

Internal Fluorocarbon Coordination as a Tool for the Protection of Active Catalytic Sites: Experimental Characterization of the $Zr\cdots F-C$ Interaction in the Group 4 Metallocene(butadiene)/ $B(C_6F_5)_3$ Betaine Ziegler Catalyst Systems

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Abstract: The Lewis acid tris(pentafluorophenyl)borane adds to the (butadiene)group 4 metallocenes **1a–d** (metallocene = Cp_2Zr , Cp_2Hf , $(MeCp)_2Zr$, $(Me_3CCp)_2Zr$) to give the metallocene–($\mu-C_4H_6$)–borate–betaine complexes **2a–d**. (Isoprene)zirconocene (**1e**) and (2-phenylbutadiene)zirconocene (**1f**) add the $B(C_6F_5)_3$ reagent regioselectively at the carbon atom C-4 to give the complexes **2e** and **2f**, respectively. The complexes **2** all show a pronounced $M\cdots F-C$ interaction with one of the six ortho- $B(C_6F_5)_3$ fluorine atoms. The resulting metallacyclic structures were characterized by X-ray diffraction of the complexes **2c** and **2e** ($Zr\cdots F \approx 2.40$ Å, angle $Zr-F-C \approx 140^\circ$). The bridging fluorine atom of the complexes in solution is characterized by an extreme upfield shift of its ^{19}F NMR resonance ($\delta \approx -210$ to -220 ppm) relative to the signals of the remaining five *o*-F resonances of the $B(C_6F_5)_3$ moiety (average $\delta \approx -135$ ppm). The ^{19}F NMR spectra of the complexes **2** are dynamic even in the noncoordinating solvent toluene- d_8 . All six *o*-fluorine signals equilibrate with coalescence temperatures around 240 K at 564 MHz to give a single resonance signal at high temperature. This fluorine equilibration process of the $-B(C_6F_5)_3$ end of the metallocene–borate–betaine complexes **2** is very likely to proceed via a rate determining cleavage of the coordinative $M\cdots F-C$ interaction. From the activation barrier of this process, obtained from the dynamic fluorine NMR spectra, $Zr\cdots F$ bond dissociation energies of ca. 8.5 kcal/mol were estimated for the complexes **2**. This magnitude of the $M\cdots F-C$ bond dissociation energy makes the internal fluorocarbon coordination a very suitable tool for protecting active electrophilic metal catalyst centers. The $Zr\cdots F-C$ bond of the complexes **2** is cleaved by the addition of the donor solvent THF with formation of acyclic 1,2- η^2 -allyl metallocene complexes.

Introduction

Hydrocarbyl group 4 metallocene cations, such as, e.g., Cp_2Zr-R^+ , are the active catalytic synthons in the homogeneous metallocene Ziegler catalysts.^{1,2} However, such very electrophilic metal complexes usually require some coordinative stabilization that results in a reduction of the electron deficiency at the metal center and thus in an increased electronic stabilization. Donor ligand addition would be an obvious way of stabilization, but this usually leads to catalytically unreactive

derivatives.^{2,3} More subtle stabilization includes the formation of ion pairs⁴ (e.g., **A** in Scheme 1)⁵ or the occurrence of an agostic interaction with an adjacent C–H bond (**B**).^{6,7} These modes of stabilizing Cp_2ZrR^+ systems have the great advantage that the catalytic activity is only marginally disturbed because these types of coordinative interactions appear to be readily cleaved in the presence of a reactive α -olefin. The interaction of the Cp_2ZrR^+ type species with C–F bonds probably is of a similar quality, resulting in an appreciable protection of the catalyst center in the dormant stage but allowing for low activation barrier decomplexation routes to be followed when necessary, e.g., upon the addition of an α -olefin monomer. A typical example of such a system is the ion pair **C**.^{4a,8} These potentially useful features of C–F bonds as protective groups in active catalyst precursors have recently led to a much

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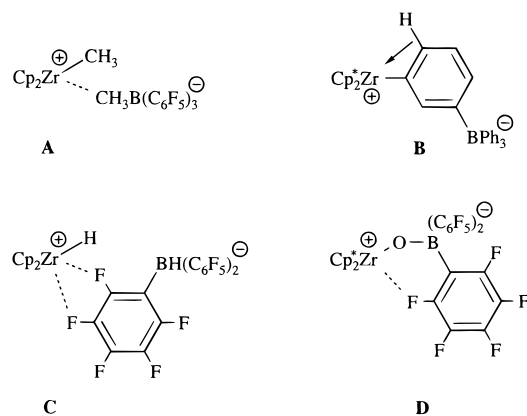
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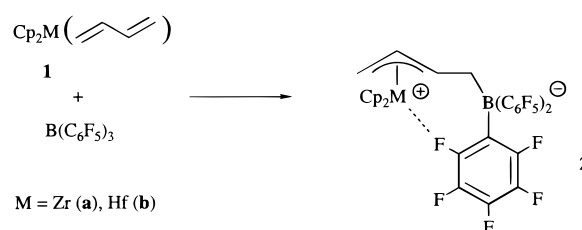
Scheme 1



increased general interest in the structural features and chemical properties of the metal \cdots F–C interaction in general.⁹ Potentially useful structural model compounds are, e.g., catalytically inactive early transition metal complexes such as **D** (see Scheme 1).^{10a}

We have recently described in a preliminary communication the zirconium complex **2a** (and its hafnium analogue). It represents a neutral dipolar organometallic catalyst system where the metallocene cation moiety is intramolecularly stabilized by a pronounced M \cdots F–C coordinative interaction.¹¹ The met-

allocene–borate–betaine system **2a** is readily formed upon the addition of the organometallic Lewis acid B(C₆F₅)₃¹² to (butadiene)zirconocene (**1a**)¹³ in a 1:1 molar ratio. Boron adds to a terminal butadiene carbon atom with formation of a metalla-cyclic (π -allyl)zirconocene complex¹⁴ that contains a Zr \cdots F–C(sp²) coordination. Complex **2a** was characterized by X-ray diffraction, and the presence of a bridging, two-coordinate fluorine atom was also revealed by ¹⁹F NMR spectroscopy^{10b} at low temperature. Addition of ethene or propene to **2a** (or the hafnium analogue **2b**) at ambient temperature resulted in the rapid formation of the respective α -olefin polymers.¹¹ We have now prepared a number of additional examples of the betaine complex type **2** with the aim of learning on an experimental basis about the nature of the metal \cdots F–C interaction¹⁵ in these complexes and its behavior. We especially hoped to arrive at a reliable estimate of the bond dissociation energy of the group 4 metal to fluorine interaction in such a coordinative situation. This was achieved using a suited series of group 4 metallocene(conjugated diene)/B(C₆F₅)₃ addition products. The results of this study are described in this article.



Synthesis and Structural Characterization of the Metallocene–Borate–Betaine Systems **2**

The metallocene–borate–betaine complexes **2a–f** were all prepared by treatment of the respective (conjugated diene) group 4 metallocene complexes **1**¹³ with an equimolar quantity of B(C₆F₅)₃ at ambient temperature. Toluene was usually employed in the preparations under donor ligand free conditions. Often the product precipitated or crystallized from the reaction solution after some period of time (usually over several days), although the addition reaction itself was instantaneous under these conditions, as revealed by experiments under direct NMR control in toluene-*d*₈. Once the products **2** were precipitated and isolated as pure solids (usually obtained in good yield, e.g., **2a**: 76%, **2c**: 78%) they are characterized by a very poor solubility in the aromatic solvent. Therefore, most of the NMR data were obtained from oversaturated solutions of the complexes **2**, generated in situ in toluene-*d*₈ from **1** and B(C₆F₅)₃. The complexes **2d** and **2f** were not isolated, but only generated in situ in the deuterated solvent and characterized spectroscopically. The parent complexes **2a** and **2b** had been described by us in a preliminary communication,¹¹ including the X-ray crystal structure analysis of **2a**. Complexes **2c** and **2e** were isolated and obtained as single crystals allowing characterization of these

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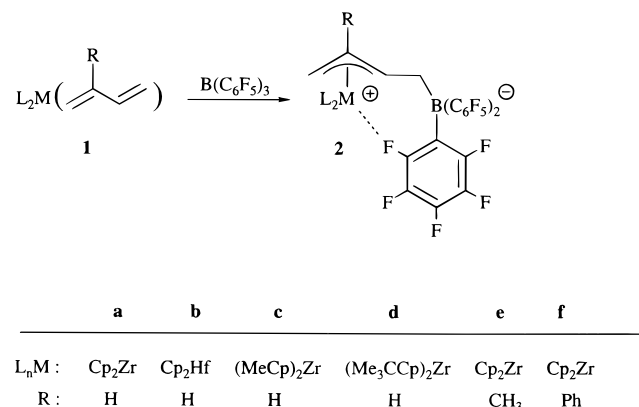
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additional examples also by X-ray diffraction. This experimental material provided a sound basis of the general structural characterization of this novel class of organometallic betaine complexes.

