

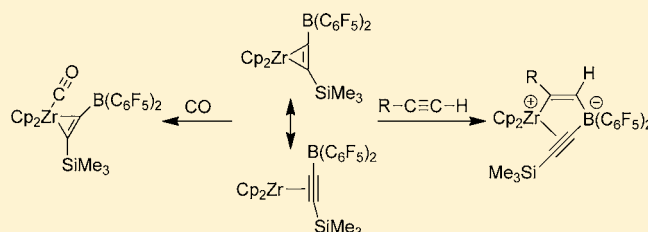
Remarkable Behavior of a Bifunctional Alkynylborane Zirconocene Complex toward Donor Ligands and Acetylenes

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Supporting Information

ABSTRACT: Treatment of a [(trimethylsilylethynyl)-alkenyl]ZrCp₂ complex with Piers' borane [HB(C₆F₅)₂] resulted in the clean formation of the Zr/B complex [η^2 -(C₆F₅)₂B-C≡C-SiMe₃]ZrCp₂ (**3**). This compound shows some unique reaction patterns. With a variety of typical donor ligands (carbon monoxide, an isonitrile, a nitrile, THF-*d*₈) it forms the respective adducts **5** (four examples characterized by X-ray diffraction). Toward terminal alkynes (RC≡CH) compound **3** behaves as a Zr(II) metal Lewis base/boron Lewis acid frustrated Lewis pair (FLP) and undergoes typical regioselective 1,2-Zr/B addition reactions to yield the metallaheterocyclic products **7** (four examples characterized by X-ray diffraction). Compound **3** also undergoes characteristic 1,4-Zr/B FLP addition to a silyl-substituted conjugated enyne (to give **9**) and also to 1,4-bis(trimethylsilyl)butadiyne to yield a metallacyclic butatriene derivative **10** (both **9** and **10** were characterized by X-ray diffraction). Eventually, compound **3** reacted with mes₂P-C≡CH to give the metallacycloallene product **15**, which was probably formed by means of 1,2-Zr/B FLP addition followed by alkynyl shift from boron to zirconium and reductive coupling. Treatment of **3** with tolane gave the closely related zirconacycloallene complex **16** by carbon carbon coupling. Both the products **15** and **16** were characterized by X-ray diffraction.



INTRODUCTION

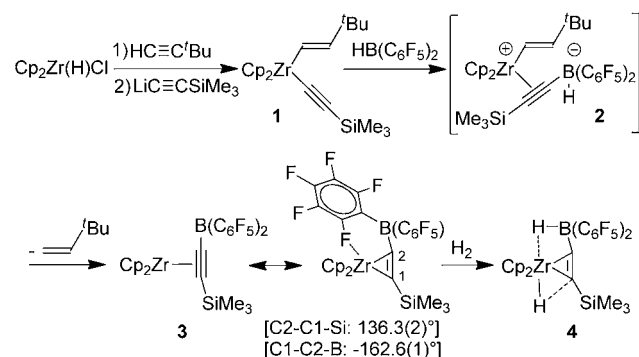
Alkyl-bridged zirconium borate complexes are of great importance in catalysis. Many examples of homogeneous single site metallocene catalysts show this feature at their ion-paired resting stage.¹ A variety of different groups bridging between, e.g., zirconium and boron have been reported² and a number of hydride bridged systems have been described.³ All these systems have in common that they contain tetracoordinated boron centers. We recently described a unique compound (**3** in Scheme 1) that has an alkynyl moiety bridging a single Cp₂Zr unit with a tricoordinate boron.^{4,5} This remarkable bonding between a reactive transition metal center and an active Lewis

acid is a situation staged for unusual chemical reactivity. In our initial report, we have described the specific reaction of **3** with dihydrogen.⁴

We prepared the (alkynylborane)zirconocene complex **3** by the following synthetic route: Hydrozirconation⁶ of *t*-butylacetylene followed by treatment with LiC≡CSiMe₃ gave the unsymmetrically functionalized (σ -alkenyl)(σ -alkynyl)-zirconocene complex **1**. Its treatment with Piers' borane [HB(C₆F₅)₂]⁷ eventually resulted in the formation of the (borylalkyne)ZrCp₂ complex **3**. This reaction probably starts by σ -alkynyl abstraction by the Lewis acidic borane followed by hydride transfer, reductive coupling and olefin extrusion (see Scheme 1).

Compound **3** was characterized by X-ray diffraction. It features a metallacyclopropene like structure as it is often observed for (alkyne)zirconocenes, but it features a very unusual arrangement of the boryl group at the η^2 -alkyne ligand. Usually, alkyne-C-substituent vectors are markedly bent away from the group 4 metal⁸ as we see it from the geometry of the attachment of the SiMe₃ substituent at C1, but in complex **3**, the C2–B vector is not showing this typical behavior but is actually slightly bent toward the zirconium center (see Scheme 1). One might argue that this is caused by the observed boryl-F...Zr contact,^{2c,9} but our further work will show (see below)

Scheme 1



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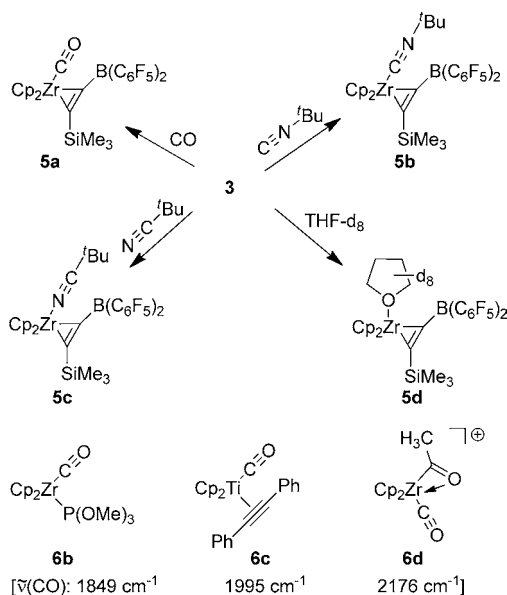
that this strange bonding geometry of a close to linear C1–C2–B arrangement is an intrinsic structural feature of the $[(C_6F_5)_2B\text{-alkyne}]$ coordination.

Compound **3** reacted with dihydrogen under mild conditions to give **4**.⁴ We have now reacted compound **3** with a variety of typical donor ligands such as CO, isonitrile or THF-*d*₈ and with a variety of alkynes (including conjugated enynes and diynes) and found a surprisingly different reaction behavior of **3** with these two groups of reagents. With the simple donors, we see “conventional” adduct formation at the zirconium atom, but the alkynes undergo a very unusual 1,2-addition reaction of the Zr/B pair of functionalities. This is reminiscent of frustrated Lewis pair (FLP) behavior,^{10,11} only that here the zirconium center takes on the role of the Lewis base.¹² In this article, we will illustrate this remarkable behavior of **3** with a series of examples.

RESULTS AND DISCUSSION

Conventional Coordination Behavior of the (Borylalkyne)–Zirconocene Complex toward Single Site Donors. The (borylalkyne)ZrCp₂ complex **3** reacts rapidly with carbon monoxide (1.5 bar) at room temperature. After a reaction time of 4 min, the mixture was worked up and we isolated the corresponding carbonyl complex **5a** as a yellow solid in 87% yield. Compound **5a** was crystallized from pentane at –35 °C. The resulting single crystals were used for the X-ray crystal structure analysis of complex **5a** (see Scheme 2 and Figure 1).

Scheme 2



The X-ray crystal structure analysis has revealed that the CO ligand has been bonded to zirconium in the major plane of the bent metallocene wedge, which is bisecting the Cp–Zr–Cp angle.¹³ In that plane it is found bonded at the lateral coordination site facing the boryl group of the acetylene ligand. The metal carbonyl unit of complex **5a** features a short C3A–O1A bond (see Table 1). The Zr1A–C3A linkage is by ca. 0.05–0.08 Å longer than that found for the Zr–C≡O moieties in $Cp_2Zr(CO)_2$ (**6a**)^{14b} or $Cp_2Zr[P(OCH_3)_3](CO)$ (**6b**).^{14a} The (alkyne)zirconocene unit features the typical intermediate situation between the Zr(η^2 -alkyne) and the metallacyclopro-

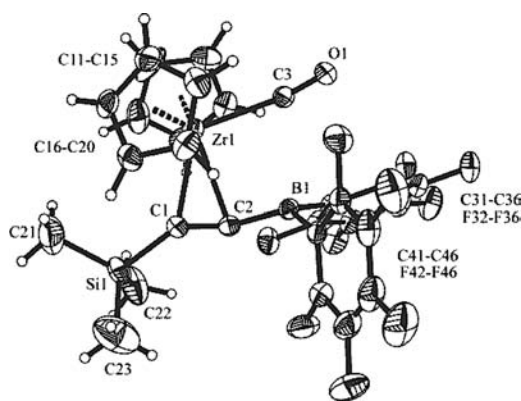


Figure 1. A view of the molecular structure of the carbonyl zirconocene complex **5a** (thermal ellipsoids are shown with 30% probability).

pane structures. The C1–Si1 vector is markedly bent away from the Zr-atom of complex **5a**, whereas the C1A–C2A–B1A unit is close to linear; actually, the C2A–B1A vector is bent slightly toward the Zr-center. We note that the C2A–B1A bond is rather short (i.e., by 0.112–0.127 Å shorter than the adjacent B1–C_{Aryl} bonds). The boron center in complex **5a** is planar tricoordinate. The $B(C_6F_5)_2$ unit has been found in a conformational orientation that brings the $-C_6F_5$ substituents to chemically (but not strictly structurally) equivalent positions above and below the σ -ligand plane (see Figure 1).

Complex **5a** shows two strong IR bands at $\tilde{\nu} = 2011$ and 1865 cm^{-1} (the spectrum is depicted in the Supporting Information). Our DFT analysis¹⁵ has shown that both are combination bands ($\tilde{\nu}_{calc} = 1997$ and 1893 cm^{-1}) involving the carbonyl ligand and the adjacent borylalkyne moiety (for details see the Supporting Information), but that the band at higher wavenumbers is close to a metal–carbonyl stretching band. Its value is close to what had been reported for the IR $\tilde{\nu}(CO)$ band (1995 cm^{-1}) of the titanocene(CO)(tolane) complex **6c** by Floriani et al.¹⁴ The IR spectrum indicates that the zirconium carbonyl complex **5a** [$\tilde{\nu}(CO)_{exptl.} = 2011$ cm^{-1}] seems to attain a somewhat intermediate position between a pure zirconium(II) carbonyl (e.g., **6b**: $\tilde{\nu}(CO) = 1849$ cm^{-1} , see Scheme 2) and a typical zirconium(IV) carbonyl complex (e.g., the “nonclassical” Zr–CO complex **6d**, $\tilde{\nu}(CO) = 2176$ cm^{-1}).^{16–18} In solution we have observed the NMR signals of a single isomer of **5a** which is probably equivalent to the structure found in the crystal. We have measured the ¹³C NMR carbonyl signal at δ 239.6 and the acetylene $\equiv CSiMe_3$ resonance at δ 126.5 ($^1J_{SiC} = 70.6$ Hz) and the $\equiv CB$ signal at 138.8 (broad). The ¹H/¹³C NMR Cp resonances were found at δ 4.81/103.6. Compound **5a** features a ²⁹Si NMR resonance at δ –3.5, a ¹¹B NMR signal at δ 6.9 and single set of *o*, *p*, *m*-¹⁹F NMR resonances for the pair of symmetry equivalent C_6F_5 groups at the boron atom.

