(\text{Zr}–\text{H}) = 2.12$ Å, theor.: 2.16 Å). The computed Zr–H distance supports the finding from

the X-ray analysis which in this case is rather problematic because of the much larger nuclear charge of zirconium compared to hydrogen. The corresponding WBO of 0.25 is relatively large and accompanied by a decrease of the B–H covalency (WBO = 0.56). The LMO of the B–H bond (see Figure 5) is spatially close to the Zr atom and shows slight distortions from its usual symmetry. The ethynyl unit connected to boron shows a significant bending out of linearity (angle C1–C2–Si11, X-ray: 158°, theor.: 159°) which is caused by the interaction of the triple bond with zirconium as also indicated by the deformation of the corresponding π -LMO (see Figure 5). Although about 20° seems to be a large deformation at first sight, a closer look to the energetics reveals that such bending deformations can easily occur. According to a comparison of the energies of $\text{Me}_3\text{SiC}\equiv\text{CH}$ in a fully relaxed geometry and in the geometry of **12a**, this deformation “costs” only 1.4 kcal/mol. The rather large WBO for C1–Zr and C2–Zr (0.41 and 0.29, respectively) indicate favorable interactions that lead to a significant weakening of the C1–C2 bond (WBO = 2.10 compared to 2.61 in $\text{Me}_3\text{SiC}\equiv\text{CH}$).

Figure 6 shows a graphical comparison of computed and X-ray structures of the metallacyclic allenoid **9a**. Opposed to the analogous hafnium compound,¹⁹ in the solid-state the *syn*-form of **9a** is found that was also the basis for the structure optimization. As can be seen in the figure, the theoretical structure very nicely agrees with that from experiment, and the only significant (but otherwise unimportant) difference is the torsion of the outer SiMe_3 group. We also did an optimization of the *anti*-form (see entry e in Figure 6) that basically resembles the previously investigated hafnium complex. The computed energy difference between *syn*-**9a** and *anti*-**9a** amounts to 0.9 kcal/mol [*anti*-form more stable, which agrees well with the experiment (see Table 2)]. The electronic structure of *syn*-**9a** is similar to that of the previously discussed hafnium compound¹⁹ but with a clear tendency for stronger carbon–metal interactions (WBO of 0.40–0.66 compared to 0.18–0.52 for **5**) and a more pronounced butenyne than allene character (WBO for C2–C3 and C3–C4 are 1.06 and 1.86 compared to 1.51 and 1.81 for **5**). This conclusion is also supported by plots of selected LMO shown in Figure 7 that exhibit stronger butenyne character. However, even the structure of *syn*-**9a** seems to be unique as it contains a rather unusual π -LMO that spreads out over C2–C4 (entry d in Figure 7). As can be seen in Figure 4 all carbon–carbon WBO are much lower than expected for both a butenyne or an allene unit, which is compatible with the mentioned stronger interactions to the metal.

The computed energy difference between **12a** and *syn*-**9a** is 17.6 kcal/mol (**9a** more stable). This sizable value indicates a high energetic driving force for the formation of the stable metallacycle from its open precursors.

Conclusions

1,1-Carboboration reactions are often observed upon treatment of e.g. group 14 acetylide compounds with trialkyl- or triallylboranes.^{31–33} The reaction requires a 1,2-migration of the metal center along the acetylide unit. Silicon derivatives and especially their heavier tin and lead analogues are prone to undergo this type of rearrangement.^{31,33,55} 1,1-Carboboration reactions have been useful in the syntheses of a variety of

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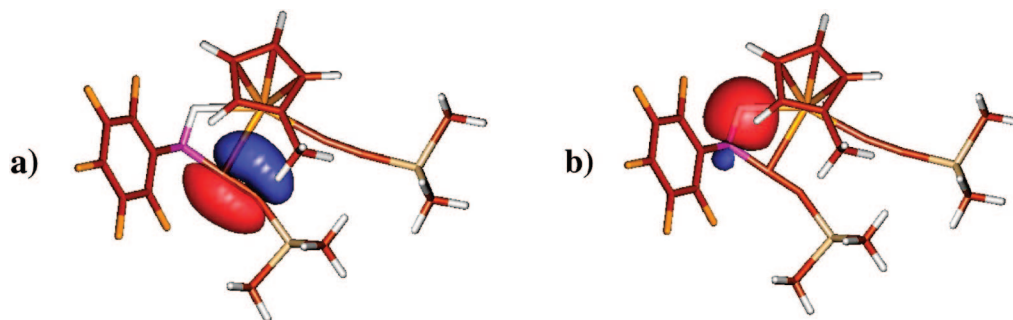


Figure 5. Isosurface (contour value of 0.05 au) plots of localized orbitals of **12a**. (a) In-plane π -LMO with bonding contributions to the Zr atom. (b) B–H σ -LMO that provides an agostic interaction with the Zr atom.