Scheme 2



The X-ray crystal structure analysis of complex **2c** shows a distorted pseudotetrahedral arrangement of ligands around zirconium.¹⁶ The (MeCp)₂Zr bent metallocene unit exhibits a conformation with one methyl group pointing to the front side of the bent metallocene wedge and the other oriented toward a lateral sector ("central,lateral:gauche" orientation).¹⁷ Carbon atoms C1, C2, and C3 of the former butadiene ligand form a distorted π-allyl group¹⁸ that is bonded to the transition metal in a central position at the front side of the bent metallocene wedge. The Zr–C1 bond is short at 2.369(4) Å. The Zr–C2 (2.512(4) Å) and Zr–C3 (2.687(3) Å) bonds are somewhat longer. The corresponding carbon–carbon distances (C1–C2 1.429(5) Å, C2–C3 1.350(5) Å) are quite different from each other, but this is a typical situation that is often encountered in substituted (π-allyl)zirconocene systems which appear to have a marked tendency toward such an unsymmetric coordination to zirconium.¹⁸

The C3–C4 bond is *syn*-attached at the distorted (π-allyl)-Zr(CpMe)₂ moiety. The C3–C4 bond length is as expected

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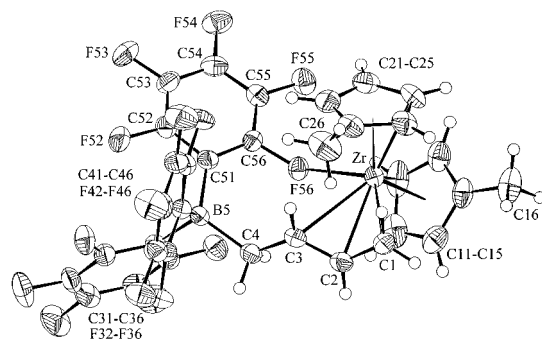


Figure 1. A view of the molecular geometry of the metallocene–borate–betaine complex **2c** in the crystal. Selected bond lengths (Å) and angles (deg): Zr–C1 2.369(4), Zr–C2 2.512(4), Zr–C3 2.687(3), Zr–C4 3.750(3), Zr–F56 2.408(2), C1–C2 1.429(5), C2–C3 1.350(5), C3–C4 1.510(5), C4–B5 1.644(5), B5–C51 1.651(5), B5–C41 1.651(5), B5–C31 1.664(5), C56–F56 1.379(4); C2–C1–Zr 78.5(2), C1–C2–Zr 67.6(2), C3–C2–Zr 82.3(2), C3–C2–C1 124.6(4), C2–C3–C4 125.2(3), C2–C3–Zr 67.8(2), C4–C3–Zr 124.2(2), C3–C4–B5 118.0(3), C56–F56–Zr 142.6(2).

for such a C(sp²)–C(sp³) linkage (1.510(5) Å).¹⁹ There is no indication of any significant C4···Zr interaction (3.750(3) Å). The B(C₆F₅)₃ group is bonded to the carbon atom C4 (B–C4: 1.644(5) Å). The three planar C₆F₅ substituents are linked to the central pseudotetrahedral boron atom in a propeller-like arrangement.²⁰ The most noteworthy structural feature of **2c** is, however, the coordination of a single *o*-fluorine atom (F56, see Figure 1) of one of the pentafluorophenyl groups at boron to the electrophilic zirconium center. Coordination of the C–F moiety through the halogen atom is indicated by the observed small F56–Zr distance (2.408(2) Å).²¹ The corresponding C56–F56 bond is slightly longer (1.379(4) Å) as compared to the average C–F bonds in **2c** (1.350 Å; the average of the remaining five ortho–C–F bonds in **2c** is 1.364 Å; the adjacent *m*-C–F bond is not interacting with zirconium, the Zr···F55 separation is 4.104 Å). The bond angle at the *μ*-F atom is 142.6(2)° (C56–F56–Zr). The C–F bond coordinates to the zirconium center in a lateral position.²² The C–F···Zr coordination closes the metallacyclic ring structure of the zirconocene–borate–betaine complex **2c**.

The addition reaction of the B(C₆F₅)₃ to (isoprene)zirconocene (**1e**) raises the question of the preferred regiochemistry. A single addition product is obtained. The X-ray crystal structure analysis identifies the obtained single regioisomer (**2e**) as bearing the methyl group at the *meso*-position (i.e., C2) of the resulting π-allyl ligand.²³ The framework of the isoprene-derived metallocene-betaine complex **2e** is almost identical to that of **2c** (see Table 1). The η³-allyl ligand is equally distorted and there

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Table 1. A Comparison of Selected Structural Parameters of Metallocene–Borate–Betaine Complexes **2** and **3**^a

	2a ^b	2c ^c	2e ^c	3 ^d
C1–C2	1.414(9)	1.430(5)	1.439(4)	1.426(6)
C2–C3	1.342(8)	1.350(5)	1.368(3)	1.362(6)
C3–C4	1.521(8)	1.510(5)	1.506(3)	1.500(6)
C4–B	1.633(9)	1.644(5)	1.649(4)	1.670(6)
C1–C2–C3	123.5(6)	124.6(4)	119.8(2)	126.3(4)
C2–C3–C4	126.9(6)	125.2(3)	126.7(2)	124.3(4)
C3–C4–B	119.0(5)	118.0(3)	117.1(2)	113.9(3)
Zr–C1	2.339(5)	2.369(4)	2.356(3)	2.337(4)
Zr–C2	2.494(6)	2.512(4)	2.580(2)	2.488(4)
Zr–C3	2.710(5)	2.687(3)	2.651(2)	2.722(4)
Zr···F	2.423(3)	2.408(2)	2.402(1)	
C– ^μ F	1.402(6)	1.379(4)	1.388(3)	
Zr– ^μ F–C	140.0(3)	142.6(2)	137.4(1)	

^a Bond lengths in Å, angles in deg. ^b From ref 11. ^c This work. ^d From ref 24.

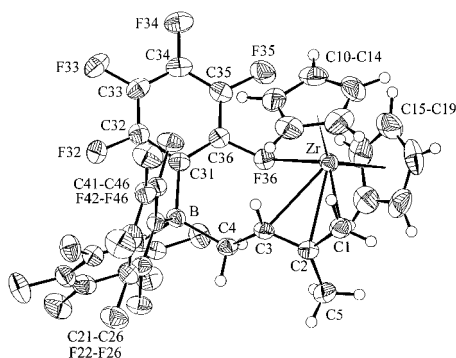
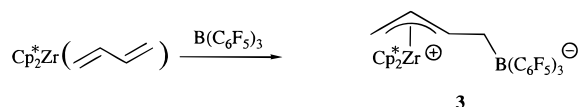


Figure 2. Molecular structure of **2e**. Selected bond lengths (Å) and angles (deg): Zr–C1 2.356(3), Zr–C2 2.580(2), Zr–C3 2.651(2), Zr–C4 3.760(2), Zr–F36 2.4020(14), Zr···F35 4.104, C1–C2 1.439(4), C2–C3 1.368(3), C3–C4 1.506(3), C2–C5 1.508(4), C4–B 1.649(4), B–C41 1.656(4), C–B31 1.658(4), B–C21 1.667(3), C36–F36 1.389(3); C2–C1–Zr 81.8(2), C1–C2–Zr 64.69(14), C3–C2–Zr 77.73(14), C3–C2–C1 119.8(2), C2–C3–C4 126.7(2), C2–C3–Zr 71.98(14), C4–C3–Zr 127.4(2), C3–C4–B 117.1(2), C36–F36–Zr 137.35(13).

is a strong C–F···Zr coordination that results in the formation of a metallacyclic ring structure (see Figure 2).

The characteristic bonding parameters of the complexes **2c** and **2e** compare well with those of the parent complex **2a**¹¹ (see Table 1). Structurally, the intramolecular coordination of the ortho C₆F₅ C–F bond to a lateral zirconocene coordination site results in typical F···Zr bond distances of 2.40–2.42 Å. The corresponding C–F bonds are slightly elongated (by ca. 0.02 Å) in the coordinated situation. The resulting bonding angle at the bridging fluorine atom (i.e., C–F–Zr) is close to 140°. The substituted (π -allyl) moiety is distorted as it is typically found in many such metallocene complexes, irrespective of the presence of an internal C–F···Zr interaction. This is evident from a comparison of the respective structural data of the complexes **2a**, **2c** and **2e** with those of the related complex **3**,²⁴ where the presence of the bulky pentamethylcyclopentadienyl ligand has sterically prohibited the formation of the C–F···Zr bond (see Table 1).



Spectroscopic Characterization and Dynamic Features

In toluene-*d*₈ solution the complexes **2** (and **3**) are chiral as it is revealed by their typical NMR spectra. This indicates the

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Table 2. Selected ¹H NMR Resonances of the H₂C¹C²HC³HC⁴H₂[B] Ligand System of the Complexes **2** and **3**^a

compd	1-H	1-H'	2-H	3-H	4-H,H'	ref
2a	1.47	1.85	5.88	5.23	2.25, 2.56	11
2b	1.11	1.57	6.04	5.25	2.29, 2.95	11
2c	1.44	1.75	5.87	4.85	2.17, 2.41	<i>b</i>
2d	1.50	3.03	6.22	6.38	1.89, 2.62	<i>b</i>
2e	0.68	2.46		4.23	–1.87, –0.27	<i>b</i>
2f	0.83	3.21		5.02	–1.73, 0.17	<i>b</i>
3	0.80	2.99	6.36	5.68	1.68, 2.28	24

^a In toluene-*d*₈ at ambient temperature. ^b This work.

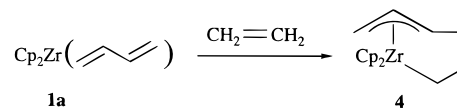
Table 3. Selected ¹³C NMR Data of the Substituted Distorted π -Allyl Ligand System of the Complexes **2** and **3**^a

compd	C-1	C-2	C-3	C-4	ref
2a	52.7	131.8	123.8	28.5	11
2b	50.7	132.0	123.6	<i>b</i>	11
2c	53.7	134.6	120.3	26.6	<i>c</i>
2d	60.3	136.0	127.5	<i>b</i>	<i>c</i>
2e	59.8	145.1	109.7	<i>b</i>	<i>c</i>
2f	60.2	147.3	107.0	24.7	<i>c</i>
3	75.4	144.5	125.0	30.4	24

^a In toluene-*d*₈ at ambient temperature. ^b Not observed. ^c This work.

presence of the (distorted) η^3 -allyl coordination geometry also in solution. Each complex exhibits the ¹H/¹³C NMR resonances of a pair of diastereotopic (η^5 -R–C₅H₄)-ligands. The ¹H NMR spectra show the inequivalency of the 1–H,H' resonances²⁵ but are not overly informative for a further detailed structural characterization and mutual comparison due to rather pronounced anisotropies that arise specifically from alterations of the substitution pattern (see Table 2).

