Articles

Structural Dichotomy in Single-Component Ziegler Catalyst Systems: Characterization of Zr···F and Zr···C-Bonded Structural Types of Group 4 Metallocene $[C_4H_6{-}B(C_6F_5)_3]$ Betaines

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The organometallic Lewis acid $B(C_6F_5)_3$ adds to the terminal $=CH_2$ group of the (butadiene)-metallocene complexes **5a** and **5b** to give the *ansa*-metallocene betaine systems $[Me_2Si(C_5H_4)_2]Zr[C_4H_6{-}B(C_6F_5)_3]$ (**6a**) and $[Me_2Si(3\text{-}MeC_5H_3)_2]Zr[C_4H_6{-}B(C_6F_5)_3]$ (**6b**), respectively, in high yield. Both complexes were characterized by X-ray diffraction. They both contain a substituted η^3-allyl ligand F of *E* configuration, and they show a characteristic (ortho aryl)-C−F···Zr interaction that stabilizes the electron-deficient metal center inside the dipolar structure. $B(C_6F_5)_3$ also adds to one butadiene terminus of (*s-cis*-η^4-C_4H_6)[$Me_2C(C_5H_4)$-(indenyl)]Zr to give a high yield of a single isomer of the respective *ansa*-metallocene $[C_4H_6{-}B(C_6F_5)_3]$ betaine complex **9**. The X-ray crystal structure analysis of **9** has revealed that in this case a (*Z*)-η^3-allyl-$CH_2B(C_6F_5)_3$ ligand is formed. This precluded the (aryl)C−F···Zr coordination. Instead, the zirconium center in **9** forms a stabilizing internal ion pair interaction between the negatively polarized [B]−*C*(4)H_2 methylene group and the positive zirconium center. The analogously structured *ansa*-metallocene [(*Z*)-$C_4H_6{-}B(C_6F_5)_3$] betaine complex **12** is obtained in high yield from $B(C_6F_5)_3$ addition to (*s-cis*-η^4-butadiene)[$Me_2C(C_5H_4)$(fluorenyl)]Zr. In solution the complexes **6**, **9**, and **12** exhibit structures that are analogous to those found in the solid state. However, treatment of (butadiene)[$Me_2Si(C_5H_4)_2$]-Zr (**5a**) with $B(C_6F_5)_3$ under kinetic control (233 K in toluene-d_8) quantitatively yields the [$Me_2Si(C_5H_4)_2$]Zr[(*Z*)-$C_4H_6{-}B(C_6F_5)_3$] betaine isomer **13**, which contains the stabilizing [B]−C(4)H_2···Zr internal ion pair interaction. Subsequent thermally induced rearrangement of the kinetic product **13** ($\Delta G^{\ddagger}_{\text{rearr}}(298\text{ K}) = 21.5 \pm 0.5$ kcal mol^{-1}) then results in the formation of the eventually observed thermodynamic *ansa*-metallocene betaine product **6a**, that contains the (*E*)-$C_4H_6{-}B(C_6F_5)_3$ ligand and exhibits internal (aryl)C−F···Zr coordination. A similar reaction sequence was observed during the addition of $B(C_6F_5)_3$ to the parent (butadiene)zirconocene system **1**: at 213 K the kinetic $Cp_2Zr[(Z)\text{-}(1{-}3\eta),\kappa C^4\text{-}C_4H_6{-}B(C_6F_5)_3]$ betaine product **14** is formed, which rapidly rearranges at temperatures above 253 K to yield the previously observed stable $Cp_2Zr[(E)\text{-}C_4H_6{-}B(C_6F_5)_3]$ betaine system **2**, which is characterized by an internal C−F···Zr bond. The *ansa*-metallocene betaines **6**, **9**, and **12** are all active homogeneous single-component Ziegler catalysts for ethene and propene polymerization. They are similarly effective as the usually employed *ansa*-metallocene dichloride/methylalumoxane catalyst systems.

Introduction

Butadiene zirconocene (**1**; Scheme 1)[1] adds the strong organometallic Lewis acid $B(C_6F_5)_3$[2] selectively at carbon atom C4 of the conjugated diene ligand. The resulting betaine system **2** was isolated at ambient temperature and characterized by spectroscopy and by X-ray diffraction.[3] Other butadiene group 4 metallocenes, such as *rac*-[(dimethylsilylene)bis(indenyl)]-zirconium, form similar $^{R}Cp_2M{-}[C_4H_6{-}B(C_6F_5)_3]$ betaines.[4] These complexes represent an interesting type of homogeneous single-component Ziegler catalyst sys-

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† Performed the X-ray crystal structure analyses.