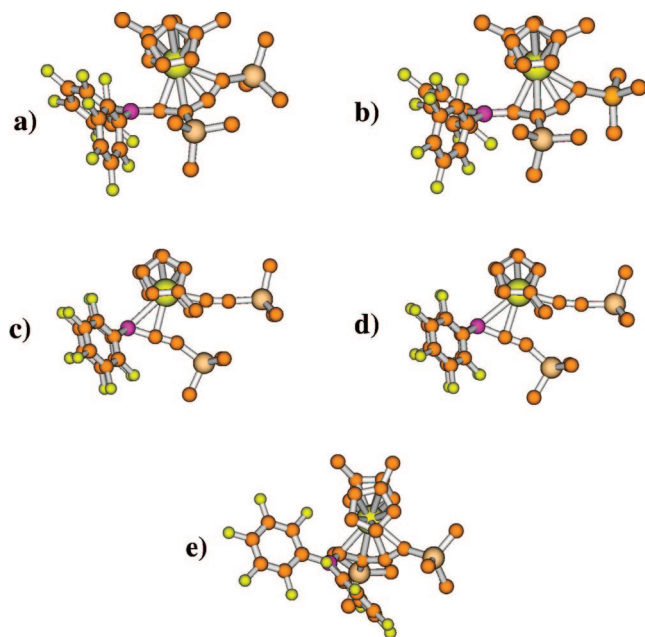


Figure 6. Comparison of TPSS-D/def2-TZVP computed (a and c) and experimental (b and d) structures of *syn*-**9a** (top) and **12a** (middle). In (e) the computed structure of *anti*-**9a** is shown.

metallaheterocyclic ring frameworks.⁵⁶ The reaction sequence observed here, which involves a related 1,1-hydroboration reaction, is probably of a general importance since it links a reaction type typically observed in main group chemistry^{31–33} with the chemistry of the transition-metal series.³⁴ The pathway of steps probably followed in our zirconium example involves acetylide abstraction, followed by 1,1-hydroboration with concomitant 1,2-metal migration along the acetylenic carbon framework, just as observed in the main-group metal examples. The similarity between the main-group and transition-metal lines of reactions in our case even goes so far, that a subsequent reversible secondary acetylide migration from Zr to B is observed, similar to reactions often found in the respective Sn or Pb chemistry.

The intermediate (**12a**) that we have observed experimentally and characterized by X-ray diffraction and DFT calculation is

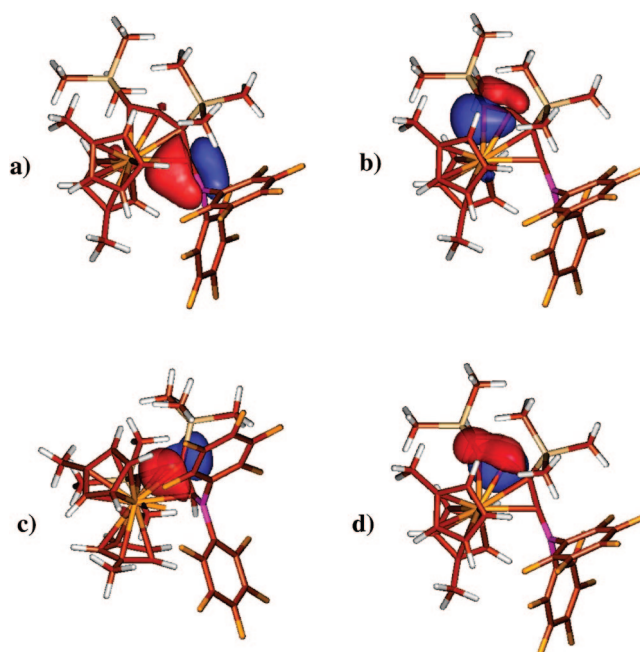
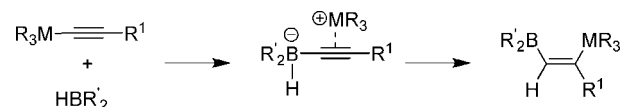


Figure 7. Isosurface (contour value of 0.05 au) plots of localized orbitals of *syn*-**9a**. (a) Three-center B–C–Zr LMO. (b) In-plane π -LMO with bonding contributions to the Zr atom. (c) Second (orthogonal) π -LMO of ethyne/allene fragment. (d) Three-center π -LMO of the allene fragment.

Scheme 8

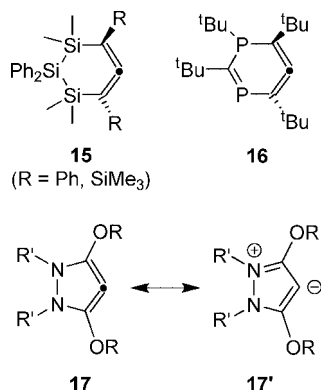


important for an understanding of the rearrangement pathway taken here. The extremely unsymmetrical coordination of the η^2 -acetylene unit to zirconium probably makes this structure a remote model of some transition-state characteristics of the rearrangement component of the incipient 1,1-hydroboration reaction. Here, the metal migration has proceeded quite far. So it seems that 1,1-hydroboration reactions might be considered as rather asynchronous, probably stepwise reactions with the 1,2-metal migration largely preceding the C–H bond-forming step (see Scheme 8).