The ¹³C NMR spectra are more characteristic in this respect. It is noteworthy that the broad C–4 ¹³C NMR resonances, when they can be located despite significant broadening by the adjacent boron nucleus, are all in a rather close range between ca. δ 25 and 28 ppm. This indicates that there is indeed no significant C⁴H₂–[B]/Zr ion pair interaction present in the complexes **2**.²⁶ The distorted π -allyl ligand is characterized by the C–2 and C–3 ¹³C NMR carbon resonances being rather close together, with the C–2 resonance usually being observed at somewhat larger δ -values (see Table 3). The respective ¹³C NMR π -allyl resonances of the model compound **4** (i.e., the 1:1 reaction product between (butadiene)zirconocene and ethylene) were previously determined as δ 35.9 (C–1), 120.1 (C–2), and 116.2 (C–3) ppm (with ¹J_{CH}-coupling constants in a uniform range: 147 Hz (C–1/H), 144 Hz (C–2/H), and 144 (C–3/H)²⁷).



The complexes **2** all contain a C–F···Zr interaction in solution. This is evident from the very typical ¹⁹F NMR spectra at low temperature. As a typical example the (CH₃–C₅H₄)₂Zr (μ -C₄H₆)-B(C₆F₅)₃ betaine **2c** exhibits different ¹⁹F NMR signals for all but one accidentally isochronous pair of fluorine atoms. A total of 14 separate ¹⁹F NMR signals of the B(C₆F₅)₃ group of complex **2c** are thus observed in toluene-*d*₈ at –80 °C,

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Table 4. ¹⁹F NMR Data of the Complexes **2** under “Static Conditions” and Activation Barriers of the Degenerate Rearrangement Leading to Combined Pairwise/Triple Exchange of *o*-, *m*-, and *p*-Fluorene Resonances^a

compd	T(K)	static situation						dynamic		
		<i>o</i> -F _{M-F}		<i>o</i> -F		<i>m</i> -F		<i>p</i> -F	T _c (K)	Δν (Hz)
2a	193	-213.2	-137.5, -134.0, -131.8, -130.6, -126.4	-165.3, -165.1, -164.7(3×), -163.6	-160.9 -159.2 -158.5	233	45 735	8.1		
2b	213	-219.5	-137.7, -134.0, -132.5, -131.3, -127.7	-166.8, -165.6(5×)	-159.6(2×) -158.9	233	52 098	8.0		
2c	193	-209.9	-137.0, -134.5, -132.6, -131.4, -127.2	-167.2, -166.6, -165.8(2×), -164.9, -162.1	-161.8 -160.5 -159.1	243	43 647	8.5		
2f	193	-214.4	-134.7, -133.8(2×), -130.5(2×)	-165.7, -165.3(3×), -162.7(2×)	-159.2 -158.9 -158.1	243	46 118	8.4		

^a In toluene-*d*₈, chemical shifts in ppm, rel. CFCl₃, δ-scale, 564 MHz.

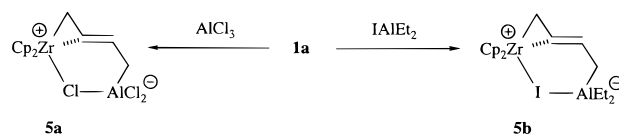
namely three *p*-fluorine signals (δ -161.8, -160.5, -159.1 ppm), five separated ¹⁹F signals originating from the six *m*-fluorine atoms [δ -167.2, -166.6, -165.8 (double intensity), -164.9, -162.1] and six *o*-fluorine resonances. The latter are separated into two groups of signals. While five of them are close together in an ordinary range (δ -137.0, -134.5, -132.6, -131.4, -127.2 ppm), the sixth resonance appears at a much lower δ value of -209.9 and is thus markedly separated from the ¹⁹F NMR chemical shifts of the other 14 C-F units. The observed extreme δ-value is characteristic of the presence of a bridging, two-coordinate fluorine atom in such an organometallic environment.¹⁰ Its observation clearly indicates that the fluorine-bridged metallacyclic structure, analogously as it was characterized in the solid state, is also favored in solution and represents the global minimum structure of the systems **2**.

The ¹⁹F NMR spectra of the complexes **2** are dynamic. Increasing the temperature from -80 °C rapidly results in broadening of all resonances and a coalescence of the respective ¹⁹F NMR signals within the ortho-, meta-, and para-F groups of resonances. Eventually, rather simple ¹⁹F NMR spectra are obtained at high temperature that contain only three (usually broad) averaged resonances for these fluorine atoms. For complex **2c** a Gibbs activation energy of ΔG[‡] (243 K) ≈ 8.5 ± 0.5 kcal/mol was estimated for the 5/1 signal exchange of the characteristic ¹⁹F NMR signals of the *o*-fluorine atoms of the three C₆F₅ ring systems at the coalescence temperature.²⁸ The analogous splitting of the ¹⁹F NMR resonances into a completely asymmetric situation is principally observed for all the complexes **2** in the noncoordinating solvent toluene-*d*₈, although the low temperature spectra are not well resolved for the complexes **2d** and **2e**. The Gibbs activation barriers of the fluorine-equilibrating degenerate rearrangement process were determined for the remaining four examples of the complex type **2** from the temperature dependent dynamic ¹⁹F NMR spectra. The respective ΔG[‡]_{automerization} values are all within a small range between 8.0 and 8.5 kcal/mol (see Table 4). As expected, the complex **3** does not show this behavior since it does not contain a bridging, two-coordinate fluorine atom.²⁴

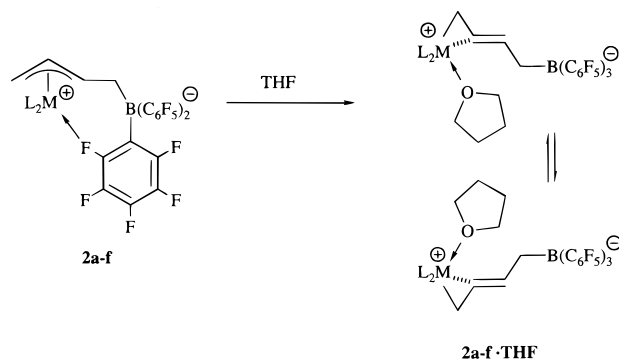
The C-F...Zr interaction does not persist in solutions of the complexes **2** in the donor solvent tetrahydrofuran. In THF-*d*₈ the (CH₃-C₅H₄)₂Zr-(μ-C₄H₆)-B(C₆F₅)₃ betaine complex **2c**·THF shows only three sharp ¹⁹F NMR resonances throughout the whole temperature range from ambient temperature to 193 K that correspond to the *o*- (δ -134.3 ppm), *m*- (δ -168.1 ppm), and *p*-fluorine atoms (δ -165.1 ppm) of the three C₆F₅ substituents that are symmetry-equivalent under these conditions. The ¹³C NMR resonances of the substituted allyl unit at

zirconium are observed at δ 45.6 (C-1), 116.0 (C-2), 143.7 (C-3), and 33.1 ppm (C-4). In THF-*d*₈ the C⁴H₂-[B] resonance of **2c**·THF is thus only slightly shifted (Δδ = + 6.5 ppm) as compared to the donor-ligand free betaine system **2c** in toluene-*d*₈ [Δδ = δ(THF-*d*₈) - δ(toluene-*d*₈)], whereas the C-2 resonance is markedly shifted to a smaller δ-value in THF-*d*₈ (δ 116.0, Δδ = -18.6 ppm) and the C-3 resonance is shifted in the opposite direction even stronger in the donor-solvent (δ 143.7, Δδ = +23.4 ppm). The donor-ligand influence on the ¹³C NMR C-1 resonance is much smaller (δ 45.6, Δδ = -8.1 ppm).

This trend is found in the whole series of the complexes **2** in THF-*d*₈. These typical shift differences (together with the observed ¹J_{CH} coupling constants, see Table 5) indicate the presence of a hitherto rather uncommon π-allyl coordination mode, where only the carbon atoms C-1 and C-2 of the allyl unit are bonded to the metal center, but the remaining sp²-



hybridized carbon atom C-3 of that unit does not show an appreciable direct metal to carbon interaction. This special type of a 1,2-η²-allyl coordination to a group 4 metal center was first detected for the dimetallic complexes **5** [¹³C NMR of **5a**: δ 42.8 (¹J_{CH} = 147 Hz, C-1), 102.6 (149 Hz, C-2), 140.5 (149 Hz, C-3), 25.4 (broad signal, C-4)], where the term “π-agostic” was proposed as a semantic description of the specific π-allyl coordination variant.²⁹



The π-interaction between carbon center C-2 and zirconium, using the characteristic set of valence orbitals at the bent

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Table 5. Selected ^{13}C NMR Data of the Complexes **2**·THF and **3** and Activation Energies of Their Enantiomerization Process^a

compd	T (K)	C-1	C-2	C-3	C-4	T_c^b	$\Delta\nu$ (Hz)	$\Delta G_{\text{inv}}^\ddagger$ ^c
2a	299	46.8 (−5.9)	114.2 (−17.6)	147.1 (+23.3)	35.0 (+6.5)	213	195	9.5
2b	299	49.3 (−1.4)	115.0 (−17.0)	147.0 (+23.4)	33.3 (d)	<i>e</i>		
2c	203	45.6 (−8.1)	116.0 (−18.6)	143.7(+23.4)	33.1(+6.5)	213	66	9.9
2d	299	48.2 (−12.1)	110.4 (−25.6)	159.3 (+31.8)	35.7 (d)	193	115	8.7
2e	299	49.2 (−10.6)	131.5 (−13.6)	129.9 (+20.2)	28.0 (d)	233	61	10.9
2f	299	47.6 (−12.6)	138.2 (−9.1)	123.8 (+16.8)	27.0 (d)	223	298	9.7
3	303	74.0 (−1.4)	138.6 (−6.1)	131.1 (+6.1)	31.0 (d)	<i>e</i>		

^a In THF-*d*₈, ^{13}C NMR shifts in ppm, δ -scale with $\Delta\delta = \delta^{13}\text{C}$ (in THF-*d*₈) − $\delta^{13}\text{C}$ (in toluene-*d*₈) in parentheses. ^b ^1H NMR coalescence temperature (600 MHz). ^c Gibbs activation energy of the enantiomerization process of the complexes **2**·THF at the coalescence temperature (in kcal/mol, ± 0.5). ^d Not determined. ^e Dynamics could not be frozen out at the lowest temperature (183 K).

metallocene framework, necessarily makes the (1,2- η^2 -allyl)-zirconocene complexes **2**·THF chiral. This is indeed observed in the NMR spectra of these systems in THF-*d*₈ solution at sufficiently low temperature. In each case the signals of a pair of diastereotopic RCp ligands is observed, in addition to the pair of diastereotypic 1-H,H' hydrogen resonances. As a typical example the chiral structure of the (1,2- η^2 -allyl)zirconium complex **2c**·THF becomes evident in the $^1\text{H}/^{13}\text{C}$ NMR spectra (at 600/150 MHz) in THF-*d*₈ at low temperature (203 K) by the occurrence of eight $\text{CH}_3\text{C}_5\text{H}_4$ methine signals at δ 6.30, 6.21 (double intensity), 6.14 (double intensity), 6.06, 5.94, 5.82/117.5, 116.0, 112.0, 110.8, 109.5, 106.9, 106.4, 106.1 ppm. The corresponding pair of methyl resonances is observed under these conditions at δ 2.00, 1.89/15.1, 14.7 ppm, and the 1-H,H' protons are diastereotopic (signals at δ 1.94 and 1.72) as are the 4-H,H' hydrogens (signals at δ 1.54 and 2.83 ppm).