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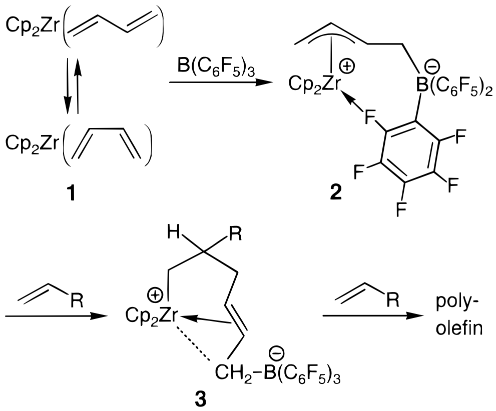
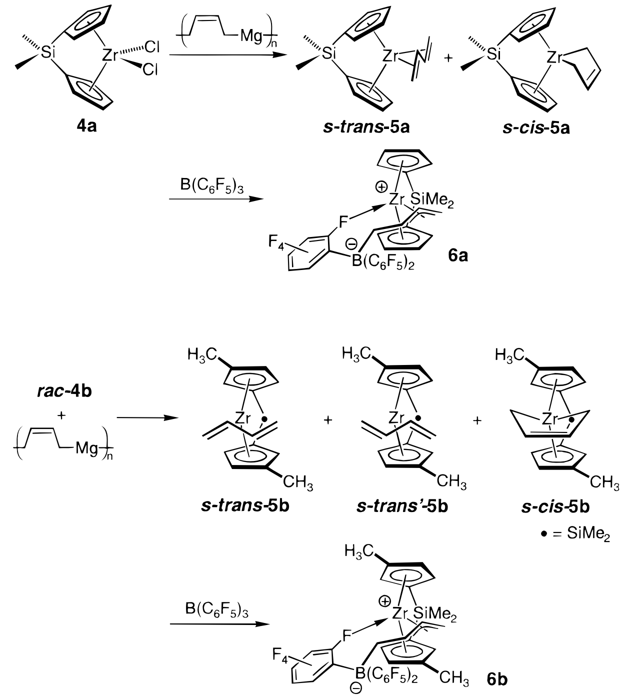
Scheme 1



tems for the polymerization of α-olefins. For several of these systems it was possible to experimentally follow the first alkene insertion step of the initiation sequence of the active polymerization process[5] and determine its kinetic[6] and stereochemical characteristics.[4a] In this primary reaction step a new C_6-bridged unsaturated betaine intermediate (**3**) is formed and experimentally observed, which is characterized by the presence of a weak metallocene–olefin π-complexation[7] and an internal ion pair interaction[8] between the metallocene and the $C^6H_2{-}B(C_6F_5)_3$ carbon end of the chain.

The starting material, the betaine **2**, is characterized by a different interaction between the positively polarized metallocene and the negative $-C^4H_2{-}B(C_6F_5)_3$ chain end:[9] here a weak stabilizing Zr···F–C interaction[10] with an *o*-F–C(Ar) bond of one of the $-C_6F_5$ groups at boron was monitored by ^{19}F NMR spectros-

Scheme 2



copy and confirmed by X-ray crystal structure analyses in several cases.[3,4b] We have now found a different type of $Zr/{-}C^4H_2{-}B(C_6F_5)_3$ interaction in a number of cases of zirconocene–$[C_4H_6{-}B(C_6F_5)_3]$ betaines, characterized by an intramolecular $Zr{\cdots}C^4H_2{-}[B]$ ion pair formation,[11] and even cases of interconversion of both types of internally stabilized betaines. The spectroscopic and structural characterization of representative examples of such metallocene–butadiene–$B(C_6F_5)_3$ betaines is described in this article, and the consequences of the mode of internal stabilization on the catalytic function of such single-component Ziegler catalyst systems was investigated.