Subsequent internal σ -ligand CC-coupling at the stage of the alleged intermediates **13**, which results from completing the 1,1-hydroboration reaction of **12**, directly leads to the observed final products **9**. Although these systems could be formulated as simple substituted Zr(II) (η^4 -1,3-butenyne)zirconocenes (**9'**),

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Scheme 9

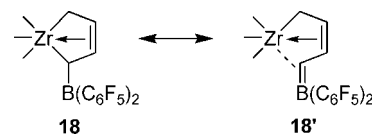


especially the results of our X-ray crystal structure analyses together with the DFT calculations show that this is not an ample description. The systems **9** exhibit a pronounced metallacyclic σ -complex character. It is probably warranted to term them as metallacycloalleneoid complexes. However, it should be emphasized that these new systems are quite different in some of their structural and spectroscopic features from real small or medium ring bent cyclic allenes.¹⁴ Although 1,2-cyclohexadiene and even 1,2-cyclopentadiene⁵⁶ were calculated to feature chiral structures with an even lower ring inversion enantiomerization barrier than the compounds **5** or **9**,^{14d,57} the extremely high reactivity of these very strained carbocycles has prevented any isolation or direct observation so far. The heterocyclic systems **15** and **16** are examples of isolable bent allenes^{58,59} (see Scheme 9). They show some similarities to our new complexes **5** and **9** but also reveal some marked differences (e.g., the ¹³C NMR shifts of the central =C= in these “organic” examples are found at substantially larger δ values as compared to those for **5** or **9**).⁶⁰ Derivatives of **17** have recently been claimed as the smallest stable cycloallenes,⁶¹ but this interpretation was criticized in favor of a description as rather aromatic pyrazolium-type zwitterions (**17'**).⁶²

One might argue that the very short B–C1 linkage and its high bond order in the complexes **9** might be an essential contribution to the remarkable persistence and stability of these compounds, similarly as it was found in the compounds **18** described by Bochmann et al.²⁵ (Scheme 10). Since Suzuki's related complex **6** is stable without this interaction,²⁰ the observed strong B–C interaction in **5** and **9** is probably a helpful but not an essential feature for obtaining such a metallacycloalleneoid structure.

It appears that the remarkable structure and stability of the complexes **5** and **9** (and their related examples) originate from

Scheme 10



making use of the unique bonding features at the group 4 bent metallocene unit to unsaturated ligands, that result in achieving a pronounced metallacyclic σ -complex character combined with an in-plane interaction between the internal carbons and the metal center across the five-membered ring. This leads to unique structures that in the case of the examples, **5**, **6**, and **9**, exhibit a pronounced metallacycloalleneoid character (or a metallacumulene or metallacycloalkyne character in the compounds **3** and **4**, respectively). However, one should probably not stress the analogy of all these unique organometallic systems with their highly strained distorted purely carbocyclic relatives too far, but concede that these five-membered metallacyclic systems represent a unique class of compounds of their own.

Experimental Section

General Procedures. Reactions with air- and moisture-sensitive compounds were carried out under an argon atmosphere using Schlenk-type glassware or a glovebox. Solvents were dried with the procedure reported by Grubbs⁶³ or, particularly deuterated solvents, were distilled from appropriate drying agents and stored under an argon atmosphere. HB(C₆F₅)₂,^{23e} [η^5 -C₅H₄(CH₃)₂]₂ZrCl₂⁶⁴ and [η^5 -C₅H₄(C(CH₃)₃)₂]₂ZrCl₂⁶⁵ were prepared according to procedures reported in the literature. The following instruments were used for physical characterization of the compounds: NMR: Bruker AC 200 P-FT (²⁹Si: 39.8 MHz {using DEPT or INEPT pulse sequence based on $J_{\text{Si,H}} = 7$ Hz}; ¹¹B: 64.2 MHz), Bruker ARX 300 (¹¹B: 96.3 MHz), Varian Inova 500 (¹H: 499.9 MHz; ¹⁹F: 470.3 MHz; ²⁹Si: 99.5 MHz {using INEPT pulse sequence based on $J_{\text{Si,H}} = 7$ Hz}), Varian Unity Plus 600 (¹H: 599.9 MHz; ¹³C: 150.8 MHz; ¹⁹F: 564.4). Most NMR assignments were supported by additional 2D experiments. The (unsystematical) X-ray crystal structure numbering scheme was also used for the listings of NMR data. The IR spectra were obtained with a Varian 3100 FT-IR (EX-CALIBUR Series) spectrometer. Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid instrument.

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,⁶⁶ absorption correction SORTAV⁶⁷ and Denzo,⁶⁸ structure solution SHELXS-97,⁶⁹ structure refinement SHELXL-97,⁷⁰ graphics XP (BrukerAXS, 2000).