The NMR spectra of complex **2c**·THF in THF-*d*₈ are dynamic. Upon raising the temperature from 203 K the signals of the diastereotopic pairs of nuclei rapidly get broadened and show coalescence due to a symmetrizing donor–ligand exchange combined with a rapid intramolecular symmetrization process of the allyl ligand, that probably proceeds via a (σ -allyl)metallocene–betaine intermediate.²⁵ From the dynamic ^1H NMR spectra a Gibbs activation energy of $\Delta G_{\text{inv}}^\ddagger$ (213 K) = 9.9 ± 0.5 kcal/mol was obtained for this enantiomerization process of **2c**·THF. The complexes **2a**·THF and **2d**–**f**·THF show a similar behavior and consequently comparable $\Delta G_{\text{inv}}^\ddagger$ values. Only the enantiomerization process of the hafnium complex **2b**·THF was so fast that we were not able to “freeze” it on the NMR time scale so far. We assume that this is due to the in general slightly stronger Hf–C σ -bond as compared to the Zr–C σ -linkage ($\Delta\Delta \approx 5$ kcal/mol)³⁰ that makes the σ -allyl intermediate of the enantiomerization process easier accessible in the case of the hafnium system.³¹

Conclusions

The metallocene–(conjugated diene)–borate–betaine complexes are dormant single component metallocene Ziegler catalyst systems.¹¹ They are rather stable, isolable species that turn into active polymerization catalysts, as we had previously shown, when they are exposed to the α -olefin monomers. Their high kinetic and thermodynamic stability in the dormant precatalyst stage originates from a well-tailored protection of the incipient metallocene cation that is a part of the overall

betaine system. The essential feature of the protection of the active catalyst system is the internal coordination of an adjacent (sp^2)C–F bond to the electrophilic zirconium center. In order to serve its purpose as a protective group of an active catalyst system the resulting metal \cdots F–C interaction must probably be within a very narrow thermodynamic bond energy range. The ensuing metal \cdots fluorine interaction must, of course, be strong enough to shield the local metallocene cation moiety from a plethora of possible irreversible deactivation pathways, be it C–H activation or other stoichiometric reactions.³² On the other hand, the Zr \cdots F–C bond strength must not be too high since it must instantaneously be cleaved as soon as the monomer is added to initiate the catalytic chain reaction. We think that the dynamic fluorine exchange, observed for the complexes **2** by dynamic ^{19}F NMR spectroscopy at low temperature in the noncoordinating solvent toluene-*d*₈, gives us a good estimate of the Zr \cdots F bond strength in these cases. This dynamic process requires that the ortho-C–F \cdots Zr linkage is cleaved. One might argue that there is one dynamic process possible that is characterized by just turning the plane of this single C_6F_5 group by 180° and bind the other ortho-C–F group to zirconium. In such a case one could argue about some remaining $\text{C}_6\text{F}_5/\text{Zr}$ interaction along the reaction coordinate; therefore, the activation energy of such a dynamic process would possibly not be a good estimate of the C–F \cdots Zr bond dissociation energy. The process, that we have observed in the ^{19}F NMR dynamics of the complexes **2** is, however, markedly different from such a scenario. We have found that *all* six *o*-fluorines, *all* six *m*-fluorines, and *all* three *p*-fluorines present in the $\text{B}(\text{C}_6\text{F}_5)_3$ residue undergo the mutual interconversion, i.e., we see a single barrier for the duplex and triplex interconversions. In such a case it is very unlikely that there is a significant stabilizing component such as an arene/Zr interaction taking place along the reaction coordinate, and, therefore, the observed Gibbs activation energy may serve as a good estimate for the strength of the C–F \cdots Zr interaction in these metallacyclic Ziegler catalyst precursors. We conclude that the thermodynamic strength of this C–F \cdots Zr interaction is in the order of 8–9 kcal/mol. We assume that the C–F bonds of fluorocarbons may potentially be suited in general to serve as coordinative protecting groups of electrophilic active metal catalyst centers if the coordination energy of the resulting C–F \cdots M bond is of this order of magnitude. The resulting coordination geometry of the M \cdots F–C interaction seems to be very flexible (the M \cdots F–C bond angle in **2** is ca. 140°). It seems to be determined by the conformational and configurational restrictions of the carbon atom framework to which the coordinating fluorine atom is attached. It appears that it is just required to bring the fluoride end of the C–F bond into the close vicinity of the electrophilic metal center to induce building up the C–F \cdots M coordination. In this regard the reaction profile of

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(32) Bertuleit, A.; Fritze, C.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, 16, 2891.

the formation of the C–F···M interaction is reminiscent of that of establishing “agostic” metal···H–C bonds.³³

The C–F···Zr interaction of **2**, whose estimated bond dissociation energy is ca. 8–9 kcal/mol, is accordingly cleaved very rapidly upon the addition of the donor solvent tetrahydrofuran. The resulting adducts, **2**·THF, still exhibit a “non-σ-allyl” ligand, namely a 1,2-η²-allyl-ligand,²⁹ as discussed above. Even with the coordinated THF ligand this is still ca. 10 kcal/mol away from a σ-allyl bonding situation. This type of a transition may represent a significant, potentially rate-limiting barrier of the first reaction step of the initiation sequence of the complexes **2** in the Ziegler catalyst cycle, only that the strong donor-ligand THF is then replaced by a weakly coordinating α-olefin. The kinetic data of the corresponding single reaction steps in the real **2**/alkene reaction systems are currently being determined in our laboratory. This may potentially lead to a better understanding of the sequence of steps followed in rapid and selective carbon carbon coupling at the enormously interesting homogeneous metallocene based Ziegler catalysts and related systems.

Experimental Section

General Information. All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. B(C₆F₅)₃ was prepared by a literature procedure.¹² The (conjugated diene)-metallocene complexes were synthesized as previously described in the literature.¹³ The preparation of the metallocene–borate–betaine complexes **2a** and **2b** was previously described by us in a preliminary communication (including the X-ray crystal structure analysis of **2a** and some α-olefin polymerization reactions).¹¹ A detailed spectroscopic characterization of these two compounds was, however, carried out recently and these data have, therefore, been included in this Experimental Section. The compounds **2d** and **2f** were not synthesized on a preparative scale and isolated, but only generated in deuterated solvents and characterized spectroscopically. The NMR spectra were recorded on a Varian Unity Plus NMR spectrometer (¹H: 600 MHz, ¹³C: 150 MHz, ¹⁹F: 564 MHz, ¹¹B: 192 MHz). In addition to 1D NMR experiments the following 2D NMR experiments were employed for a detailed characterization of the compounds: GHSQC (gradient pulsed heteronuclear single quantum coherence), GHMBC (gradient pulsed heteronuclear multiple bond coherence), and GCOSY (gradient pulsed correlated spectroscopy).³⁴ The Gibbs activation energies ΔG[‡] of the intramolecular fluorine exchange of the complexes **2** and of the allyl inversion of **2**·THF were obtained from the dynamic NMR spectra using the Gutowsky–Holm approximation³⁵ and/or by spectral simulation using the DNMR5 procedure,³⁶ with consideration of the respective statistical factors as discussed by Green et al.²⁸ For a compilation of additional instrumentation for physical characterization see ref 26.

Preparation of the Group 4 Metallocene–Borate–Betaine Complexes **2, General Procedure.** The respective (conjugated diene)group 4 metallocene complex **1** (10 mmol) is dissolved together with 10.5 mmol of B(C₆F₅)₃ in 50 mL of toluene. After 1 day at ambient temperature the precipitated betaine product **2** is collected by filtration, washed with toluene (10 mL) and pentane (50 mL), and dried in vacuo. The isolated material contains 1 molar equiv of toluene. Since the precipitated complexes **2** are only sparingly soluble in nondonor solvents, their spectra in, e.g., toluene-*d*₈ were obtained from *in situ* generated samples of the respective complexes. Typically, for this

purpose solutions (each 2 mL) of 0.10 mmol of the respective (diene)-metallocene **1** and 0.11 mmol of B(C₆F₅)₃ were prepared and equal aliquots of these were then combined. The addition reaction to give **2** was instantaneous in each case, and the spectra of **2** could, therefore, be monitored several minutes after the two components were brought together. In THF-*d*₈ in a few cases one or two additional isomers (probably conformers) of **2**·THF were observed (ca. 10%) which disappeared after some time. Therefore, only the NMR data of the final products **2**·THF are listed below.