Complex **3** reacted similarly with *t*-butylisocyanide and with pivalonitrile to give the complexes **5b** (75% isolated) and **5c** (90%), respectively. The complexes show the typical NMR spectra (see Table 2). Both complexes were characterized by X-ray diffraction (see Figure 2). Typical bonding parameters are listed in Table 1. In each case, we have found the incoming linear donor ligand become attached at the lateral zirconocene coordination site facing the C–B vector of the in-plane coordinated borylalkyne ligand. In both cases, the C2–B1 bond is markedly shortened (see Table 1) and a rotational orientation

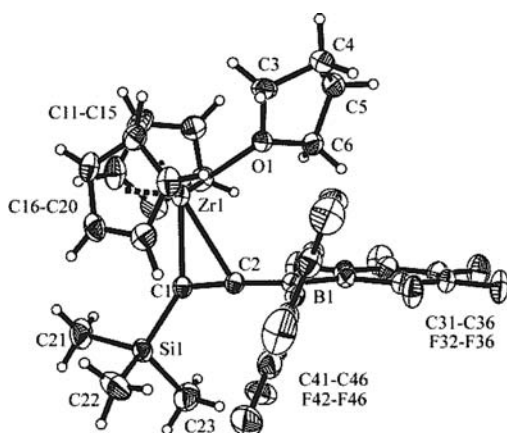
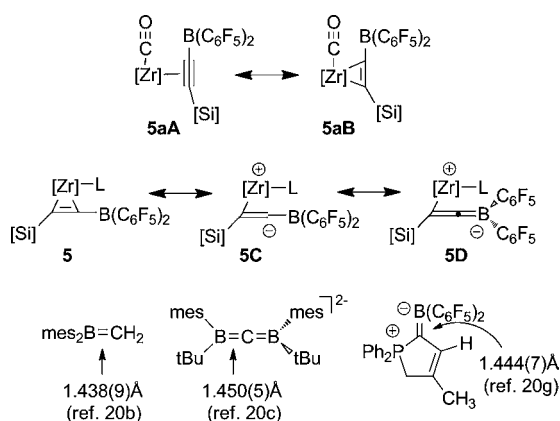


Figure 3. Molecular structure of the THF-*d*₈ adduct **5d** (thermal ellipsoids are shown with 30% probability).

Scheme 3



Scheme 4

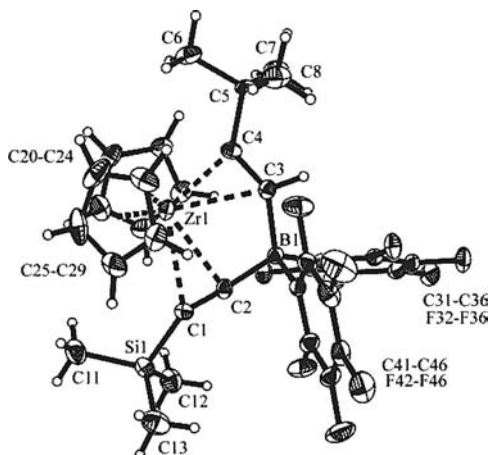
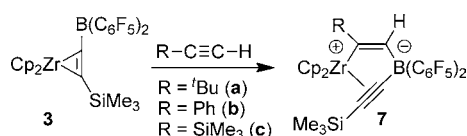


Figure 4. Molecular structure of the 1,2-Zr/B addition product **7a** to *t*-butyl acetylene (thermal ellipsoids are shown with 30% probability).

the C=C double bond range and the zirconium atom features only a weak in-plane contact to C3 (see Table 3). The Zr–

Table 3. Selected Structural Parameters of the Complexes **7a**^a

compd (R)	7a (<i>t</i> Bu)	7b (Ph) ^b	7c (SiMe ₃)	7d C(Me)=CH ₂
Zr1–C1	2.658(3)	2.752(4)	2.617(5)	2.702(5)
Zr1–C2	2.471(3)	2.461(3)	2.499(5)	2.472(4)
C1–C2	1.208(5)	1.210(5)	1.220(7)	1.207(6)
C2–B1	1.599(5)	1.598(5)	1.588(7)	1.597(6)
B1–C3	1.670(5)	1.655(5)	1.664(7)	1.669(6)
C3–C4	1.313(5)	1.331(5)	1.339(7)	1.321(6)
Zr1–C3	2.594(4)	2.677(3)	2.671(5)	2.664(4)
Zr1–C4	2.230(3)	2.197(3)	2.217(5)	2.186(4)
Si1–C1–C2	155.4(3)	156.8(3)	153.6(5)	161.2(4)
C1–C2–B1	174.7(4)	172.8(4)	174.9(5)	176.8(5)
C2–B1–C3	117.0(3)	117.5(3)	115.2(4)	116.6(4)
B1–C3–C4	144.3(3)	138.6(3)	141.7(5)	139.0(4)
C3–C4–C5	126.2(3)	123.5(3)	123.3(4) ^c	124.0(4)
Zr1–C4–C3	90.3(2)	95.6(2)	94.1(3)	95.7(3)

^aBond length in Å, angles in deg. ^bTwo independent molecules in the unit cell, values given for molecule A. ^cC3–C4–Si2.

C4(*t*Bu)=C3(H)[B] unit can be regarded as a distorted substituted vinyl zirconocene unit.²³ The boron atom in complex **7a** is tetracoordinated. It is found bonded to carbon atom C3 and to C2. The C2–B1 linkage in **7a** is rather long in contrast to the respective bond in **3** (see above), and the adjacent C1–C2 bond in **7a** is much shorter (by 0.073 Å) than the C1–C2 bond in **3**. The linear bond angle at C2 is remarkable. Together with the short C1–C2 bond length, it indicates a pronounced remaining acetylenic character of this subunit. The bonding features of **7a** are probably best described by a zwitterionic σ -vinyl/ π -acetylene structure depicted in Scheme 4. Consequently, the Zr–C1/C2 distances are rather long (see Table 3).

In solution complex **7a** shows the typical ¹³C NMR signals of a [Zr]vinyl unit [δ 217.6 (C4), δ 90.8 (1:1:1:1 q, ¹J_{CB} = 37.6 Hz, C3), =C(3)H- ¹H NMR signal at δ 6.79 (br 1:1:1:1 q, ²J_{BH} ~ 11 Hz)]. The ¹H/¹³C NMR signals of the Cp₂Zr moiety occur at δ 5.93/ δ 110.3 and the ¹³C NMR features of the C1≡C2 alkyne unit have been found at δ 108.1 (C1) and δ 110.4 (broad, C2), respectively. We have monitored a typical borate ¹¹B NMR resonance of complex **7a** at δ –23.8 with a corresponding typical set of ¹⁹F NMR resonances of the attached pair of symmetry equivalent C₆F₅ substituents [$\Delta\delta^{19}\text{F}_{m,p}$ = 4.4].

The reaction of the (borylalkyne)ZrCp₂ complex **3** with phenyl acetylene and trimethylsilylacetylene takes a similar course. We isolated the 1,2-Zr/B-addition products **7b** (R = Ph) and **7c** (R = SiMe₃) in 96% and 78% yield, respectively. Both these products were also characterized by X-ray diffraction and they showed characteristic structural parameters similar to those of **7a** (see Table 3 and Figure 5). In solution the products **7b** and **7c** show similar NMR features as **7a** (Table 4).

1,4-Addition to Conjugated Enynes and Diynes. We first reacted compound **3** with the conjugated enyne **8a** (R = H). This gave the Zr⁺/B 1,2-addition product **7d** to the terminal alkynyl moiety. Complex **7d** shows the typical structural features of this class of compounds (see Table 3, Figure 6 and Scheme 5). The 2-propenyl substituent at C4 is markedly rotated from the adjacent Zr1, C4, C3, B1 framework plane (θ C3–C4–C5–C6 –49.9(8)°, Zr1–C4–C3–B1 –3.4(6)°, C5–C6 1.358(8) Å).

The much more bulky enyne **8b** reacted with the zirconocene complex **3** in toluene at ambient temperature to

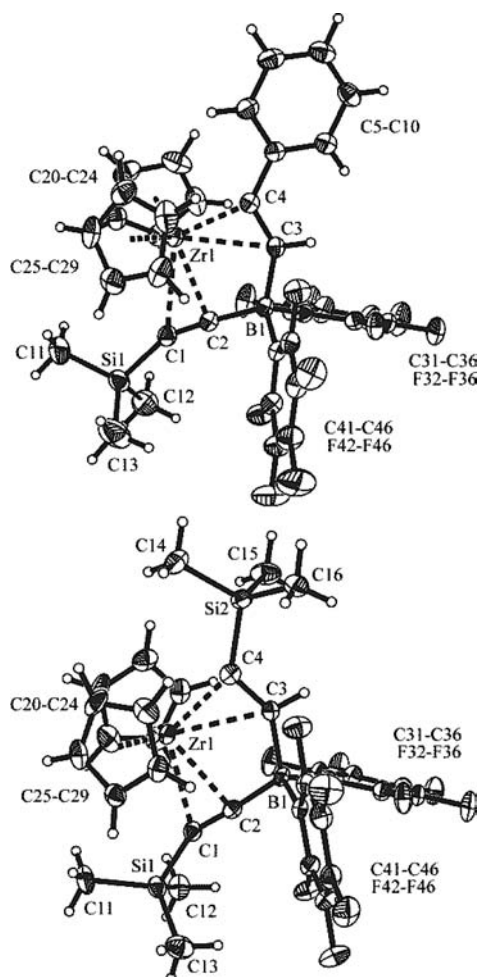


Figure 5. View of the molecular structures of complexes **7b** (top) and **7c** (bottom) (thermal ellipsoids are shown with 30% probability).

Table 4. Selected NMR Data of the Compounds **7**

compd (R)	7a ^a (^t Bu)	7b ^b (Ph)	7c ^b (SiMe ₃)	7d ^b C(Me)=CH ₂
Cp ₂ Zr (¹ H)	5.93	5.61	5.52	5.61
Cp ₂ Zr (¹³ C)	110.3	111.0	110.3	110.8
¹³ C NMR				
C1	108.1	106.5	106.4	106.2
C2	110.4	116.1	112.2	115.1
C3	90.8	93.2	108.7	93.5
C4	217.6	198.4	202.5	199.1
¹¹ B NMR				
	-23.8	-24.5	-24.8	-24.7
$\Delta\delta^{19}\text{F}_{m,p}$				
	4.4	5.4	5.6	5.4
¹ H NMR:				
Me ₃ Si	0.49	0.14	0.18	0.13
=C(3)H	6.79	7.62	8.03	7.22

^aCD₂Cl₂, 299 K. ^bC₆D₆, 299 K. Chemical shifts rel TMS (¹H, ¹³C), BF₃·OEt₂ (¹¹B).

give the product **9** that we isolated as a yellow solid in 76% yield (see Scheme 5). The X-ray crystal structure analysis (single crystals were obtained from pentane at -35 °C) showed that in this case the Zr⁺/B pair had undergone a regioselective 1,4-addition reaction to the conjugated enyne functionality of the reagent **8b**. The 1,4-addition has resulted in the formation of an allenic moiety inside the metallaheterocyclic framework of compound **9** (Figure 7). This unit contains a Zr-vinyl unit that

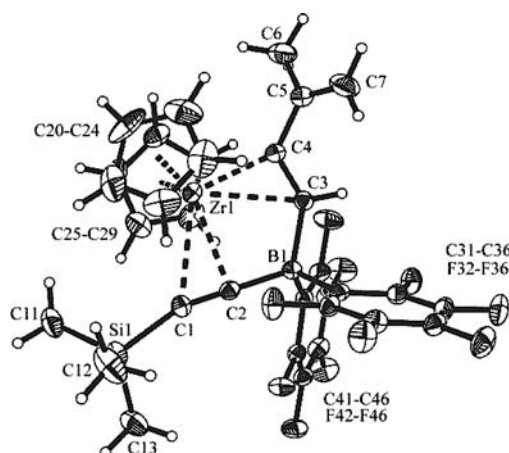


Figure 6. Molecular structure of compound **7d** (thermal ellipsoids are shown with 30% probability).