[Bis(η^5 -methylcyclopentadienyl)-bis(trimethylsilyl)ethynyl]zirconium (8a**).** Diethyl ether (100 mL) was slowly added to a cooled (–40 °C) mixture of bis(η^5 -cyclopentadienylmethyl)zirconium dichloride (**7a**) (2.00 g, 6.24 mmol) and trimethylsilyl ethynyllithium (1.30 g, 12.48 mmol). The reaction mixture was allowed to warm to room temperature (ca. 1 h) and then stirred for further 12 h. Subsequently the suspension was filtered, and the filtrate was dried

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in vacuo to get the crude product as a gray-green powder. Crystallization from pentane at $-30\text{ }^{\circ}\text{C}$ gave complex **8a** as off-white crystals (1.22 g, 44%). ^1H NMR (C_6D_6 , 600 MHz, 298 K): δ 6.16 (m, 4H, Cp^{α}), 5.61 (m, 4H, Cp^{β}), 2.29 (s, 6H, CH_3), 0.22 (s, $^2J_{\text{SiH}} = 6.8\text{ Hz}$, 18H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 151 MHz, 298 K): δ 164.9 ($\text{ZrC}\equiv$), 127.4 ($\equiv\text{CSi}$), 125.9 (Cp^{β}), 114.1 (Cp^{α}), 107.5 (Cp^{β}), 16.2 (CH_3), 0.7 ($^1J_{\text{SiC}} = 55.4\text{ Hz}$, $\text{Si}(\text{CH}_3)_3$). $^{29}\text{Si}\{\text{INEPT}\}$ NMR (C_6D_6 , 40 MHz, 298 K): δ -24.1 . IR (KBr): 2035 ($\text{C}\equiv\text{C}$) cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{ZrSi}_2$: C, 59.53; H, 7.27. Found: C, 58.54; H, 7.01.

[Bis(η^5 -*tert*-butylcyclopentadienyl)-bis(trimethylsilylethynyl)]zirconium (8b**).** Analogous procedure as described for the preparation of **8a**. Bis(η^5 -*tert*-butylcyclopentadienyl)zirconium dichloride (**7a**) (500 mg, 1.236 mmol) was reacted with trimethylsilylethynyllithium (257 mg, 2.467 mmol) in diethyl ether (30 mL; $-30\text{ }^{\circ}\text{C}$) to yield **8b** as a gray-green powder. (0.385 g, 59%). ^1H NMR (C_6D_6 , 600 MHz, 298 K): δ 6.32 (m, 4H, Cp^{α}), 5.63 (m, 4H, Cp^{β}), 1.45 (s, 18H, $\text{C}(\text{CH}_3)_3$), 0.22 (s, $^2J_{\text{SiH}} = 6.8\text{ Hz}$, 18H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 151 MHz, 298 K): δ 165.7 ($\text{ZrC}\equiv$), 142.1 (Cp^{β}), 130.1 ($\equiv\text{CSi}$), 111.5 (Cp^{α}), 106.8 (Cp^{β}), 33.0, 31.9 ($\text{C}(\text{CH}_3)_3$), 0.3 ($^1J_{\text{SiC}} = 55.4\text{ Hz}$, $\text{Si}(\text{CH}_3)_3$). $^{29}\text{Si}\{\text{INEPT}\}$ NMR (C_6D_6 , 100 MHz, 298 K): δ -24.3 . IR (KBr): 2029 ($\text{C}\equiv\text{C}$) cm^{-1} .