Reaction of (Butadiene)zirconocene (1a**) with B(C₆F₅)₃, Formation of **2a**.** (Butadiene)zirconocene (**1a**, 3.15 g, 11.43 mmol) was treated with 6.20 g (12.12 mmol) of B(C₆F₅)₃ in 100 mL of toluene analogously as described above to give 7.60 g (76%) of **2a** as an orange solid, mp 121 °C. Spectroscopic characterization of **2a**: ¹H-NMR (599.9 MHz, 303 K, toluene-*d*₈): δ = 5.88 (m, 1H, 2-H), 5.32 (s, 5H, Cp), 5.28 (s, 5H, Cp), 5.23 (m, 1H, 3-H), 2.56 (d, ²J_{HH} = 18.0 Hz, 1H, 4-H'), 2.25 (dd, ^{3/2}J_{HH} = 6.0, 18.0 Hz, 1H, 4-H), 1.85 (dd, ^{2/3}J_{HH} = 5.0, 12.0 Hz, 1H, 1-H'), 1.47 (dd, ^{2/3}J_{HH} = 5.0, 8.0 Hz, 1H, 1-H) ppm. ¹³C-NMR (150.8 MHz, 303 K, toluene-*d*₈): δ = 149.1 (d, ¹J_{CF} = 240 Hz, *o*-B(C₆F₅)₃), 138.7 (d, ¹J_{CF} = 242 Hz, *p*-B(C₆F₅)₃), 137.2 (d, ¹J_{CF} = 247 Hz, *m*-B(C₆F₅)₃), 131.8 (CH, ¹J_{CH} = 149 Hz, C-2), 123.8 (CH, C-3), 115.0 (br, C, ipso-B(C₆F₅)₃), 111.2 (CH, ¹J_{CH} = 176 Hz, Cp), 110.9 (CH, ¹J_{CH} = 175 Hz, Cp), 52.7 (CH₂, ¹J_{CH} = 151 Hz, C-1), 28.5 (br, CH₂, C-4) ppm. GCOSY (599.9 MHz, 303 K, toluene-*d*₈): δ = 5.88 (2-H)/5.23 (3-H); 1.85 (1-H')/1.47 (1-H); 5.23 (3-H)/2.56 (4-H'), 2.25 (4-H); 2.56 (4-H')/2.25 (4-H); 1.85 (1-H')/1.47 (1-H) ppm. GHSQC (599.9 MHz, 303 K, toluene-*d*₈): δ = 131.8/5.88 (C-2), 123.8/5.23 (C-3), 111.2/5.32 (Cp), 110.9/5.28 (Cp), 52.7/1.85, 1.47 (C-1), 28.5/2.25 (C-4) ppm. ¹⁹F-NMR (564.3 MHz, 238 K, toluene-*d*₈): δ = -165.4 (t, ³J_{FF} = 22 Hz, 6F, *m*-F), -161.5 (t, ³J_{FF} = 23 Hz, 3F, *p*-F) ppm (*o*-fluorines are broad due to the dynamic behavior). ¹⁹F-NMR (564.3 MHz, 193 K, toluene-*d*₈): δ = -213.2 (br, 1F, *o*-F coordinated), -165.3, -165.1, -164.7 (3×), -163.6 (each br, 6F, *m*-F), -160.9, -159.2, -158.5 (each br, 3F, *p*-F), -137.5, -134.0, -131.8, -130.6, -126.4 (each br, 5F, *o*-F) ppm. Coincidence of the *o*-F resonances at 233 K, Δν(193 K) = 45 735 Hz, ΔG[‡] = 8.1 ± 0.5 kcal/mol.

2a·THF: ¹H-NMR (599.9 MHz, 299 K, THF-*d*₈): δ = 6.14 (s, 10H, Cp), 5.85 (m, 1H, 3-H), 4.83 (dt, ³J_{HH} = 10.0, 16.0 Hz, 1H, 2-H), 2.31 (br, 2H, 4-H',H), 2.11 (d, ³J_{HH} = 10.0 Hz, 2H, 1-H',H) ppm. (193 K): δ 6.22 (s, 5H, Cp), 6.20 (s, 5H, Cp), 6.06 (br, 1H, 3-H), 4.73 (br, 1H, 2-H), 2.84, 2.09, 1.77, 1.54 (each br, each 1H, 1-H',H, 4-H',H) ppm. ¹³C-NMR (150.8 MHz, 299 K, THF-*d*₈): δ = 149.0 (d, ¹J_{CF} = 236 Hz, *o*-B(C₆F₅)₃), 147.1 (CH, C-3), 138.4 (d, ¹J_{CF} = 241 Hz, *p*-B(C₆F₅)₃), 137.3 (d, ¹J_{CF} = 231 Hz, *m*-B(C₆F₅)₃), 126.5 (C, ipso-B(C₆F₅)₃), 114.2 (CH, ¹J_{CH} = 147 Hz, C-2), 110.7 (CH, ¹J_{CH} = 175 Hz, Cp), 46.8 (CH₂, ¹J_{CH} = 148 Hz, C-1), 35.0 (br, CH₂, C-4) ppm. GCOSY (599.9 MHz, 299 K, THF-*d*₈): δ = 5.85 (3-H)/4.83 (2-H), 2.31 (4-H); 4.83 (2-H)/2.11 (1-H) ppm. GHSQC (599.9 MHz, 299 K, THF-*d*₈): δ = 147.1/5.85 (C-3), 114.2/4.83 (C-2), 110.7/6.14 (Cp), 46.8/2.11 (C-1) ppm. ¹⁹F-NMR (564.3 MHz, 299 K, THF-*d*₈): δ = -168.4 (t, ³J_{FF} = 21 Hz, 6F, *m*-F), -165.4 (t, ³J_{FF} = 21 Hz, 3F, *p*-F), -133.1 (d, ³J_{FF} = 20 Hz, 6F, *o*-F) ppm. Dynamics of the allyl inversion in THF-*d*₈: coincidence of the Cp-signals at 213 K, Δν(173 K) = 195 Hz, ΔG[‡] = 9.5 ± 0.5 kcal/mol. IR (KBr): ν̄ = 3118, 3006, 1644, 1516, 1458, 1267, 1086, 1018, 978, 820, 737 cm⁻¹.

Reaction of (Butadiene)hafnocene (1b**) with B(C₆F₅)₃, Synthesis of **2b**.** Complex **1b** (3.60 g, 9.92 mmol) was reacted with 5.20 g (10.16 mmol) of B(C₆F₅)₃ in 100 mL of toluene analogously as described above to yield 7.00 g (81%) of **2b**. Spectroscopic characterization of **2b**: ¹H-NMR (599.9 MHz, 253 K, toluene-*d*₈): δ = 6.04 (m, 1H, 2-H), 5.25 (m, 1H, 3-H), 5.13 (br, s, 10H, Cp), 2.95 (br, d, ²J_{HH} = 18.0 Hz, 1H, 4-H'), 2.29 (dd, ^{3/2}J_{HH} = 7.1, 18.0 Hz, 1H, 4-H), 1.57 (dd, ^{2/3}J_{HH} = 7.1, 12.6 Hz, 1H, 1-H'), 1.11 (tr, ^{2/3}J_{HH} = 7.1 Hz, 1H, 1-H) ppm. ¹³C-NMR (150.8 MHz, 253 K, toluene-*d*₈): δ = 149.0 (d, ¹J_{CF} = 236 Hz, *o*-B(C₆F₅)₃), 138.7 (d, ¹J_{CF} = 241 Hz, *p*-B(C₆F₅)₃), 137.1 (d, ¹J_{CF} = 231 Hz, *m*-B(C₆F₅)₃), 132.0 (CH, C-2), 123.6 (CH, C-3), 110.2, 110.1 (each CH, each Cp), 50.7 (CH₂, C-1) ppm, ipso-C of C₆F₅ and C-4 not observed. GCOSY (599.9 MHz, 253 K, toluene-*d*₈): δ = 6.04 (2-H)/5.25 (3-H); 1.57 (1-H')/1.11 (1-H); 5.25 (3-H)/2.29 (4-H); 2.95 (4-H')/2.29 (4-H); 1.57 (1-H')/1.11 (1-H) ppm. GHSQC (599.9 MHz, 253 K, toluene-*d*₈): δ = 132.0/6.04 (C-2), 123.6/5.25 (C-3), 110.2, 110.1/

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5.13 (Cp), 50.7/1.57, 1.11 (C-1) ppm. ^{19}F -NMR (564.3 MHz, 253 K, toluene- d_8): $\delta = -165.0$ (br, 6F, *m*-F), -161.0 (br, 3F, *p*-F) ppm, *o*-F broad due to dynamic behavior. ^{19}F -NMR (564.3 MHz, 213 K, toluene- d_8): $\delta = -219.5$ (br, 1F, *o*-F coordinated), -166.8 , -165.6 (5 \times), (each br, 6F, each *m*-F), -159.6 (2 \times), -158.9 (each br, 3F, each *p*-F), -137.7 , -134.0 , -132.5 , -131.3 , -127.7 (each br, 5F, each *o*-F) ppm. Dynamics of the fluorine coordination in toluene- d_8 : coalescence of the *o*-F resonances at 233 K, $\Delta\nu$ (193 K) = 52 098 Hz, $\Delta G^\ddagger = 8.0 \pm 0.5$ kcal/mol.

2b·THF: ^1H -NMR (599.9 MHz, 299 K, THF- d_8): $\delta = 6.14$ (s, 10H, Cp), 5.71 (m, 1H, 3-H), 4.91 (m, 1H, 2-H), 2.40 (br, d, $^3J_{\text{HH}} = 6.9$ Hz, 2H, 4-H',H), 1.86 (d, $^3J_{\text{HH}} = 10.0$ Hz, 2H, 1-H',H) ppm. The dynamic behavior of the allyl group could not be frozen down to 173 K. ^{13}C -NMR (150.8 MHz, 299 K, THF- d_8): $\delta = 149.0$ (d, $^1J_{\text{CF}} = 234$ Hz, *o*-B(C $_6$ F $_5$) $_3$), 147.0 (CH, $^1J_{\text{CH}} = 150$ Hz, C-2), 138.4 (d, $^1J_{\text{CF}} = 241$ Hz, *p*-B(C $_6$ F $_5$) $_3$), 137.3 (d, $^1J_{\text{CF}} = 231$ Hz, *m*-B(C $_6$ F $_5$) $_3$), 127.1 (C, ipso-B(C $_6$ F $_5$) $_3$), 115.0 (CH, $^1J_{\text{CH}} = 149$ Hz, C-3), 110.5 (CH, $^1J_{\text{CH}} = 176$ Hz, Cp), 49.3 (CH $_2$, $^1J_{\text{CH}} = 139$ Hz, C-1), 33.3 (br, CH $_2$, C-4) ppm. GCOSY (599.9 MHz, 299 K, THF- d_8): $\delta = 5.71$ (3-H)/4.91 (2-H), 2.40 (4-H); 4.91 (2-H)/1.86 (1-H) ppm. GHSQC (599.9 MHz, 299 K, THF- d_8): $\delta = 147.0/5.71$ (C-3), 115.1/4.91 (C-2), 110.5/6.14 (Cp), 49.3/1.86 (C-1), 33.3/2.40 (C-4) ppm. ^{19}F -NMR (564.3 MHz, 299 K, THF- d_8): $\delta = -168.5$ (t, $^3J_{\text{FF}} = 21$ Hz, 6F, *m*-F), -165.6 (t, $^3J_{\text{FF}} = 21$ Hz, 3F, *p*-F), -133.0 (d, $^3J_{\text{FF}} = 21$ Hz, 6F, *o*-F) ppm. IR (KBr): $\tilde{\nu} = 3118, 3006, 2967, 1644, 1611, 1519, 1460, 1282, 1084, 1025, 973, 821, 742, 683$ cm $^{-1}$.