Results and Discussion

***ansa*-Metallocene–$[C_4H_6{-}B(C_6F_5)_3]$ Betaine Structures.** For this study we have employed four *ansa*-zirconocene frameworks, namely [dimethylsilylenebis(cyclopentadienyl)]zirconium, its chiral analogue *rac*-[dimethylsilylenebis(3-methylcyclopentadienyl)]zirconium, and the carbon-bridged systems [isopropylidene–Cp(indenyl)]Zr and [isopropylidene–Cp(fluorenyl)]Zr. In each case the corresponding *ansa*-metallocene dichloride[12] was converted to the corresponding butadiene complexes by treatment with the oligomeric butadiene dianion reagent "butadiene magnesium" (em-

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ployed as a THF adduct).[13] The [dimethylsilylenebis(cyclopentadienyl)]zirconium butadiene system **5a** (Scheme 2) had previously been prepared by a different route,[14] via the bis(vinyl)zirconocene complex.[15] The butadiene−Mg route resulted in the formation of the same 1:1 mixture of the (*s-cis*-η^4-butadiene)- and (*s-trans*-η^4-butadiene)Zr[$Me_2Si(C_5H_4)_2$] complexes *s-cis*-**5a** and *s-trans*-**5a**.

Treatment of the *s-cis-*/*s-trans*-**5a** mixture with an equimolar amount of $B(C_6F_5)_3$ at ambient temperature resulted in the clean formation of the metallocene [$C_4H_6-B(C_6F_5)_3$] betaine **6a**, which was isolated in ca. 80% yield from the reaction mixture. Recrystallization from toluene at ambient temperature gave single crystals of complex **6a** that were suitable for an X-ray crystal structure analysis of the obtained product.

In the crystal state, complex **6a** (Figure 1) shows the typical structural features of such a single-component metallocene Ziegler system. It features a *syn*-substituted (i.e., of 2,3-*E*-configuration) distorted π-allyl ligand at zirconium[16] (Zr−C1 = 2.361(6) Å, Zr−C2 = 2.496(6) Å, Zr−C3 = 2.788(6) Å). The newly formed C4−B bond (1.665(9) Å) covalently connects the four former butadiene carbon atoms with the added $B(C_6F_5)_3$ moiety. One of the ortho fluorine substituents (C22−F22 = 1.388(7) Å) of the latter coordinates to the electrophilic zirconium center[10,17] in this dipolar arrangement to form a metallacycle (F22−Zr = 2.385(3) Å, C22−F22−Zr = 142.0(3)°).

Treatment of the chiral *ansa*-metallocene dichloride *rac*-[$Me_2Si(3\text{-}MeC_5H_3)_2$]$ZrCl_2$ (*rac*-**4b**) with butadiene magnesium yields a mixture of the three (η^4-butadiene)-[$Me_2Si(3\text{-}MeC_5H_3)_2Zr$]isomers *s-trans*-**5b**, *s-trans′*-**5b** and *s-cis*-**5b** (see Scheme 2) in a 82:8:10 ratio, as we had previously described.[18] The addition of tris(pentafluorophenyl)borane, proceeding analogously as described above for the *s-cis*-**5a**/*s-trans*-**5a** plus $B(C_6F_5)_3$ reaction, could here give rise to the formation of two diastereomeric metallocene [$C_4H_6-B(C_6F_5)_3$] betaine complexes (with relative configurations [a*R*(metallocene), p*R*(allyl)]* and [a*R*(metallocene), p*S*(allyl)]*).[19] The reaction between the **5b** mixture and $B(C_6F_5)_3$ proceeds rapidly. At room temperature it takes less than 10 min to go to completion. Crystallization at −40 °C furnished a single isomer of the adduct (86% isolated). Single crystals of the product **6b** were obtained from benzene at ambient temperature. The X-ray crystal structure analysis revealed the formation of the diastereomer **6b**, whose stereochemistry is described by the relative configurations (a*R*, p*S*)* (see Figure 2 and Scheme 2).