Scheme 5

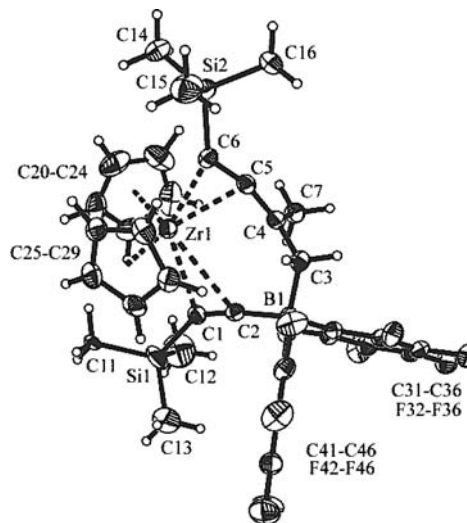
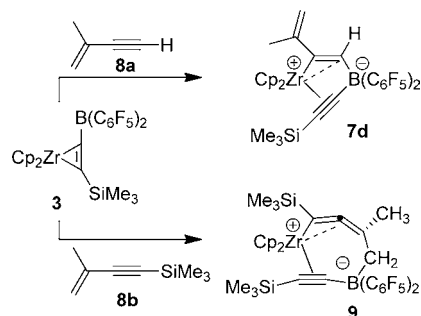


Figure 7. A view of the molecular structure of compound **9** (thermal ellipsoids are shown with 30% probability).

is part of the allenic subunit. Both the carbon atoms C6 and C5 are within bonding distance to zirconium (Zr1–C6 2.317(4) Å; Zr1–C5 2.431(4) Å) and the C6–C5 bond is rather short at 1.272(5) Å. The C5–C4 bond is longer (1.346(5) Å) but still in a C=C double bond range. The allene dihedral angle amounts to Si2–C6⋯C4–C7 -76.0°. The boron atom in compound **9** is tetracoordinate. All four B–C σ -bond lengths have been found in a narrow range (e.g., B1–C3 1.637(6) Å; B1–C2 1.628(6) Å). The C1–C2 bond is short (1.208(5) Å)

almost in a C≡C triple bond range and the B1–C2–C1 arrangement is almost linear, whereas the C2–C1–Si1 angle is much different at 142.7(6)°. The B-alkynyl unit is weakly coordinated to the zirconium atom [Zr1–C1 2.748(4) Å; Zr1–C2 2.938(4) Å].

In solution complex **9** shows the NMR signals of a pair of diastereotopic Cp-ligands at zirconium (¹H, δ 5.49, 5.37; ¹³C, δ 110.6, 109.5) and a ¹H NMR AB system of the –CH₂–[B] unit (δ 2.94, 2.24, ²J_{HH} = 15.3 Hz; ¹³C: δ 34.9). The allenic carbon NMR resonances have been located at δ 138.4 (C6), 150.3 (C5), 127.1 (C4) and the signals of the [B]–C≡C–[Si] unit were found at δ 157.5 (broad, C2) and 95.8 (C1), respectively. Compound **9** shows a borate ¹¹B NMR resonance at –14.9 and two equal intensity sets of ¹⁹F NMR signals of the pair of diastereotopic C₆F₅ substituents at boron.

The conjugated diyne 1,4-bis(trimethylsilyl)butadiyne (**8c**) undergoes a clean 1,4-addition reaction with complex **3** to give the product **10** (Scheme 6 and Figure 8). It was isolated in

Scheme 6

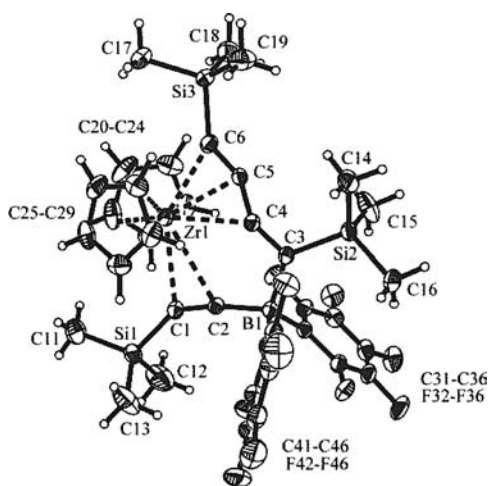
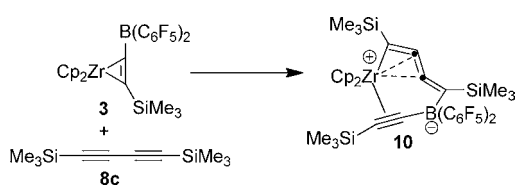


Figure 8. Molecular structure of complex **10** (thermal ellipsoids are shown with 30% probability).

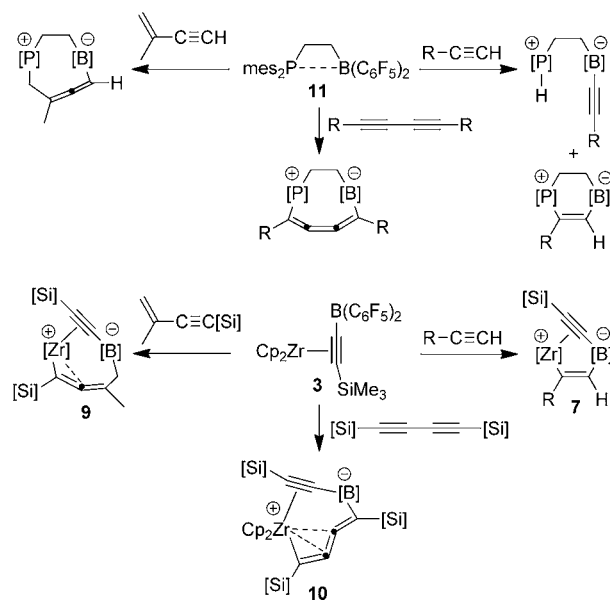
>80% yield and characterized by X-ray diffraction (single crystals were obtained from toluene at room temperature). The X-ray crystal structure analysis features a slightly distorted tetrasubstituted butatriene unit. The zirconocene moiety is found attached at one end in a Zr-vinyl type fashion. The C6–C5 bond is still rather short (1.266(4) Å) and the C5–C4 (1.337(3) Å) and C4–C3 (1.332(3) Å) bonds are longer and close to a typical C=C double bond length. This C₄ framework is slightly bent in-plane into opposite directions at carbon atoms C5 (angle C6–C5–C4 152.2(3)°) and C4 (angle C5–C4–C3 147.2(2)°) and the C4 to C6 unit has almost equidistant in-plane contacts with the zirconium atom (Zr1–C6 2.465(3) Å, Zr1–C5 2.457(2) Å, Zr1–C4 2.515(2) Å). The boron atom is attached at C3 (B1–C3 1.608(4) Å). The boron atom B1 is tetracoordinate. It has the original

C≡C–SiMe₃ substituent bonded to it (B1–C2 1.620(3) Å, C2–C1 1.219(3) Å). The C1–C2 triple bond is weakly coordinated to zirconium (Zr1–C1 2.687(3) Å, Zr1–C2 2.899(3) Å). The C2–B1 and C1–Si1 vectors are slightly bent away from the Zr-center [angles B1–C2–C1 170.0(3)°, C2–C1–Si1 141.4(2)°].

In solution compound **10** shows a sharp ¹H NMR Cp-singlet (δ 5.42 (10H); ¹³C: δ 109.4) and three SiMe₃ signals each of 9H rel. intensity (δ 0.20, 0.13, 0.08; ²⁹Si: δ –4.5, –4.8, –5.0). The ¹³C NMR resonances of the [B]–C≡C–SiMe₃ unit occur at δ 91.5 (C1) and δ 155.1 (C2), respectively, and those of the butatriene unit (C3 to C6) were found at δ 192.9, 170.2, 100.3, and 140.9. Compound **10** shows a ¹¹B NMR feature at δ –11.1 and a single set of ¹⁹F NMR resonances of the pair of C₆F₅ substituents at boron.

We find that the [B]–C≡C–[Si]ZrCp₂ complex **3** shows a remarkable reaction behavior toward acetylenes. It closely resembles a typical FLP behavior. It had previously been shown that a variety of FLPs undergo very typical addition reactions to alkynes.^{11,22} Typically, the intramolecular P/B FLP **11** may react with terminal alkynes by competing deprotonation and 1,2-addition. It typically undergoes kinetically controlled 1,4-addition reactions to the enyne **8a** (in competition with deprotonation) and to a variety of conjugated diynes (see Scheme 7).^{24,25} The observed formation of the alkyne 1,2-

Scheme 7

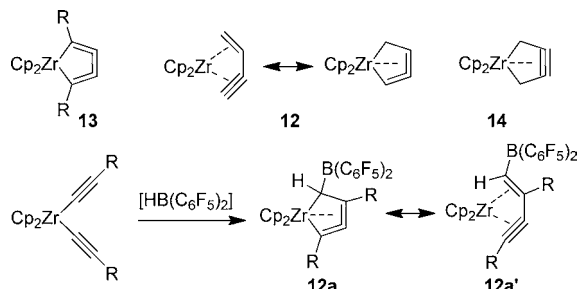


addition products **7** and the conjugated enyne and diyne 1,4-addition products (**9,10**) of the Zr/B complex **3** can be rationalized as resulting from similar Zr/B FLP addition reactions,²⁶ only that in this case the FLP is comprised by the usual strongly electrophilic borane Lewis acid and a Cp₂Zr Lewis base with zirconium in the formal oxidation state +2. Although this is certainly an unusual Lewis acid/Lewis base combination utilizing the low oxidation state early transition metal as a metal base,²⁷ the similarity between the observed reaction pattern of the P/B FLP **11** and our Zr/B complex **3** is striking.

Zirconacycloallene Formation. Olefin and acetylene zirconocene complexes often exhibit a very high metallacyclic σ-complex character. Therefore, (conjugated enyne)ZrCp₂

complexes may, to some extent, be regarded as five-membered metallacycloalleneoids **12**.²⁸ That places them into an intermediate position between U. Rosenthal's metallacyclocumulenes **13**²⁹ and N. Suzuki's metallacycloalkynes **14** (Scheme 8).³⁰ Previously, we had prepared the compounds **12a** as some

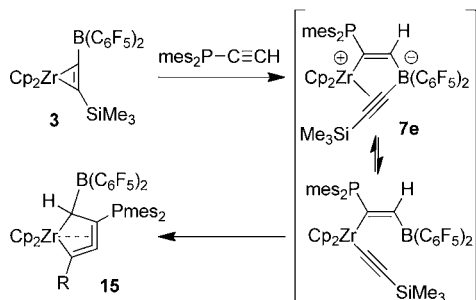
Scheme 8



of the first examples of the zirconacycloalleneoids.^{31,32} They were obtained by treatment of bis(alkynyl)metallocenes with Piers' borane $[\text{HB}(\text{C}_6\text{F}_5)_2]$ and, consequently, contained an active boryl substituent at the α -carbon atom. We have now found a way to form analogues of the systems **12a** by treatment of complex **3** with alkynes bearing bulky substituents. That created a situation where steric pressure induced C–C bond formation to construct the respective substituted enyne moiety at the zirconocene framework.