Treatment of (Butadiene)Zr(CpMe) $_2$ (1c) with B(C $_6$ F $_5$) $_3$, Preparation of 2c. **1c** (300 mg, 0.99 mmol) was treated with 550 mg (1.07 mmol) of B(C $_6$ F $_5$) $_3$ in 2 mL of toluene. After 3 days at ambient temperature 700 mg (78%) of crystalline **2c** was obtained. The crystals were suited for the X-ray crystal structure analysis, mp 107 °C. Anal. Calcd for C $_{34}$ H $_{20}$ BF $_{15}$ Zr \cdot 0.5C $_7$ H $_8$ (861.6): C, 52.28; H, 2.81. Found: C, 52.20; H, 3.09.

X-ray crystal structure analysis of **2c**: formula C $_{34}$ H $_{20}$ BF $_{15}$ Zr \cdot C $_7$ H $_8$, $M = 907.66$, $0.50 \times 0.45 \times 0.45$ mm, $a = 16.713(2)$, $b = 12.400(1)$, $c = 18.094(3)$ Å, $\beta = 99.08(1)^\circ$, $V = 3702.8(8)$ Å 3 , $\rho_{\text{calc}} = 1.628$ g cm $^{-3}$, $\mu = 4.04$ cm $^{-1}$, empirical absorption correction *via* ψ scan data ($0.976 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 7738 reflections collected ($\pm h, -k, -l$), $[(\sin\theta)/\lambda]_{\text{max}} = 0.62$ Å $^{-1}$, 7497 independent and 4536 observed reflections [$I \geq 2\sigma(I)$], 526 refined parameters, $R = 0.040$, $wR^2 = 0.083$, max. residual electron density 0.40 (−0.58) e Å $^{-3}$, hydrogens calculated and riding. Data were collected on an Enraf-Nonius MACH3 diffractometer, programs used: MolEN, SHELXS-86, SHELXL-93, DIAMOND.

Spectroscopic characterization of **2c**: ^1H -NMR (599.9 MHz, 303 K, toluene- d_8): $\delta = 5.87$ (m, 1H, 2-H), 5.50 (m, 1H, Cp), 5.31 (m, 1H, Cp), 5.23 (m, 3H, each Cp), 5.20 (m, 1H, Cp), 5.13 (m, 1H, Cp), 4.85 (m, 1H, 3-H), 4.79 (m, 1H, Cp), 2.41 (br, d, $^2J_{\text{HH}} = 17.7$ Hz, 1H, 4-H'), 2.17 (dd, $^3J_{\text{HH}} = 5.2$, 17.7 Hz, 1H, 4-H), 1.75 (dd, $^2J_{\text{HH}} = 5.2$, 11.5 Hz, 1H, 1-H'), 1.46 (s, 3H, CpMe), 1.44 (m, 1H, 1-H), 1.36 (s, 3H, CpMe) ppm. ^{13}C -NMR (150.8 MHz, 238 K, toluene- d_8): $\delta = 148.3$ (d, $^1J_{\text{CF}} = 251$ Hz, *o*-B(C $_6$ F $_5$) $_3$), 139.0 (d, $^1J_{\text{CF}} = 264$ Hz, *p*-B(C $_6$ F $_5$) $_3$), 137.3 (d, $^1J_{\text{CF}} = 253$ Hz, *m*-B(C $_6$ F $_5$) $_3$), 134.6 (CH, C-2), 120.3 (CH, C-3), 125.7 (C, Cp), 118.4 (C, CH, each Cp), 112.8, 111.4, 109.5, 109.4, 109.0, 107.9, 107.5 (each CH, each Cp), 53.7 (CH $_2$, C-1), 26.6 (br, CH $_2$, C-4), 14.3, 14.0 (CH $_3$, CpMe) ppm; ipso-C of B(C $_6$ F $_5$) $_3$ not detected. GCOSY (599.9 MHz, 303 K, toluene- d_8): $\delta = 5.87$ (2-H)/4.85 (3-H), 1.75 (1-H'), 1.44 (1-H); 4.85 (3-H)/2.41 (4-H'), 2.17 (4-H); 2.41 (4-H')/2.17 (4-H); 1.75 (1-H')/1.44 (1-H) ppm. GHSQC (599.9 MHz, 303 K, toluene- d_8): $\delta = 134.6/5.87$ (C-2), 120.3/4.85 (C-3), 118.4/5.20 (Cp), 112.8/5.13 (Cp), 111.4/5.23 (Cp), 109.5/5.23 (Cp), 109.4/4.79 (Cp), 109.0/5.31 (Cp), 107.9/5.23 (Cp), 107.5/5.50 (Cp), 53.7/1.75, 1.44 (C-1), 26.6/2.41, 2.17 (C-4), 14.3/1.46 (CpMe), 14.0/1.36 (CpMe) ppm. ^{19}F -NMR (564.3 MHz, 303 K, toluene- d_8): $\delta = -165.9$ (t, $^3J_{\text{FF}} = 21.0$ Hz, 6F, *m*-F), -162.0 (t, $^3J_{\text{FF}} = 21.0$ Hz, 3F, *p*-F) ppm; *o*-F not detected due to dynamic behavior. ^{19}F -NMR (564.3 MHz, 193 K, toluene- d_8): $\delta = -209.9$ (br, 1F, *o*-F coordinated), -167.2 , -166.6 , -165.8 (2 \times), -164.9 , -162.1 (each br, 6F, *m*-F), -161.8 , -160.5 , -159.1 (each br, 3F, *p*-F), -137.0 , -134.5 , -132.6 , -131.4 , -127.2 (each br, 5F, *o*-F) ppm; dynamics of the *o*-F coordination in toluene- d_8 : coalescence of the *o*-fluorine signals at 243

K, $\Delta\nu$ (193 K) = 43 647 Hz, $\Delta G^\ddagger = 8.5 \pm 0.5$ kcal/mol. IR (KBr): $\tilde{\nu} = 3119, 3092, 2963, 2932, 2870, 1645, 1514, 1458, 1381, 1271, 1082, 978, 812$ cm $^{-1}$.

2c·THF: ^1H -NMR (599.9 MHz, 203 K, THF- d_8): $\delta = 6.30, 6.21$ (2 \times), 6.14 (2 \times) 6.06, 5.94, 5.82 (each br, 8H, Cp), 5.63 (br, 1H, 3-H), 4.87 (br, 1H, 2-H), 2.83 (br, 1H, 4-H'), 2.00 (s, 3H, CpMe), 1.94 (under Me-group, 1-H'), 1.89 (s, 3H, CpMe), 1.72 (under THF, 1-H), 1.54 (br, 1H, 4-H) ppm. Dynamics of the allyl inversion in THF- d_8 : coalescence of the Cp-CH $_3$ signals at 213 K, $\Delta\nu$ (173 K) = 66 Hz, $\Delta G^\ddagger = 9.9 \pm 0.5$ kcal/mol. ^{13}C -NMR (150.8 MHz, 203 K, THF- d_8): $\delta = 148.7$ (d, $^1J_{\text{CF}} = 240$ Hz, *o*-B(C $_6$ F $_5$) $_3$), 143.7 (CH, C-3), 138.6 (d, $^1J_{\text{CF}} = 241$ Hz, *p*-B(C $_6$ F $_5$) $_3$), 137.9 (d, $^1J_{\text{CF}} = 231$ Hz, *m*-B(C $_6$ F $_5$) $_3$), 126.7 (C, ipso-B(C $_6$ F $_5$) $_3$), 117.5, 116.0, 112.0, 110.8, 109.5, 106.9, 106.4, 106.1 (each CH, each Cp), 116.0 (CH, C-2), 45.6 (CH $_2$, C-1), 33.1 (br, CH $_2$, C-4), 15.1, 14.7 (each CH $_3$, each CpMe) ppm. GCOSY (599.9 MHz, 203 K, THF- d_8): $\delta = 5.63$ (3-H)/4.87 (2-H), 1.54 (4-H); 4.87 (2-H)/1.94 (1-H'), 1.72 (1-H); 2.83 (4-H')/1.54 (4-H), 1.94 (1-H')/1.72 (1-H) ppm. GHSQC (599.9 MHz, 203 K, THF- d_8): $\delta = 143.7/5.63$ (C-3), 117.5/6.06 (Cp), 116.2/4.87 (C-2), 116.0/6.21 (Cp), 112.0/5.82 (Cp), 110.8/6.14 (Cp), 109.5/6.14 (Cp), 106.9/6.30 (Cp), 106.4/6.21 (Cp), 106.1/5.94 (Cp), 45.6/1.94, 1.54 (C-4), 15.1/1.89 (MeCp), 14.7/2.00 (MeCp) ppm. ^{19}F -NMR (564.3 MHz, 299 K, THF- d_8): $\delta = -168.1$ (t, $^3J_{\text{FF}} = 21$ Hz, 6F, *m*-F), -165.1 (t, $^3J_{\text{FF}} = 21$ Hz, 3F, *p*-F), -134.3 (d, $^3J_{\text{FF}} = 20$ Hz, 6F, *o*-F) ppm.