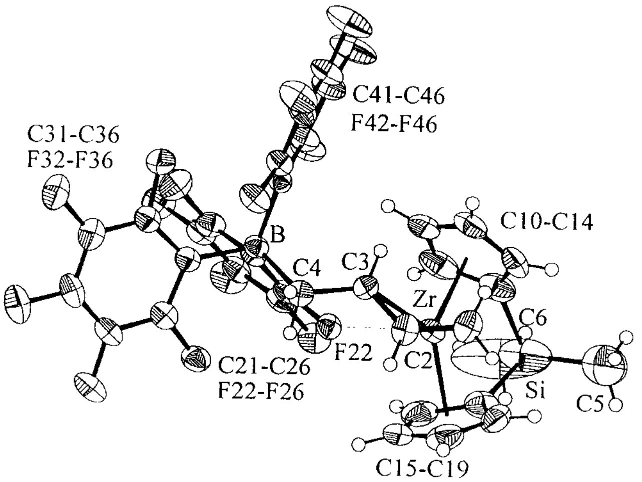

Figure 1. Molecular structure of the metallocene [$C_4H_6-B(C_6F_5)_3$] betaine **6a**. Selected bond lengths (Å) and angles (deg): Zr−C1 = 2.361(6), Zr−C2 = 2.496(6), Zr−C3 = 2.788(6), Zr−F22 = 2.385(3), C1−C2 = 1.433(9), C2−C3 = 1.359(8), C3−C4 = 1.511(8), C4−B = 1.665(9), B−C21 = 1.657(9), B−C31 = 1.668(9), B−C41 = 1.662(9), C22−F22 = 1.388(7), Si−C5 = 1.827(14), Si−C6 = 1.852(13), Si−C14 = 1.864(8), Si−C15 = 1.871(8); C1−C2−C3 = 126.0(6), C2−C3−C4 = 124.9(6), C3−C4−B = 119.9(5), C4−B−C21 = 115.0(5), C4−B−C31 = 107.5(5), C4−B−C41 = 105.3(5), C21−B−C31 = 104.9(5), C21−B−C41 =112.0(5), C31−B−C41 = 112.4(5), C22−F22−Zr =142.0(3), C14−Si−C5 = 112.8(5), C14−Si−C6 = 110.2(6), C14−Si−C15 = 94.0(3), C5−Si−C6 = 114.2(9), C5−Si−C15 = 111.9(6), C6−Si−C15 = 112.2(6).

The molecular structure of **6b** is quite analogous to that of **6a** and that of the parent compound **2**. The $C_4H_6-B(C_6F_5)_3$ ligand is 1−3-η^3-coordinated to zirconium and exhibits an *E*-configuration of the distorted π-allyl moiety. Characteristically, one of the ortho fluorine substituents of a C_6F_5 group at boron is again coordinated to the zirconium center. A comparison of typical structural data of representative examples of this structural type of metallocene [$C_4H_6-B(C_6F_5)_3$] betaines is provided in Table 1.

Treatment of the *ansa*-metallocene dichloride [isopropylidene−Cp(1-indenyl)]$ZrCl_2$ (**7**) with butadiene

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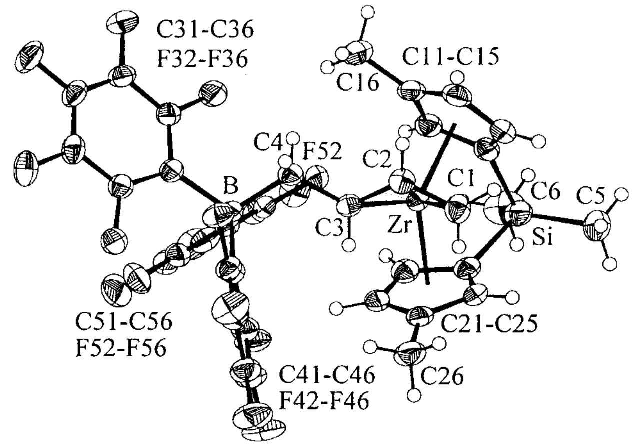


Figure 2. Molecular structure of **6b**. Selected bond lengths (Å) and angles (deg): Zr−C1 = 2.364(2), Zr−C2 = 2.501(2), Zr−C3 = 2.639(2), Zr−F52 = 2.403(1), C1−C2 = 1.424(3), C2−C3 = 1.361(3), C3−C4 = 1.507(3), C4−B = 1.649(3), B−C31 = 1.661(3), B−C41 = 1.656(3), B−C51 = 1.652(3), C52−F52 = 1.397(2), Si−C5 = 1.844(3), Si−C6 = 1.851(3), Si−C11 = 1.869(2), Si−C21 = 1.870(2); C1−C2−C3 = 123.8(2), C2−C3−C4 = 125.0(2), C3−C4−B = 116.9(2), C4−B−C31 = 108.5(2), C4−B−C41 = 104.6(2), C4−B−C51 = 114.6(2), C31−B−C41 = 113.2(2), C31−B−C51 = 103.3(2), C41−B−C51 = 112.8(2), C52−F52−Zr = 138.5(1), C11−Si−C5 = 111.3(1), C11−Si−C6 = 111.4(1), C11−Si−C21 = 94.2(1), C5−Si−C6 = 114.3(2), C5−Si−C21 = 112.1(1), C6−Si−C21 = 111.9(1).