We reacted the $([\text{B}]\text{C}\equiv\text{C}[\text{Si}])\text{ZrCp}_2$ complex **3** with dimesitylphosphino-ethyne. At room temperature in toluene solution the reaction took ca. 3 h to go completion and we isolated the product **15** as a red solid in 74% yield (see Scheme 9). Single crystals of **15** were obtained from a saturated solution

Scheme 9



in pentane at $-35\text{ }^\circ\text{C}$ (see Figure 9). The X-ray crystal structure analysis has shown that the carbon frameworks of both acetylene derived substituents had undergone C–C coupling to form a substituted enyne ligand framework at the zirconocene unit that has attained a pronounced σ -complex character. It is a typical zirconacycloalleneoid complex. The zirconium atom is bonded to all four enyne ligand carbon atoms. The Zr1–C1 (2.387(6) Å) and Zr1–C2 (2.353(5) Å) bonds are short, the Zr1–C3 (2.584(5) Å) and Zr1–C4 (2.492(5) Å) bonds are longer. The C1–C2 linkage is short at 1.257(7) Å, reminding us of its alkyne origin. The C2–C3 bond (1.372(7) Å) is in the typical C=C double bond range and the adjacent C3–C4 bond is a (short) σ -bond at 1.463(7) Å. The ligand C–C–C angles amount to $159.0(5)^\circ$ (C1–C2–C3) and $117.9(5)^\circ$ (C2–C3–C4). Carbon atom C1 bears a SiMe_3 substituent and the Pmes_2 group is found attached at C3

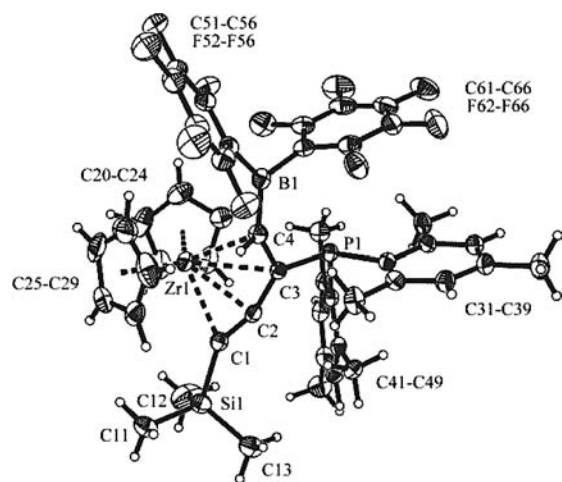


Figure 9. Molecular structure of the zirconacycloalleneoid complex **15** (thermal ellipsoids are shown with 30% probability).

of the framework. The $\text{B}(\text{C}_6\text{F}_5)_2$ substituent is bonded to carbon atom C4, which is to be regarded as a metalated (i.e., zirconated) α -boryl carbanion.^{17,18} Consequently, the C4–B1 linkage is rather short at 1.472(9) Å. The zirconacycloalleneoid framework of **15** is nonplanar. It has attained a conformation that has the bulky Pmes_2 and $\text{B}(\text{C}_6\text{F}_5)_2$ substituents oriented in a cisoid position (θ P1–C3–C4–B1 $21.5(8)^\circ$).³¹ The allenoid dihedral angle amounts to θ Si1–C1–C3–P1 $51.1(8)^\circ$.

Complex **15** features the $^1\text{H}/^{13}\text{C}$ NMR signals of a pair of diastereotopic Cp ligands. It shows a ^{11}B NMR resonance at δ 40.0 and a ^{31}P NMR signal at δ -25.1 that shows a coupling to a fluorine of an adjacent C_6F_5 group ($J_{\text{PF}} \sim 22$ Hz). The $\text{CH}[\text{B}]$ unit shows a ^{13}C NMR signal at δ 90.7 and a ^1H NMR resonance at δ 2.97 ($^3J_{\text{PH}} = 24.0$ Hz). The ^{13}C NMR signals of the C1, C2, and C3 allenoid moiety occur at δ 124.7 (C[Si]), 130.0 (=C=), and 100.9 (C[P]), respectively. We assume that the formation of compound **15** was initiated by 1,2-Zr/B FLP addition to the dimesitylphosphino-ethyne reagent (to generate **7e**, see Scheme 9), which was followed by alkynyl transfer from boron to zirconium and subsequent reductive coupling to give the zirconacycloalleneoid product.

The reaction of complex **3** with diphenylacetylene takes a similar course. After reacting the two components in a 1:1 molar ratio in toluene, we isolated the product **16** as dark violet solid in close to 80% yield. The X-ray crystal structure analysis (see Figure 10) has revealed that also in this case a zirconacycloalleneoid type compound was formed, but its structure differed slightly from that of **15**. Again, the acetylene has formally been inserted into the carbon–boron bond of the $[\text{B}]\text{C}\equiv\text{C}[\text{Si}]$ ligand of **3**, probably by an analogous reaction pathway as assumed for the formation of **15**, namely, via the 1,2-Zr/B FLP addition product **7f** and its follow-up product **17** (see Scheme 10).³¹ Compound **16** features a Zr-allenoid subunit that contains the C1–C2 (1.270(4) Å) and C2–C3 (1.349(4) Å) bonds that feature a decreasing contact to zirconium (Zr1–C1 2.285(3) Å, Zr1–C2 2.426(3) Å, Zr1–C3 3.040(3) Å). The central allene angle amounts to C1–C2–C3 $170.9(3)^\circ$ and the allenoid dihedral angle was found at θ Si1–C1–C3–C31 $73.7(4)^\circ$. Carbon atom C1 bears the $-\text{SiMe}_3$ substituent, and a phenyl group is attached at C3. The C3–C4 bond is long at 1.501(4) Å. Carbon atom C4 has the second phenyl group attached and the $\text{B}(\text{C}_6\text{F}_5)_2$ substituent. The B1–C4 bond is rather short at 1.464(5) Å pointing to some

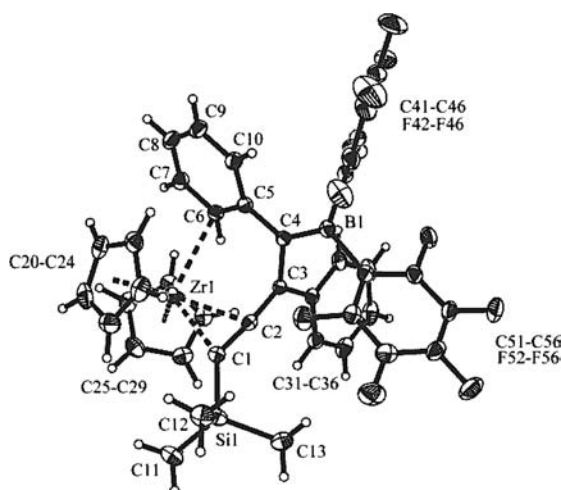
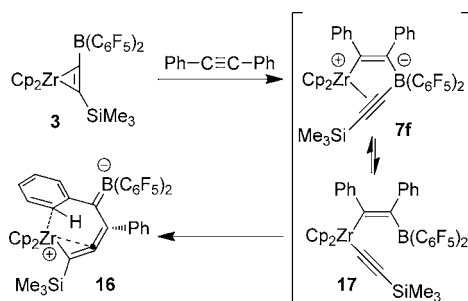


Figure 10. Molecular structure of compound **16** (thermal ellipsoids are shown with 30% probability).

Scheme 10



carbanion character of this sp^2 -carbon center ($\Sigma C4^{CBC} = 359.8^\circ$) α to the boryl group ($\Sigma B^{CCC} = 359.9^\circ$). In contrast to **15**, there is no direct Zr1/C4 interaction but the metal contact is shifted to the adjacent phenyl substituent (e.g., Zr1–C6 2.639(3) Å; the Zr1–C5 (3.305 Å) and Zr1–C7 (3.318 Å) contacts are much longer). So, compound **16** may be regarded as zirconacycloallene compound^{28,33} that has opened its heterocyclic core by incorporation of the conjugated phenyl substituent at C4.

CONCLUSIONS

The unique $([B]-C\equiv C-[Si])ZrCp_2$ complex **3** shows quite some different reaction patterns toward a variety of reagents. With simple donors (CO, isonitrile, etc.), it forms typical d-metal/ligand adducts. In detail, they show some special bonding features arising from the participation of the metallacyclopropene structure in the description of the bonding features of the $(\eta^2$ -alkyne)zirconocene unit in **3** (and **5**), but in principle, the adducts **5** behave as donor-ligand d^2 -ZrCp₂ complexes.

In the reaction with acetylenes, the system reacts rather differently. Often Cp₂Zr(II) complexes react with pairs of acetylene reagents by zirconacyclopentadiene formation.³⁴ This is not the predominant reaction type observed here. Instead, both the zirconium complex subunit and the borane moiety are actively involved in the reaction with the added alkynes. We have observed an interesting new reaction pattern of a cooperative 1,2-addition of the zirconium metal center and the boron Lewis acid to the respective C≡C triple bonds. In some cases, even Zr/B 1,4-addition to conjugated enyne or

diyne reagents has been observed. This reaction type is quite unusual. It requires the zirconocene unit to act as a metal Lewis base to undergo these addition reactions in conjunction with the boron Lewis acid functionality. The Cp₂Zr unit of **3** acting as a Lewis base is in accord with its typical zirconium(II) behavior in the coordination chemistry with CO, etc. (see above). The overall reaction can be regarded as a novel type of FLP addition reaction to acetylenic substrates, and consequently, the system **3** may be regarded to provide a basis for making Zr/B FLP reactions available. Zirconium containing FLPs had previously been described, but in them the boron Lewis acid had been substituted for the electrophilic Cp₂ZrX⁺ Lewis acid. Typically, Zr⁺/P systems have been involved in that chemistry.¹² Our new system is different in the way that we have formally substituted the main group element Lewis base (phosphane or amine in typical P/B or N/B FLPs) by a Lewis basic zirconocene unit and have kept the strongly electrophilic borane Lewis acid.

The resulting Zr/B FLP system (**3**) may then show a variety of typical FLP reactions, such as H₂-cleavage^{4,35,36} or the here studied alkyne addition reactions, but in a competition, some quite normal donor ligand adduct formation can also be observed. The alkyne addition reactions, making use of the cooperative Zr/B FLP reaction mode in this apparently typical behavior of **3**, eventually have opened some new pathways to synthesizing interesting new examples of the unique zirconacycloallene compounds,^{28,31,33} which makes this Zr/B FLP behavior actually synthetically useful.

EXPERIMENTAL SECTION

General Remarks. All manipulations were performed in oven- or flame-dried glassware under an argon atmosphere in a glovebox or by standard Schlenk techniques unless specified otherwise. For detailed general experimental information, see the Supporting Information.

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT;³⁷ data reduction Denzo-SMN;³⁸ absorption correction, Denzo;³⁹ structure solution SHELXS-97;⁴⁰ structure refinement SHELXL-97⁴¹ and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and *wR*² values are given for all reflections. *Exceptions and special features:* A disordered over two position SiMe₃ group was found in the asymmetric unit of compound **5a**. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Compound **7b** crystallized with two molecules in the asymmetric unit. One pentane molecule and one SiMe₃ group disordered over two positions were found in the asymmetric unit. Several restraints (SADI, SIMU and SAME) were used in order to improve refinement stability. For compound **7c**, an unidentified disordered solvent molecule was found in the asymmetric unit and could not be satisfactorily refined. The program SQUEEZE⁴² was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. Compound **9** present two SiMe₃ groups and one Cp group disordered over two positions. Several restraints (SADI, SIMU and SAME) were used in order to improve refinement stability.