Reaction of **8a with Bis(pentafluorophenyl)borane; Formation of Complex **9a**.** Toluene (30 mL) was added to a mixture of **8a** (150 mg, 0.338 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.338 mmol). The resulting red solution was stirred under argon at $60\text{ }^{\circ}\text{C}$ for 5 h. Subsequently the volatiles were removed in vacuo to obtain the crude product as an orange-red solid. Crystallization from pentane solution (30 mL) at $-30\text{ }^{\circ}\text{C}$ yielded **9a** as orange-red crystals (70 mg, 26%), suitable for X-ray diffraction. Two isomers were detected by NMR experiments: ratio major/minor $\approx 3:1$ (213 K). Anal. Calcd for $\text{C}_{34}\text{H}_{33}\text{BF}_{10}\text{Si}_2\text{Zr}$: C, 51.70; H, 4.21. Found: C, 50.78; H, 4.19. 353 K: ^1H NMR (C_7D_8 , 500 MHz, 353 K): δ 5.50, 5.34, 5.27, 4.45 (each m, each 1H, Cp^{α}), 5.43, 5.39, 5.22, 4.82 (each m, each 1H, Cp^{β}), 2.57 (s, 1H, 1-H), 1.85, 1.59 (each s, each 3H, CH_3), 0.10, 0.04 (each s, each 9H, $\text{Si}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 470 MHz, 353 K): δ -126.2 (2F, o), -155.9 (1F, p), -163.1 (2F, m) (C_6F_5), -129.5 (2F, o), -155.3 (1F, p), -162.9 (2F, m) (C_6F_5) [C_6F_5 : $\text{C}_6\text{F}_5 = 1:1$]. 213 K: **Major isomer.** ^1H NMR (C_7D_8 , 600 MHz, 213 K): δ 5.51(β), 5.40(β), 5.17(α), 4.41(α) (each m, each 1H, Cp^{α}), 5.37(β), 5.07(α), 4.86(α), 4.55(β) (each m, each 1H, Cp^{β}), 2.08 (s, 1H, 1-H), 1.76 (s, 3H, CH_3^{A}), 1.34 (s, 3H, CH_3^{B}), 0.08 (s, 9H, 4-Si(CH_3) $_3$), -0.05 (s, 9H, 2-Si(CH_3) $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 151 MHz, 213 K): δ 138.8 (C3), 119.0, 117.2 ($\text{C}_6\text{F}_5^{\text{I}}$), 117.9 (Cp^{IA}), 116.9 (C4), 115.6 (Cp^{IB}), 112.7 ($\text{Cp}^{\alpha\text{B}}$), 111.6 ($\text{Cp}^{\alpha\text{B}}$), 109.4 ($\text{Cp}^{\alpha\text{A}}$), 106.7 ($\text{Cp}^{\alpha\text{A}}$), 104.1 ($\text{Cp}^{\beta\text{B}}$), 103.6 ($\text{Cp}^{\beta\text{B}}$, $\text{Cp}^{\beta\text{A}}$), 100.0 ($\text{Cp}^{\beta\text{A}}$), 95.0 (C2), 88.3 (C1), 16.2 (CH_3^{A}), 14.1 (CH_3^{B}), 1.4 (4-Si(CH_3) $_3$), 0.9 (2-Si(CH_3) $_3$), n.o. (C_6F_5). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 470 MHz, 223 K): δ -126.4 (o), -127.4 (o), -155.2 (p), -161.7 (m), -162.0 (m) (each 1F, C_6F_5), -130.0 (br, 2F, o), -154.0 (1F, p), -161.1 (very br, without integral value) (C_6F_5). $^{29}\text{Si}\{\text{DEPT}\}$ NMR (C_7D_8 , 100 MHz, 223 K): -2.4 (2-Si), -6.5 (4-Si). **Minor isomer.** ^1H NMR (C_7D_8 , 600 MHz, 213 K): δ 6.32(α), 5.62(α), 5.31(β), 3.69(β) (each m, each 1H, Cp^{α}), 5.53(β), 5.23(α), 4.92(α), 4.92(β) (each m, each 1H, Cp^{β}), 3.88 (s, 1H, 1-H), 1.87 (s, 3H, CH_3^{A}), 1.78 (s, 3H, CH_3^{B}), 0.31 (s, 9H, 2-Si(CH_3) $_3$), -0.02 (s, 9H, 4-Si(CH_3) $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 151 MHz, 213 K): δ 141.4 (C3), 129.7 (C4), 121.6 (Cp^{IA}), 117.6 (Cp^{IB}), 114.7 ($\text{C}_6\text{F}_5^{\text{I}}$), 114.1 ($\text{Cp}^{\alpha\text{A}}$), 108.5 ($\text{Cp}^{\alpha\text{B}}$), 107.3 ($\text{Cp}^{\alpha\text{B}}$), 105.9 ($\text{Cp}^{\beta\text{B}}$), 104.1 ($\text{Cp}^{\beta\text{A}}$), 103.9 ($\text{Cp}^{\alpha\text{A}}$), 102.6 ($\text{Cp}^{\beta\text{A}}$), 101.9 ($\text{Cp}^{\beta\text{B}}$), 93.2 (C2), 73.0 (C1), 15.9 (CH_3^{B}), 15.4 (CH_3^{A}), 1.0 (4-Si(CH_3) $_3$), -0.3 (2-Si(CH_3) $_3$), n.o. (C_6F_5) [the ^{13}C chemical shifts were extracted from 2D $^1\text{H}/^{13}\text{C}$ correlation experiments; see Supporting Information]. $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 470 MHz, 223 K): δ -123.2 (br, 2F, o), -153.4 (1F, p), -162.7 (2F, m) (C_6F_5), -127.7 (br, 2F, o), -154.0 (1F, p), -162.4 (2F, m) (C_6F_5). $^{29}\text{Si}\{\text{DEPT}\}$ NMR (C_7D_8 , 100 MHz, 223 K): 2.3 (2-Si), -7.4 (4-Si).

X-ray Crystal Structure Analysis of **9a.** Formula $\text{C}_{34}\text{H}_{33}\text{BF}_{10}\text{Si}_2\text{Zr}$, $M = 789.81$, yellow-orange crystal $0.25\text{ mm} \times 0.15\text{ mm} \times$

0.07 mm , $a = 40.6692(5)$, $b = 9.6463(2)$, $c = 21.1243(4)\text{ \AA}$, $\beta = 120.872(1)^{\circ}$, $V = 7113.0(2)\text{ \AA}^3$, $\rho_{\text{calc}} = 1.475\text{ g cm}^{-3}$, $\mu = 0.452\text{ mm}^{-1}$, empirical absorption correction ($0.895 \leq T \leq 0.969$), $Z = 8$, monoclinic, space group C2/c (No. 15), $\lambda = 0.71073\text{ \AA}$, $T = 223(2)\text{ K}$, ω and φ scans, 31271 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60\text{ \AA}^{-1}$, 6273 independent ($R_{\text{int}} = 0.120$) and 3475 observed reflections [$I \geq 2\sigma(I)$], 441 refined parameters, $R = 0.052$, $wR^2 = 0.134$, max (min.) residual electron density 0.59 (-0.69) e \AA^{-3} , poor crystals with limited diffracting power, hydrogen atoms calculated and refined as riding atoms.