Table 1. Comparison of Selected Structural Data of the Metallocene [C_4H_6−$B(C_6F_5)_3$] Betaine Complexes 6a,b and 2[a]

	metallocene		
	[$Me_2Si(C_5H_4)_2$]Zr (**6a**)	[$Me_2Si(3\text{-}MeC_5H_3)_2$]Zr (**6b**)	Cp_2Zr (**2**)
C1−C2	1.433(9)	1.424(3)	1.414(9)
C2−C3	1.359(8)	1.361(3)	1.342(8)
C3−C4	1.511(8)	1.507(3)	1.521(8)
C4−B	1.665(9)	1.649(3)	1.633(9)
C1−C2−C3	126.0(6)	123.8(2)	123.5(6)
C2−C3−C4	124.9(6)	125.0(2)	126.9(6)
C3−C4−B	119.9(5)	116.9(2)	119.0(5)
Zr−C1	2.361(6)	2.364(2)	2.339(5)
Zr−C2	2.496(6)	2.501(2)	2.494(6)
Zr−C3	2.788(6)	2.639(2)	2.710(5)
Zr−F	2.385(3)	2.403(1)	2.423(3)
C(Ar)−F−Zr	142.0(3)	138.5(1)	140.0(3)
C(Ar)−F	1.388(7)	1.397(2)	1.402(6)

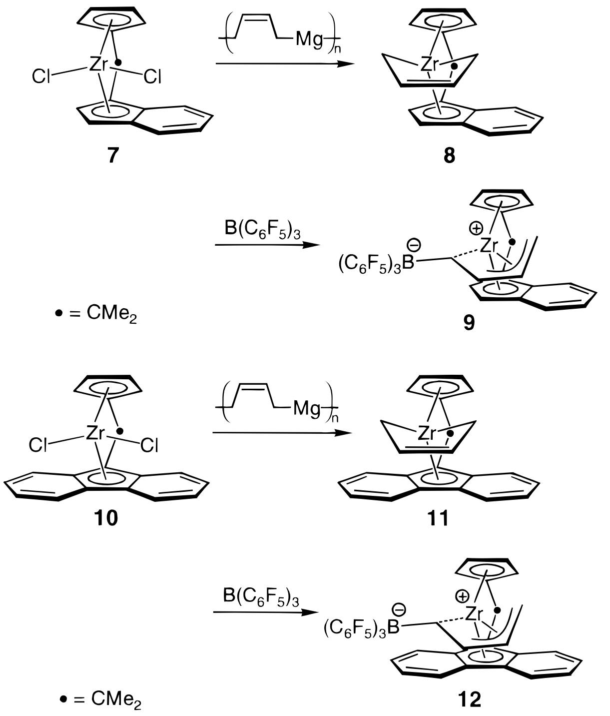
[a] Bond lengths in Å and angles in deg. For **6a**,**b**, data are from this work; for **2**, data are from ref 3.

Table 2. Comparison of Selected ^1H and ^{13}C NMR Data of the η^4-Butadiene Zirconocenes 5, 8, and 11

compd	conditions	isomer	H_{meso}	H_{syn}	H_{anti}	=CH−	$=CH_2$
5a	*a*	*s-trans*	2.92	3.12	1.34	95.8	59.5
		s-cis	4.79	3.44	−0.83	111.6	50.5
5b[d]	*b*	*s-trans*	2.29	2.97	1.33	99.0	59.6
		s-trans′	2.55	3.21	1.05	97.4	62.8
		s-cis	4.81	3.35	−0.55	112.2	51.4
			4.68	3.30	−1.11	112.1	50.6
8	*c*	(*s-cis*)	5.20	3.14	−0.82	117.7	56.7
			4.10	2.03	−1.31	112.6	49.6
11	*e*	(*s-cis*)	3.90	1.67	−0.97	122.5	52.7

[a] Conditions: benzene-d_6, 298 K. [b] Conditions: toluene-d_8, 253 K. [c] Conditions: toluene-d_8, 298 K. [d] **5b** values from ref 18. [e] Conditions: toluene-d_8, 288 K.