Preparation of Complex 5a. (*Caution: carbon monoxide is a toxic gas and must be handled with due care*). A dark red solution of complex **3** (100 mg, 0.145 mmol) in toluene (1.5 mL) was evacuated and exposed to carbon monoxide (1.5 bar) for 4 min. During this time, the dark red color of the reaction solution changed to yellowish brown. Then, all volatiles were removed in *vacuum* and the obtained residue was washed with *n*-pentane (5 mL). Compound **5a** was isolated as a pale yellow solid (88.0 mg, 0.127 mmol, 87%). Crystals suitable for an X-ray crystal structure analysis were obtained by crystallization of a

saturated *n*-pentane solution of **5a** at $-35\text{ }^{\circ}\text{C}$. Analysis calcd for $\text{C}_{28}\text{H}_{19}\text{BF}_{10}\text{OSiZr}$: C, 48.63; H, 2.77. Found: C, 48.72; H, 2.87. IR (KBr): 2011 (s), 1865 (s) cm^{-1} . ^1H NMR (600 MHz, C_6D_6 , 299 K): δ 4.81 (s, 10H, Cp), 0.25 (s, $^2J_{\text{SiH}} = 6.8$ Hz, 9H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 299 K): δ 239.6 (C \equiv O), 148.1 (dm, $^1J_{\text{FC}} \sim 239$ Hz, C_6F_5), 140.2 (dm, $^1J_{\text{FC}} \sim 252$ Hz, C_6F_5), 138.8 (br, =CB)^t, 137.6 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 126.5 ($^1J_{\text{SiC}} = 70.6$ Hz, =CSi), 116.2 (br, *i*- C_6F_5), 103.6 (Cp), 0.9 ($^1J_{\text{SiC}} = 54.6$ Hz, SiMe₃), [^t tentatively assigned]. ^{29}Si DEPT (119 MHz, C_7D_8 , 299 K): δ -3.5 ($\nu_{1/2} \sim 2$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_7D_8 , 299 K): δ 6.9 ($\nu_{1/2} \sim 300$ Hz). ^{11}B NMR (192 MHz, C_7D_8 , 299 K): δ 6.9 ($\nu_{1/2} \sim 300$ Hz). ^{19}F NMR (564 MHz, C_7D_8 , 299 K): δ -127.7 (m, 2F, *o*- C_6F_5), -156.6 (t, $^3J_{\text{FF}} = 20.6$ Hz, 1F, *p*- C_6F_5), -163.6 (m, 2F, *m*- C_6F_5), [$\Delta\delta^{19}\text{F}_{\text{mp}} = 7.0$].

X-ray Crystal Structure Analysis of Complex 5a. Formula $\text{C}_{28}\text{H}_{19}\text{BF}_{10}\text{OSiZr}$, $M = 691.55$, yellow crystal, $0.23 \times 0.07 \times 0.05$ mm, $a = 11.1528(1)$, $b = 14.9749(3)$, $c = 17.9193(3)$ Å, $\alpha = 98.461(1)$, $\beta = 97.158(1)$, $\gamma = 103.779(1)^{\circ}$, $V = 2835.0(1)$ Å³, $\rho_{\text{calc}} = 1.620$ g·cm⁻³, $\mu = 0.518$ mm⁻¹, empirical absorption correction (0.890 $\leq T \leq 0.974$), $Z = 4$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 23 458 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.59$ Å⁻¹, 9819 independent ($R_{\text{int}} = 0.040$) and 8151 observed reflections [$I > 2\sigma(I)$], 779 refined parameters, $R = 0.059$, $wR^2 = 0.132$, max (min) residual electron density 0.68 (-0.67) e·Å⁻³, hydrogen atoms were calculated and refined as riding atoms.

Preparation of Complex 5b. (Caution: many isocyanides are toxic and must be handled with due care). ^tButyl isocyanide (13.0 mg, 0.16 mmol, 1 equiv, 18.3 μL) was added to a dark red solution of complex **3** (110 mg, 0.16 mmol, 1 equiv) in toluene (2 mL). The dark red color of the solution was immediately changed to light red and the reaction mixture was stirred for 10 min at room temperature. After this time all volatiles were removed under reduced pressure and the obtained material was washed with *n*-pentane (5 mL). Complex **5b** was isolated as a light red solid (90.0 mg, 0.120 mmol, 75%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane solution of **5b** at $-35\text{ }^{\circ}\text{C}$. Analysis calcd for $\text{C}_{32}\text{H}_{28}\text{BF}_{10}\text{NSiZr}$: C, 51.47; H, 3.78; N, 1.88. Found: C, 50.22; H, 3.79; N, 1.60. IR (KBr): 2154 (m) cm^{-1} . ^1H NMR (600 MHz, C_6D_6 , 299 K): δ 5.12 (s, 10H, Cp), 0.91 (s, 9H, ^tBu), 0.45 (s, $^2J_{\text{SiH}} = 6.7$ Hz, 9H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 299 K): δ 167.7 (C \equiv N), 155.6 (br, =CB)^t, 148.1 (dm, $^1J_{\text{FC}} \sim 238$ Hz, C_6F_5), 139.9 (=CSi), 139.5 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 137.5 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 118.3 (br, *i*- C_6F_5), 104.6 (Cp), 58.2 (^tBu), 29.1 (^tBu), 1.2 ($^1J_{\text{SiC}} = 53.6$ Hz, SiMe₃), [^t tentatively assigned]. ^{29}Si DEPT (119 MHz, C_6D_6 , 299 K): δ -4.3 ($\nu_{1/2} \sim 2$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_6D_6 , 299 K): δ 11.1 ($\nu_{1/2} \sim 280$ Hz). ^{11}B NMR (192 MHz, C_6D_6 , 299 K): δ 11.1 ($\nu_{1/2} \sim 280$ Hz). ^{19}F NMR (564 MHz, C_6D_6 , 299 K): δ -127.1 (m, 2F, *o*- C_6F_5), -159.0 (t, $^3J_{\text{FF}} = 20.6$ Hz, 1F, *p*- C_6F_5), -164.7 (m, 2F, *m*- C_6F_5), [$\Delta\delta^{19}\text{F}_{\text{mp}} = 5.7$].

X-ray Crystal Structure Analysis of Complex 5b. Formula $\text{C}_{32}\text{H}_{28}\text{BF}_{10}\text{NSiZr}$, $M = 746.67$, orange crystal, $0.20 \times 0.10 \times 0.03$ mm, $a = 11.6698(2)$, $b = 15.5587(2)$, $c = 18.0772(2)$ Å, $\beta = 92.406(1)^{\circ}$, $V = 3279.33(8)$ Å³, $\rho_{\text{calc}} = 1.512$ g·cm⁻³, $\mu = 0.452$ mm⁻¹, empirical absorption correction (0.915 $\leq T \leq 0.986$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 29 432 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.60$ Å⁻¹, 8030 independent ($R_{\text{int}} = 0.044$) and 6327 observed reflections [$I > 2\sigma(I)$], 421 refined parameters, $R = 0.044$, $wR^2 = 0.095$, max (min) residual electron density 0.38 (-0.39) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 5c. Pivalonitrile (13.0 mg, 0.16 mmol, 1 equiv, 18.3 μL) was added to a dark red solution of complex **3** (110 mg, 0.16 mmol, 1 equiv) in toluene (2 mL). The dark red color of the solution was immediately changed light red and the reaction mixture was stirred for 10 min at room temperature. After this time, all volatiles were removed under reduced pressure and the obtained material was washed with *n*-pentane (5 mL). Complex **5c** was isolated as a light red solid (108 mg, 0.145 mmol, 90%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane and dichloromethane solution of **5c** at $-35\text{ }^{\circ}\text{C}$. Analysis calcd for $\text{C}_{32}\text{H}_{28}\text{BF}_{10}\text{NSiZr}$: C, 51.47; H, 3.78; N, 1.88. Found: C,

51.22; H, 3.75; N, 1.80. IR (KBr): 2259 (m) cm^{-1} . ^1H NMR (600 MHz, C_6D_6 , 299 K): δ 5.36 (s, 10H, Cp), 0.65 (s, 9H, ^tBu), 0.41 (s, $^2J_{\text{SiH}} = 6.6$ Hz, 9H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 299 K): δ 170.5 (=CB)^t, 156.9 (=CSi), 148.1 (dm, $^1J_{\text{FC}} \sim 238$ Hz, C_6F_5), 147.0 (N \equiv C), 139.5 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 137.5 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 118.5 (br, *i*- C_6F_5), 107.8 (Cp), 29.9 (^tBu), 26.5 (^tBu), 1.2 ($^1J_{\text{SiC}} = 52.8$ Hz, SiMe₃), [^t tentatively assigned]. ^{29}Si DEPT (119 MHz, C_6D_6 , 299 K): δ -5.3 ($\nu_{1/2} \sim 2$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_6D_6 , 299 K): δ 17.2 ($\nu_{1/2} \sim 320$ Hz). ^{11}B NMR (192 MHz, C_6D_6 , 299 K): δ 17.2 ($\nu_{1/2} \sim 320$ Hz). ^{19}F NMR (564 MHz, C_6D_6 , 299 K): δ -127.9 (m, 2F, *o*- C_6F_5), -159.0 (t, $^3J_{\text{FF}} = 20.6$ Hz, 1F, *p*- C_6F_5), -164.8 (m, 2F, *m*- C_6F_5), [$\Delta\delta^{19}\text{F}_{\text{mp}} = 5.8$].

X-ray Crystal Structure Analysis of Complex 5c. Formula $\text{C}_{32}\text{H}_{28}\text{BF}_{10}\text{NSiZr}$, $M = 746.67$, orange crystal, $0.21 \times 0.18 \times 0.03$ mm, $a = 11.6849(2)$, $b = 15.5589(2)$, $c = 18.1675(3)$ Å, $\beta = 92.132(1)^{\circ}$, $V = 3300.64(9)$ Å³, $\rho_{\text{calc}} = 1.503$ g·cm⁻³, $\mu = 0.449$ mm⁻¹, empirical absorption correction (0.911 $\leq T \leq 0.986$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 9814 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.60$ Å⁻¹, 5703 independent ($R_{\text{int}} = 0.036$) and 4318 observed reflections [$I > 2\sigma(I)$], 421 refined parameters, $R = 0.052$, $wR^2 = 0.114$, max (min) residual electron density 0.49 (-0.32) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 5d. THF-*d*₈ (1 mL) was added to complex **3** (60.0 mg) and the in situ generated red solution of **5d** was directly used for the NMR experiment. Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated THF-*d*₈ solution of **5d** at $-35\text{ }^{\circ}\text{C}$. Isolated yield was not calculated due to the instability of the compound. ^1H NMR (600 MHz, $\text{C}_4\text{D}_8\text{O}$, 299 K): δ 5.82 (s, 10H, Cp), 3.59 ($\text{C}_4\text{D}_7\text{HO}$), 1.73 ($\text{C}_4\text{D}_7\text{HO}$), 0.22 (s, $^2J_{\text{SiH}} = 6.5$ Hz, 9H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, $\text{C}_4\text{D}_8\text{O}$, 299 K): δ 185.0 (br, =CB), 174.7 (=CSi), 147.9 (dm, $^1J_{\text{FC}} \sim 240$ Hz, C_6F_5), 140.1 (dm, $^1J_{\text{FC}} \sim 248$ Hz, C_6F_5), 137.8 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 118.9 (br, *i*- C_6F_5), 109.8 (Cp), 67.4 (quint, $\text{C}_4\text{D}_8\text{O}$), 25.2 (quint, $\text{C}_4\text{D}_8\text{O}$), 1.0 ($^1J_{\text{SiC}} = 52.1$ Hz, SiMe₃). ^{29}Si DEPT (119 MHz, $\text{C}_4\text{D}_8\text{O}$, 299 K): δ -3.7 ($\nu_{1/2} \sim 2$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, $\text{C}_4\text{D}_8\text{O}$, 299 K): δ 23.4 ($\nu_{1/2} \sim 400$ Hz). ^{11}B NMR (192 MHz, $\text{C}_4\text{D}_8\text{O}$, 299 K): δ 23.4 ($\nu_{1/2} \sim 400$ Hz). ^{19}F NMR (564 MHz, $\text{C}_4\text{D}_8\text{O}$, 299 K): δ -128.3 (m, 2F, *o*- C_6F_5), -159.1 (t, $^3J_{\text{FF}} = 20.0$ Hz, 1F, *p*- C_6F_5), -164.4 (m, 2F, *m*- C_6F_5), [$\Delta\delta^{19}\text{F}_{\text{mp}} = 5.3$].