Reaction of (Butadiene)Zr(CpCMe $_3$) $_2$ (1d) with B(C $_6$ F $_5$) $_3$, in Situ Generation of 2d. Complex **2d** was obtained by combining a solution of 38 mg (0.10 mmol) of **1d** in 1 mL of toluene- d_8 with a solution of 54 mg (0.10 mmol) of B(C $_6$ F $_5$) $_3$ in 1 mL of toluene at ambient temperature. An aliquot was used for the spectroscopic characterization. Complex **2d**·THF was analogously generated by combining two THF- d_8 solutions of these substrates. Spectroscopic characterization of **2d**: ^1H -NMR (599.9 MHz, 303 K, toluene- d_8): $\delta = 6.38$ (m, 1H, 3-H), 6.22 (m, 1H, 2-H), 6.26 (m, 1H, Cp), 6.23 (m, 1H, Cp), 5.92 (m, 1H, Cp), 5.71 (m, 1H, Cp), 5.63 (m, 2H, Cp), 5.42 (m, 1H, Cp), 4.87 (m, 1H, Cp), 3.03 (dd, $^2J_{\text{HH}} = 5.0$, 12.4 Hz, 1H, 1-H'), 2.62 (br, 1H, 4-H'), 1.89 (br, t, $^2J_{\text{HH}} = 11.2$ Hz, 1H, 4-H), 1.50 (dd, $^2J_{\text{HH}} = 5.0$, 8.2 Hz, 1H, 1-H), 0.39, 0.31 (each s, each 9H, each ^tBu) ppm. ^{13}C -NMR (150.8 MHz, 303 K, toluene- d_8): $\delta = 149.0$ (d, $^1J_{\text{CF}} = 250$ Hz, *o*-B(C $_6$ F $_5$) $_3$), 139.1 (d, $^1J_{\text{CF}} = 250$ Hz, *p*-B(C $_6$ F $_5$) $_3$), 137.5 (d, $^1J_{\text{CF}} = 250$ Hz, *m*-B(C $_6$ F $_5$) $_3$), 136.0 (CH, C-2), 127.5 (CH, C-3), 116.5, 115.2, 114.9, 109.7, 109.6, 109.4 (2 \times), 107.0 (each CH, each Cp), 60.3 (CH $_2$, C-1), 32.7, 32.1 (each C, each ^tBu), 30.1, 27.8 (each CH $_3$, each Cp^tBu) ppm; ipso-C of B(C $_6$ F $_5$) $_3$ and quat. C $_3$ H $_4$ CMe $_3$ carbon signals not detected. GCOSY (599.9 MHz, 303 K, toluene- d_8): $\delta = 6.38$ (3-H)/6.22 (2-H), 2.62 (4-H'), 1.89 (4-H); 6.22 (2-H)/3.03 (1-H'), 1.50 (1-H); 3.03 (1-H')/1.50 (1-H); 2.62 (4-H')/1.89 (4-H). GHSQC (599.9 MHz, 303 K, toluene- d_8): $\delta = 136.0/6.22$ (C-2), 127.5/6.38 (C-3), 116.5/6.26 (Cp), 115.2/5.71 (Cp), 114.9/6.23 (Cp), 109.7/4.87 (Cp), 109.6/5.63 (Cp), 109.4/5.92, 5.42 (Cp), 107.0/5.63 (Cp), 60.3/3.03, 1.50 (C-1), 30.1/0.39 (Cp^tBu), 27.8/0.31 (Cp^tBu) ppm. ^{19}F -NMR (564.3 MHz, 303 K, toluene- d_8): $\delta = -166.7$ (t, $^3J_{\text{FF}} = 21$ Hz, 6F, *m*-F), -162.8 (t, $^3J_{\text{FF}} = 21$ Hz, 3F, *p*-F), 134.3 (d, $^3J_{\text{FF}} = 21$ Hz, 6F, *o*-F) ppm. The fluorine signals began to separate at 193 K but the dynamic behavior could not be frozen completely. IR (KBr): $\tilde{\nu} = 3122, 3006, 2976, 2908, 2873, 1646, 1518, 1459, 1367, 1265, 1087, 978, 806, 679$ cm $^{-1}$.

2d·THF: ^1H -NMR (599.9 MHz, 299 K, THF- d_8): $\delta = 6.32$ (m, 1H, 3-H), 6.25, 6.17 (each m, each 4H, each Cp), 4.74 (m, 1H, 2-H), 2.41 (br, 2H, 4-H',H), 2.26 (d, $^3J_{\text{HH}} = 9.6$ Hz, 2H, 1-H',H), 1.21 (s, 18H, ^tBu) ppm. (173K): $\delta = 6.48$ –6.38 (m, 8H, Cp), 5.79 (br, 1H, 3-H), 4.76 (br, 1H, 2-H), 3.05, 2.26, 1.89, 1.65 (each br, each 1H, 1-H',H, 4-H',H), 1.27, 1.08 (each s, each 9H, ^tBu) ppm. Dynamics of the allyl inversion in THF- d_8 : coalescence of the Cp-C(CH $_3$) $_3$ signals at 193 K, $\Delta\nu$ (173 K) = 115 Hz, $\Delta G^\ddagger = 8.7 \pm 0.5$ kcal/mol. ^{13}C -NMR (150.8 MHz, 299 K, THF- d_8): $\delta = 159.3$ (CH, $^1J_{\text{CH}} = 149$ Hz, C-3), 149.0 (d, $^1J_{\text{CF}} = 240$ Hz, *o*-B(C $_6$ F $_5$) $_3$), 138.9 (d, $^1J_{\text{CF}} = 241$ Hz, *p*-B(C $_6$ F $_5$) $_3$), 137.5 (C, Cp), 137.3 (d, $^1J_{\text{CF}} = 240$ Hz, *m*-B(C $_6$ F $_5$) $_3$), 126.9 (C, ipso-B(C $_6$ F $_5$) $_3$), 112.8, 107.1 (each CH, $^1J_{\text{CH}} = 175$ Hz, each Cp), 110.4 (CH, $^1J_{\text{CH}} = 148$ Hz, C-2), 48.2 (CH $_2$, $^1J_{\text{CH}} = 146$ Hz, C-1), 35.7 (br, CH $_2$, C-4), 34.1 (C, ^tBu), 31.5 (CH $_3$, $^1J_{\text{CH}} = 125$ Hz, ^tBu) ppm. GCOSY (599.9 MHz, 299 K, THF- d_8): $\delta = 6.32$ (3-H)/4.74 (2-H), 2.41 (4-H); 4.74 (2-H)/2.26 (1-H) ppm. GHSQC (599.9 MHz, 299 K, THF- d_8):

$\delta = 159.3/6.32$ (C-3), 112.8/6.25 (Cp), 110.4/4.74 (C-2), 107.1/6.17 (Cp), 48.2/2.26 (C-1), 37.7/2.41 (C-4), 31.5/1.21 (^tBuCp) ppm. ¹⁹F-NMR (564.3 MHz, 299 K, THF-*d*₈): $\delta = -168.3$ (t, ³J_{FF} = 21 Hz, 6F, *m*-F), -165.3 (t, ³J_{FF} = 21 Hz, 3F, *p*-F), -133.4 (d, ³J_{FF} = 20 Hz, 6F, *o*-F) ppm.

Reaction of (Isoprene)zirconocene (1e) with B(C₆F₅)₃, Preparation of the Betaine System 2e. 1e (300 mg, 1.04 mmol) was treated with 550 mg (1.07 mmol) of B(C₆F₅)₃ in 2 mL of toluene analogously as described above. The product 2e was obtained as a crystalline material after 3 days at ambient temperature. The crystals were suited for an X-ray crystal structure analysis. Yield 680 mg (73%), mp 67 °C. Anal. Calcd for C₃₃H₁₈BF₁₅Zr·C₇H₈ (893.6): C, 53.76, H, 2.93. Found: C, 53.2; H, 2.93. X-ray crystal structure analysis of 2e: formula C₃₃H₁₈BF₁₅Zr·C₇H₈, *M* = 893.64, 0.50 × 0.40 × 0.30 mm, *a* = 16.080(2), *b* = 12.098(1), *c* = 18.342(1) Å, $\beta = 98.44(1)^\circ$, *V* = 3529.5(6) Å³, $\rho_{\text{calc}} = 1.682$ g cm⁻³, $\mu = 4.22$ cm⁻¹, empirical absorption correction *via* ψ scan data (0.981 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group *P*2₁/*n* (no. 14), $\lambda = 0.71073$ Å, *T* = 223 K, $\omega/2\theta$ scans, 7416 reflections collected ($-h, -k, \pm l$), $[(\sin\theta)/\lambda]_{\text{max}} = 0.62$ Å⁻¹, 7156 independent and 5550 observed reflections [*I* ≥ 2 $\sigma(I)$], 516 refined parameters, *R* = 0.034, *wR*² = 0.092, max. residual electron density 1.03 (−0.52) e Å⁻³, hydrogens calculated and riding. Spectroscopic characterization of 2e: ¹H-NMR (599.9 MHz, 299 K, toluene-*d*₈): $\delta = 5.29, 4.84$ (each s, each 5H, Cp), 4.23 (d, ³J_{HH} = 13.1 Hz, 1H, 3-H), 2.46 (d, ²J_{HH} = 9.2 Hz, 1H, 1-H'), 1.16 (s, 3H, 5-H), 0.68 (d, ²J_{HH} = 9.2 Hz, 1H, 1-H), -0.27 (br, 1H, 4-H'), -1.87 (br, 1H, 4-H) ppm. ¹³C-NMR (150.8 MHz, 299 K, toluene-*d*₈): $\delta = 148.6$ (d, ¹J_{CF} = 250 Hz, *o*-B(C₆F₅)₃), 145.1 (C, C-2), 139.5 (d, ¹J_{CF} = 250 Hz, *p*-B(C₆F₅)₃), 137.6 (d, ¹J_{CF} = 250 Hz, *m*-B(C₆F₅)₃), 109.7 (CH, C-3), 109.9, 106.4 (each CH, Cp), 59.8 (CH₂, C-1), 27.7 (CH₃, C-5) ppm. GCOSY (599.9 MHz, 299 K, toluene-*d*₈): $\delta = 4.23$ (3-H)/ -0.27 (4-H'); 2.46 (1-H')/0.68 (1-H); -0.27 (4-H')/1.87 (4-H) ppm. GHSQC (599.9 MHz, 299 K, toluene-*d*₈): $\delta = 109.9/5.29$ (Cp), 109.7/4.23 (C-3), 106.4/4.84 (Cp), 59.8/2.64, 0.68 (C-1), 27.7/1.16 (C-7) ppm; ipso-C of B(C₆F₅)₃ and C-4 not detected. ¹⁹F-NMR (564.3 MHz, 299 K, toluene-*d*₈): $\delta = -167.5$ (d, ³J_{FF} = 21 Hz, 6F, *m*-F), -165.5 (t, ³J_{FF} = 21 Hz, 3F, *p*-F), -132.0 (t, ³J_{FF} = 21 Hz, 6F, *o*-F) ppm, the fluorine resonances began to be resolved at 188K, but the low temperature limiting spectra could not be reached before the solution solidified. IR (KBr): $\tilde{\nu} = 3115, 2964, 2926, 2864, 1643, 1514, 1458, 1381, 1273, 1084, 980, 822$ cm⁻¹.