Scheme 3



magnesium results in the formation of a single *s-cis*-η^4-butadiene *ansa*-metallocene diastereoisomer (**8**).[20] From the NMR data (see Table 2) and the results of an X-ray crystal structure analysis (the data of which will not be discussed in detail due to its rather poor quality; see the Supporting Information), the isomer has likely been formed in which the conjugated diene ligand has its open side oriented toward the Cp ring of the *ansa* backbone (see Scheme 3).[21]

Addition of $B(C_6F_5)_3$ has resulted in clean carbon−boron coupling with formation of an *ansa*-metallocene [C_4H_6−$B(C_6F_5)_3$] betaine (**9**; Figure 3), which was isolated in >80% yield. Single crystals of **9** were obtained from benzene at room temperature. Analysis revealed that in this case a structurally different betaine system was obtained. In complex **9** the resulting substituted η^3-allyl moiety exhibits a *Z* configuration. It shows rather different bonding parameters than the (*E*)-allyl unit in, for example, the complexes **6**. In **9** the three carbon atoms of the (allyl)zirconocene unit are much more evenly linked with the central metal atom[22] (for details see Table 3). The *Z* configuration of the C_4H_6−[B] moiety brings carbon atom C4 rather close to zirconium. The resulting C4−Zr distance (2.498(2) Å)

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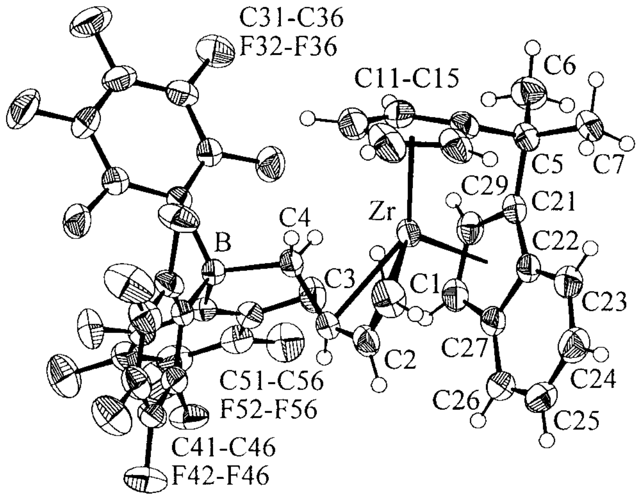

Figure 3. Molecular structure of the betaine complex **9**. Selected bond lengths (Å) and angles (deg): Zr−C1 = 2.333(3), Zr−C2 = 2.521(2), Zr−C3 = 2.508(2), Zr−C4 = 2.498(2), C1−C2 = 1.406(4), C2−C3 = 1.370(3), C3−C4 =1.489(3), C4−B = 1.670(3), B−C31 = 1.657(3), B−C41 = 1.643(3), B−C51 = 1.644(3), C5−C6 = 1.524(3), C5−C7 = 1.528(3), C5−C11 = 1.523(3), C5−C21 = 1.529(3); C1−C2−C3 = 127.1(3), C2−C3−C4 = 126.9(2), C3−C4−B = 115.5(2), C4−B−C31 = 110.7(2), C4−B−C41 = 100.5(2), C4−B−C51 = 115.4(2), C31−B−C41 = 114.9(2), C31−B−C51 = 102.8(2), C41−B−C51 = 113.1(2), C11−C5−C6 = 112.2(2), C11−C5−C7 = 112.2(2), C11−C5−C21 = 99.3(2), C6−C5−C7 = 107.9(2), C6−C5−C21 = 111.2(2), C7−C5−C21 = 114.0(2).