X-ray Crystal Structure Analysis of Complex 5d. Formula $\text{C}_{31}\text{H}_{27}\text{BF}_{10}\text{OSiZr}$, $M = 735.65$, orange crystal, $0.25 \times 0.22 \times 0.15$ mm, $a = 34.4119(4)$, $b = 9.5110(1)$, $c = 18.9714(3)$ Å, $\beta = 91.286(1)^{\circ}$, $V = 6207.61(14)$ Å³, $\rho_{\text{calc}} = 1.574$ g·cm⁻³, $\mu = 0.478$ mm⁻¹, empirical absorption correction (0.889 $\leq T \leq 0.931$), $Z = 8$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 20 448 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.60$ Å⁻¹, 7587 independent ($R_{\text{int}} = 0.038$) and 6498 observed reflections [$I > 2\sigma(I)$], 409 refined parameters, $R = 0.036$, $wR^2 = 0.090$, max (min) residual electron density 0.35 (-0.32) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 7a. 3,3-Dimethyl-1-butene (6.0 mg, 0.075 mmol, 9 μL , 1 equiv) was added to a solution of complex **3** (50.0 mg, 0.075 mmol) in toluene (1 mL). The dark red color of the solution was immediately changed to light yellow and the reaction mixture was stirred for 10 min at room temperature. After this time, all volatiles were removed under reduced pressure and the obtained material was washed with *n*-pentane (3 mL). Complex **7a** was isolated as a light yellow solid (40.0 mg, 54 μmol , 72%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a concentrated CH_2Cl_2 solution of **7a** at $-35\text{ }^{\circ}\text{C}$. Analysis calcd for $\text{C}_{33}\text{H}_{29}\text{BF}_{10}\text{SiZr}$: C, 53.15; H, 3.92. Found: C, 53.17; H, 3.75. ^1H NMR (600 MHz, CD_2Cl_2 , 299 K): δ 6.79 (br 1:1:1:1 q, $^2J_{\text{BH}} \sim 11$ Hz, 1H, =CH), 5.93 (s, 10H, Cp), 1.31 (s, 9H, ^tBu), 0.49 (s, $^2J_{\text{SiH}} = 7.0$ Hz, 9H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 299 K): δ 217.6 (=CZr), 148.1 (dm, $^1J_{\text{FC}} \sim 239$ Hz, C_6F_5), 139.3 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 137.4 (dm, $^1J_{\text{FC}} \sim 249$ Hz, C_6F_5), 123.1 (br m, *i*- C_6F_5), 110.4 (br m, =CB)^t, 110.3 (Cp), 108.1 (br m, =CSi), 90.8 (1:1:1:1 q, $^1J_{\text{CB}} = 37.6$ Hz, =CH), 41.4 (br m, ^tBu), 32.5 (^tBu), 0.1 ($^1J_{\text{SiC}} = 56.6$ Hz, SiMe₃), [^t from the ghmbc experiment]. ^{29}Si DEPT (119 MHz,

CD₂Cl₂, 299 K): δ -9.8 ($\nu_{1/2} \sim 2$ Hz). ¹¹B{¹H} NMR (192 MHz, CD₂Cl₂, 299 K): δ -23.8 ($\nu_{1/2} \sim 13$ Hz). ¹¹B NMR (192 MHz, CD₂Cl₂, 299 K): δ -23.8 ($\nu_{1/2} \sim 25$ Hz). ¹⁹F NMR (564 MHz, CD₂Cl₂, 299 K): δ -133.8 (m, 2F, *o*-C₆F₅), -160.9 (t, ³J_{FF} = 20.4 Hz, 1F, *p*-C₆F₅), -165.3 (m, 2F, *m*-C₆F₅), [$\Delta\delta^{19}\text{F}_{m,p} = 4.4$].

X-ray Crystal Structure Analysis of Complex 7a. Formula C₃₃H₂₉BF₁₀SiZr, *M* = 745.68, yellow crystal, 0.35 × 0.23 × 0.17 mm, *a* = 10.2083(1), *b* = 10.8557(2), *c* = 16.1270(3) Å, α = 94.417(1), β = 93.355(1), γ = 116.351(1)°, *V* = 1588.09(4) Å³, $\rho_{\text{calc}} = 1.559$ g·cm⁻³, $\mu = 0.466$ mm⁻¹, empirical absorption correction (0.853 ≤ *T* ≤ 0.925), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, *T* = 223(2) K, ω and φ scans, 14 290 reflections collected ($\pm h$, $\pm k$, $\pm l$), [($\sin \theta$)/ λ] = 0.59 Å⁻¹, 5455 independent (*R*_{int} = 0.031) and 5285 observed reflections [*I* > 2 σ (*I*)], 425 refined parameters, *R* = 0.046, *wR*² = 0.103, max (min) residual electron density 1.56 (-1.15) e·Å⁻³, the hydrogen at C3 atom was refined freely; others were calculated and refined as riding atoms.

Preparation of Complex 7b. Compound 7b was prepared by the same procedure as described for 7a. Compound 3 (100 mg, 0.15 mmol) reacted with phenylacetylene (17.0 mg, 0.16 mmol, 1.1 equiv) to give compound 7b as a light-yellow solid (111 mg, 0.145 mmol, 96%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane solution of 7b at -35 °C. Analysis calcd for C₃₅H₂₅BF₁₀SiZr: C, 54.90; H, 3.29. Found: C, 54.66; H, 3.63. ¹H NMR (500 MHz, C₆D₆, 299 K): δ 7.62 (br m, 1H, =CH), 7.49 (m, 2H, *o*-Ph), 7.33 (m, 2H, *m*-Ph), 7.20 (m, 1H, *p*-Ph), 5.61 (s, 10H, Cp), 0.14 (s, ²J_{SiH} = 7.0 Hz, 9H, SiMe₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, 299 K): δ 198.4 (=CZr), 148.3 (dm, ¹J_{FC} ~ 240 Hz, C₆F₅), 145.5 (*i*-Ph), 139.7 (dm, ¹J_{FC} ~ 246 Hz, C₆F₅), 138.6 (dm, ¹J_{FC} ~ 248 Hz, C₆F₅), 129.0 (*m*-Ph), 127.8 (*p*-Ph), 127.4 (*o*-Ph), 122.4 (br m, *i*-C₆F₅), 116.1 (1:1:1:1 q, ¹J_{CB} = 52.6 Hz, =CB), 111.0 (Cp), 106.5 (br, =CSi), 93.2 (1:1:1:1 q, ¹J_{CB} = 39.8 Hz, =CH), 0.3 (¹J_{SiC} = 56.5 Hz, SiMe₃). ²⁹Si DEPT (99 MHz, C₆D₆, 299 K): δ -9.9 ($\nu_{1/2} \sim 2$ Hz). ¹¹B{¹H} NMR (160 MHz, C₆D₆, 299 K): δ -24.5 ($\nu_{1/2} \sim 17$ Hz). ¹¹B NMR (160 MHz, C₆D₆, 299 K): δ -24.5 ($\nu_{1/2} \sim 24$ Hz). ¹⁹F NMR (470 MHz, C₆D₆, 299 K): δ -133.8 (m, 2F, *o*-C₆F₅), -158.4 (t, ³J_{FF} = 20.9 Hz, 1F, *p*-C₆F₅), -163.8 (m, 2F, *m*-C₆F₅), [$\Delta\delta^{19}\text{F}_{m,p} = 5.4$].

X-ray Crystal Structure Analysis of Complex 7b. Formula C₃₅H₂₅BF₁₀SiZr·0.5 × C₅H₁₂, *M* = 801.74, yellow crystal, 0.27 × 0.10 × 0.03 mm, *a* = 10.5805(1), *b* = 31.8728(4), *c* = 21.7498(3) Å, β = 102.941(1)°, *V* = 7148.4(2) Å³, $\rho_{\text{calc}} = 1.490$ g·cm⁻³, $\mu = 0.420$ mm⁻¹, empirical absorption correction (0.895 ≤ *T* ≤ 0.987), *Z* = 8, monoclinic, space group *P*_{2₁/n (No. 14), $\lambda = 0.71073$ Å, *T* = 223(2) K, ω and φ scans, 82 752 reflections collected ($\pm h$, $\pm k$, $\pm l$), [($\sin \theta$)/ λ] = 0.59 Å⁻¹, 12 520 independent (*R*_{int} = 0.072) and 9697 observed reflections [*I* > 2 σ (*I*)], 987 refined parameters, *R* = 0.046, *wR*² = 0.100, max (min) residual electron density 0.44 (-0.41) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.}

Preparation of Complex 7c. Compound 7c was prepared by the same procedure as described for 7a. Compound 3 (80.0 mg, 0.12 mmol) reacted with (trimethylsilyl)acetylene (12.0 mg, 0.12 mmol, 1.1 equiv) to give compound 7c as a light-yellow solid (72.0 mg, 0.094 mmol, 78%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane solution of 7c at -35 °C. Analysis calcd for C₃₂H₂₉BF₁₀Si₂Zr: C, 50.45; H, 3.84. Found: C, 50.78; H, 3.37. ¹H NMR (600 MHz, C₆D₆, 299 K): δ 8.03 (br 1:1:1:1 q, ²J_{BH} = 11.8 Hz, 1H, =CH), 5.52 (s, 10H, Cp), 0.28 (s, ²J_{SiH} = 6.4 Hz, 9H, =SiMe₃), 0.18 (s, ²J_{SiH} = 7.0 Hz, 9H, =SiMe₃). ¹³C{¹H} NMR (151 MHz, C₆D₆, 299 K): δ 202.5 (=CZr), 148.4 (dm, ¹J_{FC} ~ 240 Hz, C₆F₅), 139.6 (dm, ¹J_{FC} ~ 250 Hz, C₆F₅), 137.7 (dm, ¹J_{FC} ~ 246 Hz, C₆F₅), 122.3 (br m, *i*-C₆F₅), 112.2 (br 1:1:1:1 q, ¹J_{CB} ~ 55 Hz, =CB), 110.3 (Cp), 108.7 (1:1:1:1 q, ¹J_{CB} = 34.3 Hz, =CH), 106.4 (br, =CSi), 0.6 (¹J_{SiC} = 52.0 Hz, =SiMe₃), -0.1 (¹J_{SiC} = 56.5 Hz, =SiMe₃). ²⁹Si DEPT (119 MHz, C₆D₆, 299 K): δ -2.3 (broad, =Si), -9.4 ($\nu_{1/2} \sim 3$ Hz, =Si). ¹¹B{¹H} NMR (192 MHz, C₆D₆, 299 K): δ -24.8 ($\nu_{1/2} \sim 13$ Hz). ¹¹B NMR (192 MHz, C₆D₆, 299 K): δ -24.8 ($\nu_{1/2} \sim 25$ Hz). ¹⁹F NMR (564 MHz, C₆D₆, 299 K): δ -133.8 (m, 2F, *o*-C₆F₅), -158.2 (t, ³J_{FF} = 20.6 Hz, 1F, *p*-C₆F₅), -163.8 (m, 2F, *m*-C₆F₅), [$\Delta\delta^{19}\text{F}_{m,p} = 5.6$].