Reaction of **8b with Bis(pentafluorophenyl)borane; Formation of Complex **9b**.** Analogous procedure as described for the preparation of **9a**. The reaction of **8b** (229 mg, 0.437 mmol) and bis(pentafluorophenyl)borane (150 mg, 0.437 mmol) in toluene (30 mL) at $60\text{ }^{\circ}\text{C}$ for 2 h and subsequent crystallization ($-30\text{ }^{\circ}\text{C}$, pentane) of the crude product yielded **9b** as yellow crystals (215 mg, 57%), suitable for X-ray diffraction. Two isomers were detected by NMR experiments: ratio major/minor $\approx 3:1$ (223 K). Anal. Calcd for $\text{C}_{40}\text{H}_{45}\text{BF}_{10}\text{Si}_2\text{Zr}$: C, 54.97; H, 5.19. Found: C, 55.04; H, 5.14. 353 K: ^1H NMR (C_7D_8 , 500 MHz, 353 K): δ 6.06, 6.03, 5.46 (br), 3.94 (each m, each 1H, Cp^{α}), 5.78, 5.58, 5.54, 4.78 (each m, each 1H, Cp^{β}), 2.65 (s, 1H, 1-H), 1.07, 1.55 (each s, each 9H, $\text{C}(\text{CH}_3)_3$), 0.16, 0.07 (each s, each 9H, $\text{Si}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 470 MHz, 353 K): δ -126.9 (2F, o), -156.1 (1F, p), -163.1 (2F, m) (C_6F_5), -128.7 (2F, o), -154.3 (1F, p), -163.0 (2F, m) (C_6F_5) [C_6F_5 : $\text{C}_6\text{F}_5 = 1:1$]. 223 K: **Major isomer.** ^1H NMR (C_7D_8 , 500 MHz, 223 K): δ 6.08, 5.75, 5.00, 3.84 (each m, each 1H, Cp^{α}), 5.74, 5.65, 5.58, 4.61 (each m, each 1H, Cp^{β}), 2.03 (s, 1H, 1-H), 1.04 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{A}}$), 1.02 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{B}}$), 0.14 (s, 9H, 4-Si(CH_3) $_3$), -0.00 (s, 9H, 2-Si(CH_3) $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 126 MHz, 223 K): δ 140.9 (C3), 136.7 (Cp^{IA}), 136.1 (Cp^{IB}), 119.4 (C4), 117.9 (br, $\text{C}_6\text{F}_5^{\text{I}}$), 109.7 (Cp^{α}), 106.8 (Cp^{β}), 105.9 (Cp^{β}), 105.4 (Cp^{α}), 105.4 (Cp^{α}), 103.2 (Cp^{α}), 101.1 (Cp^{β}), 99.2 (C2), 99.0 (Cp^{β}), 86.9 (C1), 31.9^a, 31.7 ($\text{C}(\text{CH}_3)_3^{\text{B}}$), 33.0^a, 30.8 ($\text{C}(\text{CH}_3)_3^{\text{A}}$), 1.8 (4-Si(CH_3) $_3$), 0.5 (2-Si(CH_3) $_3$), n.o. (C_6F_5). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 470 MHz, 223 K): δ -128.1 (o), -129.8 (o), -152.4 (p), -161.0 (m), -162.9 (m) (each 1F, C_6F_5), -126.5 (o), -126.9 (o), -155.1 (p), -161.1 (m), -162.2 (m) (each 1F, C_6F_5). $^{29}\text{Si}\{\text{DEPT}\}$ NMR (C_7D_8 , 100 MHz, 223 K): -2.8 (2-Si), -4.6 (4-Si). **Minor isomer.** ^1H NMR (C_7D_8 , 500 MHz, 223 K): δ 6.42, 5.99, 5.92, 3.24 (each m, each 1H, Cp^{α}), 5.78, 5.75, 5.45, 5.00 (each m, each 1H, Cp^{β}), 4.13 (s, 1H, 1-H), 1.09 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{A}}$), 0.98 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{B}}$), 0.33 (s, 9H, 2-Si(CH_3) $_3$), 0.05 (s, 9H, 4-Si(CH_3) $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 126 MHz, 223 K): δ 145.0 (C3), 139.5 (Cp^{IA}), 136.1 (Cp^{IB}), 130.6 (C4), 116.9, 115.3 ($\text{C}_6\text{F}_5^{\text{I}}$), 111.8 (Cp^{α}), 109.5 (Cp^{β}), 105.4 (Cp^{α}), 104.7 (Cp^{β}), 102.9 (Cp^{α}), 101.7 (Cp^{β}), 100.6 (Cp^{β}), 99.0 (Cp^{α}), 94.4 (C2), 72.0 (C1), 33.6^a, 30.7 ($\text{C}(\text{CH}_3)_3^{\text{A}}$), 32.1, 31.8^a ($\text{C}(\text{CH}_3)_3^{\text{B}}$), 1.3 (4-Si(CH_3) $_3$), -0.4 (2-Si(CH_3) $_3$), n.o. (C_6F_5). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_7D_8 , 470 MHz, 223 K): δ -124.0 (br, 2F, o), -153.6 (1F, p), -162.9 (2F, m) (C_6F_5), n.o. (o), -153.9 (1F, p), -162.3 (2F, m) (C_6F_5). $^{29}\text{Si}\{\text{DEPT}\}$ NMR (C_7D_8 , 100 MHz, 223 K): 2.2 (2-Si), -5.8 (4-Si).