2e·THF: ¹H-NMR (599.9 MHz, 299 K, THF-*d*₈): $\delta = 6.06$ (s, 10H, Cp), 5.48 (t, ³J_{HH} = 7.3 Hz, 1H, 3-H), 2.18 (d, ³J_{HH} = 7.3 Hz, 1H, 2H, 4-H',H), 2.15 (s, 2H, 1-H',H), 1.35 (s, 3H, 5-H) ppm. (173 K): $\delta = 6.20, 6.10$ (each br, each 5H, Cp), 5.46 (br, 1H, 3-H), 2.20, 2.03, 1.62, 1.52 (each br, each 1H, 1-H',H, 4-H',H), 1.31 (br, 3H, Me) ppm. Dynamics of the allyl inversion in THF-*d*₈: coalescence of the Cp-signals at 233 K, $\Delta\nu(173 \text{ K}) = 61$ Hz, $\Delta G^\ddagger = 10.9 \pm 0.5$ kcal/mol. ¹³C-NMR (150.8 MHz, 299 K, THF-*d*₈): $\delta = 149.0$ (d, ¹J_{CF} = 240 Hz, *o*-B(C₆F₅)₃), 138.5 (d, ¹J_{CF} = 240 Hz, *p*-B(C₆F₅)₃), 137.9 (d, ¹J_{CF} = 240 Hz, *m*-B(C₆F₅)₃), 131.5 (C, C-2), 129.9 (CH, C-3), 126.8 (ipso-B(C₆F₅)₃), 111.6 (CH, Cp), 49.2 (CH₂, C-1), 28.0 (br, CH₂, C-4), 20.1 (CH₃, C-5) ppm. GCOSY (599.9 MHz, 299 K, THF-*d*₈): $\delta = 5.48$ (3-H)/2.18 (4-H) ppm. GHSQC (599.9 MHz, 299 K, THF-*d*₈): $\delta = 129.9/5.48$ (C-3), 111.6/6.06 (Cp), 49.2/2.15 (C-1), 20.1/1.35 (C-5) ppm. ¹⁹F-NMR (564.3 MHz, 303 K, toluene-*d*₈): $\delta = -168.3$ (t, ³J_{FF} = 21 Hz, 6F, *m*-F), -165.5 (t, ³J_{FF} = 21 Hz, 3F, *p*-F), -132.7 (d, ³J_{FF} = 21 Hz, 6F, *o*-F) ppm.

Reaction of (2-Phenylbutadiene)zirconocene (1f) with B(C₆F₅)₃, Generation of 2f. This complex was only in situ generated in the respective deuterated solvents and then spectroscopically characterized: 35 mg (0.10 mmol) of 1f in 1 mL of toluene-*d*₈ was combined

with a solution of 54 mg (0.10 mmol) of B(C₆F₅)₃ in 1 mL of toluene-*d*₈ at ambient temperature. An aliquot was used for the NMR measurements. Complex 2f·THF was analogously generated in THF-*d*₈. Spectroscopic characterization of 2f: ¹H-NMR (599.9 MHz, 299 K, toluene-*d*₈): $\delta = 7.11-6.89$ (m, 5H, Ph), 5.33, 4.72 (each s, each 5H, Cp), 5.02 (d, ³J_{HH} = 14.0 Hz, 1H, 3-H), 3.21 (d, ²J_{HH} = 10.7 Hz, 1H, 1-H'), 0.83 (d, ²J_{HH} = 10.7 Hz, 1H, 1-H), 0.17 (br, 1H, 4-H'), -1.73 (br, 1H, 4-H) ppm. ¹³C-NMR (150.8 MHz, 299 K, toluene-*d*₈): $\delta = 148.5$ (d, ¹J_{CF} = 240 Hz, *o*-B(C₆F₅)₃), 147.3 (C, C-2), 139.4 (d, ¹J_{CF} = 240 Hz, *p*-B(C₆F₅)₃), 139.3 (C, Ph), 137.7 (d, ¹J_{CF} = 240 Hz, *m*-B(C₆F₅)₃), 130.0, 129.3, 129.1, 128.2, 125.7 (each CH, Ph), 109.5, 107.1 (each CH, Cp), 107.0 (CH, C-3), 60.2 (CH₂, C-1), 24.7 (br, CH₂, C-4) ppm. GCOSY (599.9 MHz, 299 K, toluene-*d*₈): $\delta = 5.02$ (3-H)/0.17 (4-H'); 3.21 (1-H')/0.83 (1-H); 0.17 (4-H')/ -1.73 (4-H) ppm. GHSQC (599.9 MHz, 299 K, toluene-*d*₈): $\delta = 109.5/5.33$ (Cp), 107.1/4.72 (Cp), 107.0/5.02 (C-3), 60.2/3.21, 0.83 (C-1), 24.7/0.17 (C-4) ppm, (phenyl resonances under solvent signals). GHMBC (599.9 MHz, 299 K, toluene-*d*₈): $\delta = 147.3$ (C-2)/3.21 (1-H'), 7.11 (Ph), 139.3 (C, Ph)/6.90 (Ph), 3.21 (1-H'), 0.83 (1-H), 107.1 (C-3)/3.21 (1-H'), 0.83 (1-H) ppm; ipso-C of B(C₆F₅)₃ not detected. ¹⁹F-NMR (564.3 MHz, 299 K, toluene-*d*₈): $\delta = -165.2$ (d, ³J_{FF} = 21 Hz, 6F, *m*-F), -159.6 (t, ³J_{FF} = 21 Hz, 3F, *p*-F), -133.9 (d, ³J_{FF} = 21 Hz, 6F, *o*-F) ppm. ¹⁹F-NMR (564.3 MHz, 193 K, toluene-*d*₈): $\delta = -214.4$ (br., 1F, *o*-F coordinating), $-165.7, -165.3$ (3x), -162.7 (2x) (each br, 6F, *m*-F), $-159.2, -158.9, -158.1$ (each br, 3F, *p*-F), $-134.7, -133.8$ (3x), -130.5 (2x) (each br, 5F, *o*-F) ppm. Dynamics of the fluorine coordination in toluene-*d*₈: *o*-F coalescence at 243 K, $\Delta\nu(193 \text{ K}) = 46$ 118 Hz, $\Delta G^\ddagger = 8.4 \pm 0.5$ kcal/mol.

2f·THF: ¹H-NMR (599.9 MHz, 299 K, THF-*d*₈): $\delta = 7.30-7.00$ (m, 5H, Ph), 5.98 (s, 10H, Cp), 5.26 (t, ³J_{HH} = 7.7 Hz, 1H, 3-H), 2.56 (br, 2H, 4-H',H), 2.41 (s, 2H, 1-H',H) ppm. (193 K): $\delta = 7.31-7.17$ (br, 5H, Ph), 6.31, 5.81 (each br, each 5H, Cp), 5.17 (br, 1H, 3-H), 2.25, 2.08, 1.79, 1.37 (each br, each 1H, 1-H',H, 4-H',H) ppm. Dynamics of the allyl inversion in THF-*d*₈: coalescence of the Cp-signals at 223 K, $\Delta\nu(173 \text{ K}) = 298$ Hz, $\Delta G^\ddagger = 9.7 \pm 0.5$ kcal/mol. ¹³C-NMR (150.8 MHz, 299 K, THF-*d*₈): $\delta = 149.0$ (d, ¹J_{CF} = 240 Hz, *o*-B(C₆F₅)₃), 139.4 (C, Ph), 138.2 (C, C-2), 138.0 (d, ¹J_{CF} = 240 Hz, *p*-B(C₆F₅)₃), 137.1 (d, ¹J_{CF} = 240 Hz, *m*-B(C₆F₅)₃), 129.1, 128.9, 128.5, 128.4, 126.7 (each CH, Ph), 123.8 (CH, ¹J_{CH} = 135 Hz, C-3), 116.4 (ipso-B(C₆F₅)₃), 111.8 (CH, ¹J_{CH} = 175 Hz, Cp), 47.6 (CH₂, ¹J_{CH} = 147 Hz, C-1), 27.0 (br, CH₂, C-4) ppm. GCOSY (599.9 MHz, 299 K, THF-*d*₈): $\delta = 5.26$ (3-H)/2.56 (4-H) ppm. GHSQC (599.9 MHz, 299 K, THF-*d*₈): $\delta = 129.1/7.24$ (Ph), 128.9/7.27 (Ph), 128.5/7.27 (Ph), 128.4/6.96 (Ph), 126.7/7.26 (Ph), 123.8/5.26 (C-3), 111.8/5.98 (Cp), 47.6/2.41 (C-1), 27.0/2.56 (C-4) ppm. ¹⁹F-NMR (564.3 MHz, 303 K, toluene-*d*₈): $\delta = -168.7$ (tr, ³J_{FF} = 21 Hz, 6F, *m*-F), -166.2 (tr, ³J_{FF} = 21 Hz, 3F, *p*-F), -132.8 (d, ³J_{FF} = 21 Hz, 6F, *o*-F) ppm.

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Supporting Information Available: Details of the X-ray crystal structure analyses of the complexes 2c and 2e, including listings of bond lengths and angles and positional parameters (18 pages). See any current masthead page for ordering and Internet access instructions.

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