X-ray Crystal Structure Analysis of Complex 7c. Formula C₃₂H₂₉BF₁₀Si₂Zr, *M* = 761.76, yellow crystal, 0.22 × 0.20 × 0.04 mm, *a* = 11.1086(3), *b* = 16.2478(4), *c* = 21.5154(6) Å, α = 98.084(1), β = 104.561(1), γ = 94.600(1)°, *V* = 3694.09(2) Å³, $\rho_{\text{calc}} = 1.370$ g·cm⁻³, $\mu = 0.433$ mm⁻¹, empirical absorption correction (0.910 ≤ *T* ≤ 0.982), *Z* = 4, triclinic, space group *P* $\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, *T* = 223(2) K, ω and φ scans, 34 403 reflections collected ($\pm h$, $\pm k$, $\pm l$), [($\sin \theta$)/ λ] = 0.59 Å⁻¹, 12 699 independent (*R*_{int} = 0.069) and 9801 observed reflections [*I* > 2 σ (*I*)], 841 refined parameters, *R* = 0.066, *wR*² = 0.173, max (min) residual electron density 0.77 (-0.98) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 7d. Compound 7d was prepared by the same procedure as described for 7a. Compound 3 (350 mg, 0.530 mmol) reacted with 2-methylbut-1-en-3-yne (38.0 mg, 0.538 mmol, 1.1 equiv) to give compound 7d as a light-yellow solid (293 mg, 0.402 mmol, 75%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane solution of 7d at -35 °C. Analysis calcd for C₃₂H₂₅BF₁₀SiZr: C, 52.68; H, 3.45. Found: C, 52.40; H, 3.38. ¹H NMR (600 MHz, C₆D₆, 299 K): δ 7.22 (br m, =CH), 5.61 (s, 10H, Cp), 5.21 (m, 1H, =CH₂^E), 4.79 (d, ²J_{HH} = 2.6 Hz, 1H, =CH₂^Z), 2.14 (m, 3H, Me), 0.13 (s, ²J_{SiH} = 6.9 Hz, 9H, SiMe₃). ¹³C{¹H} NMR (151 MHz, C₆D₆, 299 K): δ 199.1 (=CZr), 149.4 (br, MeC=), 148.3 (dm, ¹J_{FC} ~ 242 Hz, C₆F₅), 139.6 (dm, ¹J_{FC} ~ 253 Hz, C₆F₅), 137.6 (dm, ¹J_{FC} ~ 249 Hz, C₆F₅), 122.5 (br m, *i*-C₆F₅), 117.2 (=CH₂), 115.1 (br 1:1:1:1 q, ¹J_{CB} = 52.8 Hz, =CB), 110.8 (Cp), 106.2 (br m, =CSi), 93.5 (br 1:1:1:1 q, ¹J_{CB} = 39.8 Hz, =CH), 23.3 (Me), -0.4 (¹J_{SiC} = 56.4 Hz, SiMe₃). ²⁹Si DEPT (119 MHz, C₆D₆, 299 K): δ -10.0 ($\nu_{1/2} \sim 3$ Hz). ¹¹B{¹H} NMR (192 MHz, C₆D₆, 299 K): δ -24.7 ($\nu_{1/2} \sim 15$ Hz). ¹¹B NMR (192 MHz, C₆D₆, 299 K): δ -24.7 ($\nu_{1/2} \sim 25$ Hz). ¹⁹F NMR (564 MHz, C₆D₆, 299 K): δ -134.0 (m, 2F, *o*-C₆F₅), -158.5 (t, ³J_{FF} = 20.9 Hz, 1F, *p*-C₆F₅), -163.9 (m, 2F, *m*-C₆F₅), [$\Delta\delta^{19}\text{F}_{m,p} = 5.4$].

X-ray Crystal Structure Analysis of Complex 7d. Formula C₃₂H₂₅BF₁₀SiZr, *M* = 729.64, pale yellow crystal, 0.35 × 0.15 × 0.02 mm, *a* = 10.4621(2), *b* = 14.9667(3), *c* = 19.5364(4) Å, β = 96.105(1)°, *V* = 3041.7(1) Å³, $\rho_{\text{calc}} = 1.593$ g·cm⁻³, $\mu = 0.485$ mm⁻¹, empirical absorption correction (0.848 ≤ *T* ≤ 0.990), *Z* = 4, monoclinic, space group *P*_{2₁/n (No. 14), $\lambda = 0.71073$ Å, *T* = 223(2) K, ω and φ scans, 17 327 reflections collected ($\pm h$, $\pm k$, $\pm l$), [($\sin \theta$)/ λ] = 0.59 Å⁻¹, 5142 independent (*R*_{int} = 0.052) and 4381 observed reflections [*I* > 2 σ (*I*)], 410 refined parameters, *R* = 0.055, *wR*² = 0.139, max (min) residual electron density 0.84 (-0.39) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.}

Preparation of Complex 9. A toluene (2 mL) solution of 2-methyl-4-trimethylsilyl-1-butene-3-yne (50.0 mg, 0.36 mmol, 1.2 equiv) was added to a dark red solution of 3 (200 mg, 0.30 mmol) in the same solvent (3 mL). The reaction mixture was stirred at room temperature and after 1 h the dark red color of the reaction mixture was changed to yellowish-brown. After this time, all volatiles were removed under reduced pressure and the obtained material was washed with *n*-pentane (3 mL). Compound 9 was isolated as a yellow solid (220 mg, 0.27 mmol, 76%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane solution of 9 at -35 °C. Analysis calcd for C₃₅H₃₃BF₁₀Si₂Zr: C, 52.43; H, 4.15. Found: C, 52.37; H, 4.24. ¹H NMR (500 MHz, C₆D₆, 299 K): δ = 5.49 (s, 5H, Cp^a), 5.37 (s, 5H, Cp^b), 2.94 (d, ²J_{HH} = 15.3 Hz, 1H, CH₂), 2.24 (d, ²J_{HH} = 15.3 Hz, 1H, CH₂), 1.86 (s, 3H, Me), 0.28 (br s, ²J_{SiH} = 6.8 Hz, 9H, =SiMe₃), 0.15 (s, ²J_{SiH} = 6.6 Hz, 9H, =SiMe₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, 299 K): δ = 157.5 (br, =CB), 150.3 (=C=), 138.4 (=CZr), 127.1 (=CMe), 110.6 (Cp^a), 109.5 (Cp^b), 95.8 (=CSi), 34.9 (br, CH₂), 23.6 (Me), 1.7 (br, ¹J_{SiC} = 56.5 Hz, =SiMe₃), 1.0 (¹J_{SiC} = 54.0 Hz, =SiMe₃), [C₆F₅ not listed; tentatively assigned]. ²⁹Si DEPT (99 MHz, C₆D₆, 299 K): δ -2.6 ($\nu_{1/2} \sim 2$ Hz, =Si), -4.1 ($\nu_{1/2} \sim 2$ Hz, =Si). ¹¹B{¹H} NMR (160 MHz, C₆D₆, 299 K): δ -14.9 ($\nu_{1/2} \sim 70$ Hz). ¹¹B NMR (160 MHz, C₆D₆, 299 K): δ -14.9 ($\nu_{1/2} \sim 80$ Hz). ¹⁹F NMR (470 MHz, C₆D₆, 299 K): δ -130.7 (m, 2F, *o*), -160.4 (t, ³J_{FF} = 20.6 Hz, 1F, *p*), -164.9 (m, 2F, *m*)(C₆F₅), -130.9 (2F, *o*), -159.7 (t, ³J_{FF} = 20.7 Hz, 1F, *p*), -164.4 (m, 2F, *m*)(C₆F₅), [$\Delta\delta^{19}\text{F}_{m,p} = 4.5$, $\Delta\delta^{19}\text{F}_{m,p} = 4.7$].

X-ray crystal Structure Analysis of Complex 9. Formula $C_{35}H_{33}BF_{10}Si_2Zr$, $M = 801.82$, yellow crystal, $0.20 \times 0.10 \times 0.10$ mm, $a = 14.3941(3)$, $b = 10.2369(3)$, $c = 23.7522(5)$ Å, $\beta = 91.691(2)^\circ$, $V = 3498.4(2)$ Å³, $\rho_{\text{calc}} = 1.522$ g·cm⁻³, $\mu = 0.461$ mm⁻¹, empirical absorption correction ($0.913 \leq T \leq 0.955$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 25 995 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.59$ Å⁻¹, 6105 independent ($R_{\text{int}} = 0.047$) and 4883 observed reflections [$I > 2\sigma(I)$], 563 refined parameters, $R = 0.051$, $wR^2 = 0.126$, max (min) residual electron density 1.42 (−0.43) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 10. A toluene (1 mL) solution of 1,4-bis(trimethylsilyl)buta-1,3-diyne (30.0 mg, 0.15 mmol, 1 equiv) was added to a dark red solution of complex 3 (100 mg, 0.15 mmol) in the same solvent (1 mL). The dark red color of the reaction mixture was changed to light yellow. The reaction mixture was stirred for 5 min at room temperature. Then all volatiles were removed under reduced pressure and the obtained material was washed with *n*-pentane (5 mL). Compound 10 was isolated as a light yellow solid (103 mg, 0.122 mmol, 82%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated toluene solution of 10 at room temperature. Analysis calcd for $C_{37}H_{37}BF_{10}Si_3Zr$: C, 51.80; H, 4.35. Found: C, 53.49; H, 4.46. ¹H NMR (500 MHz, C_6D_6 , 299 K): $\delta = 5.42$ (s, 10H, Cp), 0.20 (s, ²J_{SiH} = 6.8 Hz, 9H, ^{Zr}SiMe₃), 0.13 (s, ²J_{SiH} = 6.8 Hz, 9H, ^BSiMe₃), 0.08 (s, ²J_{SiH} = 6.8 Hz, 9H, [≡]SiMe₃). ¹³C{¹H} NMR (126 MHz, C_6D_6 , 299 K): $\delta = 192.9$ (br m, =CSi^B), 170.3, 100.3 (=C=C=), 155.1 (br m, ≡CB), 148.2 (dm, ¹J_{FC} ~ 239 Hz, C_6F_5), 140.9 (br, =CSi^{Zr}), 139.4 (dm, ¹J_{FC} ~ 242 Hz, C_6F_5), 137.6 (dm, ¹J_{FC} ~ 244 Hz, C_6F_5), 122.8 (br m, *i*- C_6F_5), 109.4 (Cp), 91.5 (br, =CSi), 1.01 (¹J_{SiC} = 56.1 Hz), 0.97 (¹J_{SiC} = 55.2 Hz) (=ZrSiMe₃), −0.8 (¹J_{SiC} = 51.8 Hz, ^BSiMe₃), [[†] tentatively assigned]. ²⁹Si DEPT (99 MHz, C_6D_6 , 299 K): $\delta = -4.5$ ($\nu_{1/2} \sim 2$ Hz, [≡]Si), −4.8 (^BSi), −5.0 ($\nu_{1/2} \sim 2$ Hz, ^{Zr}Si). ¹¹B{¹H} NMR (160 MHz, C_6D_6 , 299 K): $\delta = -11.1$ ($\nu_{1/2} \sim 70$ Hz). ¹¹B NMR (160 MHz, C_6D_6 , 299 K): $\delta = -11.1$ ($\nu_{1/2} \sim 80$ Hz). ¹⁹F NMR (470 MHz, C_6D_6 , 299 K): $\delta = -130.0$ (m, 2F, *o*- C_6F_5), −159.5 (t, ³J_{FF} = 20.7 Hz, 1F, *p*- C_6F_5), −164.9 (m, 2F, *m*- C_6F_5), [$\Delta\delta^{19}F_{m,p} = 5.4$].