X-ray Crystal Structure Analysis of **9b.** Formula $\text{C}_{40}\text{H}_{45}\text{BF}_{10}\text{Si}_2\text{Zr} \times \text{C}_5\text{H}_{12}$, $M = 946.12$, yellow crystal $0.35\text{ mm} \times 0.30\text{ mm} \times 0.25\text{ mm}$, $a = 12.0655(1)\text{ \AA}$, $b = 14.5258(2)\text{ \AA}$, $c = 15.7909(3)\text{ \AA}$, $\alpha = 111.166(1)^{\circ}$, $\beta = 94.238(1)^{\circ}$, $\gamma = 111.542(1)^{\circ}$, $V = 2331.55(6)\text{ \AA}^3$, $\rho_{\text{calc}} = 1.348\text{ g cm}^{-3}$, $\mu = 0.357\text{ mm}^{-1}$, empirical absorption correction ($0.885 \leq T \leq 0.916$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073\text{ \AA}$, $T = 223(2)\text{ K}$, ω and φ scans, 22053 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67\text{ \AA}^{-1}$, 11248 independent ($R_{\text{int}} = 0.046$) and 8750 observed reflections [$I \geq 2\sigma(I)$], 546 refined parameters, $R = 0.045$, $wR^2 = 0.116$, max (min.) residual electron density 0.49 (-0.68) e \AA^{-3} , hydrogen atoms calculated and refined as riding atoms.

Preparation of Compound **12a.** At $-30\text{ }^{\circ}\text{C}$ toluene (10 mL) was slowly added to a mixture of compound **8a** (200 mg, 0.450 mmol) and bis(pentafluorophenyl)borane (156 mg, 0.450 mmol). The suspension was stirred at $-30\text{ }^{\circ}\text{C}$ for 30 min. The volume of the solution was reduced to 5 mL; meanwhile, the solution was

briefly allowed to warm to room temperature. After removing the magnetic stirrer and cooling the reaction mixture again to $-30\text{ }^{\circ}\text{C}$, the solution was covered with pentane (5 mL). Subsequently the reaction mixture was stored at $-30\text{ }^{\circ}\text{C}$ for 12 h, to obtain pure **12a** as crystals suitable for X-ray diffraction.

X-ray Crystal Structure Analysis of 12a. Formula $\text{C}_{34}\text{H}_{33}\text{BF}_{10}\text{Si}_2\text{Zr}$, $M = 789.81$, yellow crystal $0.30\text{ mm} \times 0.20\text{ mm} \times 0.06\text{ mm}$, $a = 10.0841(3)\text{ \AA}$, $b = 15.8190(5)\text{ \AA}$, $c = 11.5732(4)\text{ \AA}$, $\beta = 104.946(1)^{\circ}$, $V = 1783.7(1)\text{ \AA}^3$, $\rho_{\text{calc}} = 1.471\text{ g cm}^{-3}$, $\mu = 0.451\text{ mm}^{-1}$, empirical absorption correction ($0.877 \leq T \leq 0.973$), $Z = 2$, monoclinic, space group $P2_1/m$ (No. 11), $\lambda = 0.71073\text{ \AA}$, $T = 223(2)\text{ K}$, ω and φ scans, 12284 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66\text{ \AA}^{-1}$, 4394 independent ($R_{\text{int}} = 0.069$) and 3035 observed reflections [$I \geq 2\sigma(I)$], 237 refined parameters, $R = 0.056$, $wR^2 = 0.136$, max (min.) residual electron density 1.48 (-0.52) e \AA^{-3} , hydrogen atom at B1 from difmap, others calculated and refined as riding atoms (at C13 and C43 with AFIX 33), C42 refined with thermal restraints (ISOR).