X-ray Crystal Structure Analysis of Complex 10. Formula $C_{37}H_{37}BF_{10}Si_3Zr \cdot 1.5 \times C_6H_6$, $M = 975.13$, yellow crystal, $0.30 \times 0.20 \times 0.13$ mm, $a = 11.4217(1)$, $b = 12.4543(1)$, $c = 18.0412(3)$ Å, $\alpha = 91.971(1)^\circ$, $\beta = 102.497(1)^\circ$, $\gamma = 108.450(1)^\circ$, $V = 2362.05(5)$ Å³, $\rho_{\text{calc}} = 1.371$ g·cm⁻³, $\mu = 0.379$ mm⁻¹, empirical absorption correction ($0.894 \leq T \leq 0.952$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 21 729 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.59$ Å⁻¹, 8153 independent ($R_{\text{int}} = 0.038$) and 7602 observed reflections [$I > 2\sigma(I)$], 559 refined parameters, $R = 0.039$, $wR^2 = 0.096$, max (min) residual electron density 0.32 (−0.48) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 15. A toluene (1 mL) solution of ethynyl(dimesityl)phosphane (67.0 mg, 0.22 mmol) was added to complex 3 (150 mg, 0.22 mmol) in the same solvent (2 mL). The reaction mixture was stirred at room temperature for 3 h, during this time the dark red color of the reaction mixture changed to red. Then all volatiles were removed under reduced pressure and the obtained material was washed with cold *n*-pentane (5 mL). Compound 15 was isolated as a red solid (160 mg, 0.167 mmol, 74%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane solution of 15 at −35 °C. Analysis calcd for $C_{47}H_{42}BF_{10}PSiZr$: C, 58.93; H, 4.42. Found: C, 59.22; H, 4.57. ¹H NMR (600 MHz, C_6D_6 , 299 K): $\delta = 6.90$ (br, 1H, *m*-Mes^a), 6.62 (br, 1H, *m*-Mes^b), 6.56 (d, ⁴J_{PH} = 5.8 Hz, 2H, *m'*-Mes^{a,b}), 5.51 (d, $J = 0.5$ Hz, 5H, Cp^a), 5.02 (s, 5H, Cp^b), 3.37 (s, 3H, *o*-Me^{Mes^a}), 2.97 (d, ³J_{PH} = 24.0 Hz, 1H, CH), 2.77 (s, 3H, *o*-Me^{Mes^b}), 2.64 (s, 3H, *o'*-Me^{Mes^b}), 2.15 (s, 3H, *p*-Me^{Mes^a}), 1.99 (d, $J = 2.4$ Hz, 3H, *o'*-Me^{Mes^a}), 1.94 (s, 3H, *p*-Me^{Mes^b}), 0.06 (s, ²J_{SiH} = 6.8 Hz, 9H, SiMe₃). ¹³C{¹H} NMR (126 MHz, C_6D_6 , 299 K): $\delta = 145.7$ (d, ²J_{FC} = 4.6 Hz, *o*-Mes^b), 145.7 (d, ²J_{FC} = 39.8 Hz, *o'*-Mes^b), 143.0 (d, ²J_{FC} = 2.7 Hz, *o*-Mes^a), 142.0 (d, ²J_{FC} = 36.5 Hz, *o'*-Mes^a), 139.7 (d, ⁴J_{FC} = 1.4 Hz, *p*-Mes^b), 138.0 (*p*-Mes^a), 132.0 (*m*-Mes^a), 131.5 (*m*-Mes^b), 131.0 (d, ¹J_{FC} = 29.2 Hz, *i*-Mes^a), 130.0 (d, ²J_{FC} = 3.4 Hz, =C=), 129.9 (d, ³J_{FC} = 6.5 Hz, *m'*-

Mes^a), 129.5 (d, ³J_{FC} = 7.8 Hz, *m'*-Mes^b), 128.8 (d, ¹J_{PC} = 20.1 Hz, *i*-Mes^b), 124.7 (=CSi), 107.5 (Cp^b), 105.9 (m, Cp^a), 100.9 (d, ¹J_{PC} = 30.7 Hz, =CP^a), 90.7 (br m, CH), 25.5 (br, *o*-Me^{Mes^a}), 23.9 (*o*-Me^{Mes^b}), 23.3 (d, ³J_{PC} = 30.4 Hz, *o'*-Me^{Mes^b}), 22.9 (d, ³J_{PC} = 30.1 Hz, *o'*-Me^{Mes^a}), 20.74 (*p*-Me^{Mes^b}), 20.68 (*p*-Me^{Mes^a}), 1.4 (¹J_{SiC} = 54.7 Hz, SiMe₃), [C_6F_5 not listed; [†] tentatively assigned]. ²⁹Si DEPT (119 MHz, C_6D_6 , 299 K): $\delta = -6.5$ (d, ⁴J_{PSi} = 2.4 Hz). ³¹P{¹H} NMR (243 MHz, C_6D_6 , 299 K): $\delta = -25.1$ (d, ³J_{PF} ~ 21.9 Hz). ³¹P{¹H, ¹⁹F_{sat}: −127.9} NMR (243 MHz, C_6D_6 , 299 K): $\delta = -25.0$ ($\nu_{1/2} \sim 4$ Hz). ³¹P NMR (243 MHz, C_6D_6 , 299 K): $\delta = -25.1$ (br t, ³J_{PH} ~ 22 Hz). ¹¹B{¹H} NMR (192 MHz, C_6D_6 , 299 K): $\delta = 40.0$ ($\nu_{1/2} \sim 1000$ Hz). ¹¹B NMR (192 MHz, C_6D_6 , 299 K): $\delta = 40.0$ ($\nu_{1/2} \sim 1100$ Hz). ¹⁹F NMR (564 MHz, C_6D_6 , 299 K): $\delta = -127.9$ (m, *o*), −129.9 (m, *o'*), −158.3 (t, ³J_{FF} = 20.5 Hz, *p*), −163.0 (m, *m'*), −165.0 (m, *m*) (each 1F, C_6F_5), −130.7 (br m, 2F, *o*), −154.7 (t, ³J_{FF} = 20.9 Hz, 1F, *p*), −162.4 (br, 2F, *m*) (C_6F_5), [$\Delta\delta^{19}F_{m,p} = 4.7, 6.7, \Delta\delta^{19}F_{m,p} = 7.7$].

X-ray Crystal Structure Analysis of Complex 15. Formula $C_{47}H_{42}BF_{10}PSiZr$, $M = 957.90$, red crystal, $0.12 \times 0.08 \times 0.05$ mm, $a = 12.3208(2)$, $b = 18.0860(3)$, $c = 19.0287(5)$ Å, $\beta = 97.545(1)^\circ$, $V = 4203.5(2)$ Å³, $\rho_{\text{calc}} = 1.514$ g·cm⁻³, $\mu = 0.407$ mm⁻¹, empirical absorption correction ($0.952 \leq T \leq 0.979$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 29 228 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.59$ Å⁻¹, 7310 independent ($R_{\text{int}} = 0.077$) and 5313 observed reflections [$I > 2\sigma(I)$], 563 refined parameters, $R = 0.069$, $wR^2 = 0.162$, max (min) residual electron density 0.73 (−0.47) e·Å⁻³, the hydrogen at C4 atom was refined freely; others were calculated and refined as riding atoms.

Preparation of Complex 16. Under the exclusion of light toluene (3 mL) was added to a mixture of toluene (22.0 mg, 0.12 mmol, 1 equiv) and complex 3 (80.0 mg, 0.12 mmol) at −70 °C. The reaction mixture was stirred at −70 °C for 30 min. Then the reaction solution was warmed to room temperature and stirred for another 40 min. After this time all volatiles were removed under reduced pressure and the obtained material was washed with cold *n*-pentane (3 mL). Compound 16 was isolated as a dark violet solid (80.0 mg, 0.095 mmol, 79%). Crystals suitable for the X-ray crystal structure analysis were obtained by crystallization of a saturated *n*-pentane solution of 16 at −35 °C. Analysis calcd for $C_{41}H_{29}BF_{10}SiZr$: C, 58.50; H, 3.47. Found: C, 58.00; H, 3.31. ¹H NMR (600 MHz, C_7D_8 , 213 K): $\delta = 7.82$ (1H, *o*), 7.24 (1H, *m*), 6.99 (1H, *o*), 6.83 (2H, *m/p*) (each m, Ph), 7.11(*o*), 6.86(*m*), 6.57(*m*), 6.31(*p*), 5.21(*o*) (br m, each 1H, Ph^{Zr}), 4.74 (s, 5H, Cp^a), 4.66 (s, 5H, Cp^b), 0.30 (s, 9H, SiMe₃). ¹³C{¹H} NMR (151 MHz, C_7D_8 , 213 K): δ n.o. (=C=, C=B), 159.8(*i*), 141.2(*m*), 137.9(*m*), 125.4(*o*), 118.6(*p*), 83.6(*o*) (Ph^{Zr}), 139.2(*i*), 130.1(*o*), 129.7(*m*), 127.9(*p*)¹, 127.7(*m*)¹, 122.3(*o*) (Ph), 115.7 (=CPh), 132.4 (¹J_{SiC} = 64.6 Hz, =CSi), 110.1 (Cp^b), 109.3 (Cp^a), 0.8 (¹J_{SiC} = 54.2 Hz, SiMe₃), [C_6F_5 not listed; [†] tentatively assigned; ¹ from the ghmbc experiment]. ¹¹B{¹H} NMR (192 MHz, C_7D_8 , 213 K): $\delta = 34.5$ ($\nu_{1/2} \sim 1300$ Hz). ¹¹B NMR (192 MHz, C_7D_8 , 213 K): $\delta = 34.5$ ($\nu_{1/2} \sim 1300$ Hz). ²⁹Si DEPT (119 MHz, C_7D_8 , 213 K): $\delta = -3.0$ ($\nu_{1/2} \sim 1$ Hz). ¹⁹F NMR (564 MHz, C_7D_8 , 213 K): $\delta = -130.8$, −132.2 (each 1F, *o*), −156.7 (1F, *p*), −162.5 (2F, *m*) (each br, BC_6F_5), [$\Delta\delta^{19}F_{m,p} = 5.8$ Hz], −131.6 (2F, *o*), −157.6 (1F, *p*), −163.7, −164.7 (each 1F, *m*) (each br, BC_6F_5), [$\Delta\delta^{19}F_{m,p} = 6.1, 7.1$ Hz].

X-ray Crystal Structure Analysis of Complex 16. Formula $C_{41}H_{29}BF_{10}SiZr$, $M = 841.76$, red crystal, $0.12 \times 0.07 \times 0.02$ mm, $a = 35.8746(3)$, $b = 10.5981(1)$, $c = 23.2071(3)$ Å, $\beta = 125.385(1)^\circ$, $V = 7193.53(13)$ Å³, $\rho_{\text{calc}} = 1.554$ g·cm⁻³, $\mu = 0.422$ mm⁻¹, empirical absorption correction ($0.951 \leq T \leq 0.991$), $Z = 8$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 29 228 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.59$ Å⁻¹, 7302 independent ($R_{\text{int}} = 0.077$) and 5631 observed reflections [$I > 2\sigma(I)$], 490 refined parameters, $R = 0.048$, $wR^2 = 0.098$, max (min) residual electron density 0.30 (−0.36) e·Å⁻³, hydrogen atoms calculated and refined as riding atoms.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details and physical characterization of the new compounds, crystallographic data, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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