NMR Monitored Reaction of 8a and Bis(pentafluorophenyl)borane. Characterization of 10a, 12a, and 14a. A mixture of **8a** (30 mg, 0.068 mmol) and bis(pentafluorophenyl)borane (23.4 mg, 0.068 mmol) was added in a NMR tube, which was cooled to $-78\text{ }^{\circ}\text{C}$. Then deuterated toluene (0.8 mL) was injected very carefully, and the NMR tube was sealed under vacuum, still at $-78\text{ }^{\circ}\text{C}$. Subsequently, the NMR tube was removed from the cooling bath, agitated at room temperature only for a few seconds, and cooled to $-78\text{ }^{\circ}\text{C}$ again. For NMR measurements the temperature was raised in successive steps, starting at $-60\text{ }^{\circ}\text{C}$. **Intermediate 10a.** ^1H NMR (C_7D_8 , 500 MHz, 243 K): δ 5.21 (m, 4H, Cp^{β}), 5.17 (m, 4H, Cp^{α}), 0.88 (s, 6H, CH_3), 0.41 (s, $^2J_{\text{Si,H}} = 6.8\text{ Hz}$, 18H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 126 MHz, 243 K): δ 184.5 ($=\text{CSi}$), 137.4 ($=\text{C}=\text{C}$), 112.0 (Cp^i), 106.7 (Cp^{α}), 99.4 (Cp^{β}), 13.3 (CH_3), 0.8 ($^1J_{\text{Si,C}} = 53.6\text{ Hz}$, $\text{Si}(\text{CH}_3)_3$). ^{19}F NMR (C_7D_8 , 470 MHz, 243 K): δ -131.3 (2F, o), -162.5 (1F, p), -163.8 (2F, m) (each br, C_6F_5). $^{29}\text{Si}\{\text{INEPT}\}$ NMR (C_7D_8 , 100 MHz, 243 K): δ -7.5 . **Compound 12a.** After the characterization of compound **10a** by NMR experiments, the temperature of the spectrometer was warmed stepwise to $0\text{ }^{\circ}\text{C}$. Then the NMR tube was ejected, shaken at room temperature (only for seconds) to dissolve the precipitate, and immediately injected into the NMR spectrometer again, which was cooled to $-40\text{ }^{\circ}\text{C}$. The obtained reaction mixture contained ca. 70% of compound **12a**. ^1H NMR (C_7D_8 , 500 MHz, 233 K): δ 5.62 (m, 2H, Cp^{α}), 5.49 (m, 2H, Cp^{β}), 5.35 (m, 2H, Cp^{β}), 5.19 (m, 2H, Cp^{α}),

1.87 (s, 6H, CH_3), 0.40 (s, 9H, $\text{Si}(\text{CH}_3)_3^{\text{A}}$), 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3^{\text{B}}$), -0.65 (br 1:1:1:1 q [partially relaxed], $^1J_{\text{B,H}} \approx 65\text{ Hz}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 126 MHz, 233 K): δ 137.1, 111.9 ($=\text{CSi}$), 124.6 (Cp^i), 119.2 (Cp^{α}), 112.5 (Cp^{α}), 107.1 (Cp^{β}), 106.8 (Cp^{β}), 15.8 (CH_3), 0.4 ($\text{Si}(\text{CH}_3)_3^{\text{B}}$), -0.1 ($\text{Si}(\text{CH}_3)_3^{\text{A}}$), n.o. ($2 \times \text{C}=\text{C}$, C_6F_5). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_7D_8 , 160 MHz, 233 K): δ -27.4 ($\nu_{1/2} \approx 60\text{ Hz}$). ^{11}B NMR (C_7D_8 , 160 MHz, 233 K): δ -27.4 (d, $^1J_{\text{B,H}} \approx 60\text{ Hz}$). ^{19}F NMR (C_7D_8 , 470 MHz, 233 K): δ -131.2 (br, 2F, o), -156.6 (1F, p), -162.4 (br, 2F, m) (C_6F_5). $^{29}\text{Si}\{\text{INEPT}\}$ NMR (C_7D_8 , 100 MHz, 233 K): δ -9.7 (Si^{A}), -25.4 (Si^{B}). **Intermediate 14a.** After the characterization of compound **12a** by NMR experiments, the temperature of the spectrometer was warmed stepwise to $25\text{ }^{\circ}\text{C}$, until the reaction mixture contained ca. 30% of the intermediate **14a** and ca. 65% of the product **9b**. Subsequently, the NMR experiments were carried out at $-50\text{ }^{\circ}\text{C}$. ^1H NMR (C_7D_8 , 500 MHz, 223 K): δ 8.21 (br m, 1H, 2-H), 5.49 (m, 2H, Cp^{α}), 5.37 (m, 2H, Cp^{α}), 5.32 (m, 2H, Cp^{β}), 5.10 (m, 2H, Cp^{β}), 1.27 (s, 6H, CH_3), 0.25 (s, 9H, 1-Si(CH_3)₃), 0.14 (s, 9H, 5-Si(CH_3)₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 126 MHz, 233K): δ 201.5 (C1), 122.5 (Cp^i), 112.9 (Cp^{α}), 112.3 (br, C_2)^a, 110.6 (Cp^{α}), 108.1 (Cp^{β}), 106.8 (Cp^{β}), 105.8 (br, C5), 14.3 (CH_3), 0.7 (1-Si(CH_3)₃), -0.1 (5-Si(CH_3)₃), n.o. (C4, C_6F_5) [^a assigned by ghsqc experiment; see Supporting Information]. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_7D_8 , 160 MHz, 223 K): δ -25.3 ($\nu_{1/2} \approx 40\text{ Hz}$). ^{11}B NMR (C_7D_8 , 160 MHz, 223 K): δ -25.3 (s, $\nu_{1/2} \approx 40\text{ Hz}$). ^{19}F NMR (C_7D_8 , 470 MHz, 233 K): δ -133.5 (2F, o), -158.0 (1F, p), -163.8 (2F, m) (each m, C_6F_5). $^{29}\text{Si}\{\text{INEPT}\}$ NMR (C_7D_8 , 100 MHz, 223 K): δ -3.2 (1-Si), -10.0 (5-Si).

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Supporting Information Available: CIF files giving details of the X-ray crystal structure analyses (**9a**, **9b**, and **12a**) and text giving additional information about spectroscopic data and details of the X-ray crystal structure determinations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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