Table 3. Selected Structural Data of the *ansa*-Metallocene [(*Z*)-(1−3-η^3),κ*C*^{4}-C_4H_6−B(C_6F_5)$_3$] Betaines 9 and 12[a]

	metallocene	
	[Me_2C(Cp)(indenyl)]Zr (**9**)	[Me_2C(Cp)(fluorenyl)]Zr (**12**)
C1−C2	1.406(4)	1.431(4)
C2−C3	1.370(3)	1.355(4)
C3−C4	1.489(3)	1.491(4)
C4−B	1.670(3)	1.691(4)
C1−C2−C3	127.1(3)	126.9(3)
C2−C3−C4	126.9(2)	125.7(3)
C3−C4−B	115.5(2)	118.6(2)
Zr−C1	2.333(3)	2.322(3)
Zr−C2	2.521(2)	2.506(3)
Zr−C3	2.508(2)	2.545(3)
Zr−C4	2.498(2)	2.542(3)

[a] Bond lengths in Å and angles in deg.

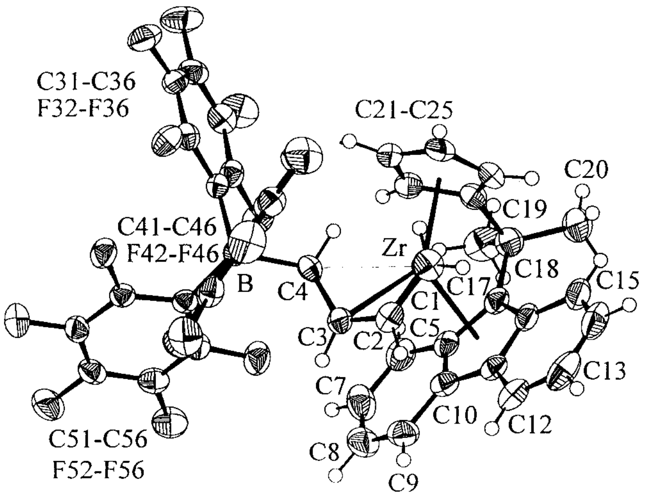

Figure 4. Molecular structure of **12**. Selected bond lengths (Å) and angles (deg) (for additional data see Table 3): Zr−C1 = 2.322(3), Zr−C2 = 2.506(3), Zr−C3 = 2.545(3), Zr−C4 = 2.542(3), C1−C2 = 1.431(4), C2−C3 = 1.355(4), C3−C4 = 1.491(4), C4−B = 1.691(4), B−C31 = 1.668(4), B−C41 = 1.644(4), B−C51 = 1.638(4), C18−C19 = 1.537(5), C18−C20 = 1.531(5), C18−C17 = 1.547(4), C18−C21 = 1.530(4); C1−C2−C3 = 126.9(3), C2−C3−C4 = 125.7(3), C3−C4−B = 118.6(2), C4−B−C31 = 107.6(2), C4−B−C41 = 101.7(2), C4−B−C51 = 115.6(2), C31−B−C41 = 112.8(2), C31−B−C51 = 104.1(2), C41−B−C51 = 115.0(2), C17−C18−C19 = 114.0(3), C17−C18−C20 = 113.7(3), C17−C18−C21 = 98.6(2), C19−C18−C20 = 107.1(3), C19−C18−C21 = 111.4(3), C20−C18−C21 = 111.9(3).

is in the typical range of an internal [B]−CH_2···[Zr] ion pair interaction.[8,11] Consequently, the bulky B(C_6F_5)$_3$ unit is oriented away from the metal center (dihedral angle C2−C3−C4−B = −133.5(2)°), so that a direct −C_6F_5···Zr interaction, as was typically found in **2** and **6**, is no longer observed in **9**. In the specific case of the [Me_2C(Cp)(indenyl)]Zr framework of **9**, in principle four different *C*$_1$-symmetric metallocene [(*Z*)-(1−3-η^3)-C_4H_6−B(C_6F_5)$_3$] betaines could have been formed. In the crystal we have only observed a single diastereomer, which has the (*Z*)-C_4H_6− subunit oriented analogously as in its immediate precursor, the (*s*-*cis*-butadiene)-[Me_2C(Cp)(indenyl)]Zr complex **8**.

The reaction of [Me_2C(Cp)(fluorenyl)]$ZrCl_2$ (**10**) with butadiene magnesium yields the *s*-*cis*-η^4-butadiene *ansa*-metallocene complex **11**. A single isomer is obtained in which the butadiene ligand is also probably oriented with its open side toward the small Cp ring (see Table 2). Subsequent treatment of **11** with B(C_6F_5)$_3$ gave the *ansa*-metallocene [C_4H_6−B(C_6F_5)$_3$] betaine **12**, which was isolated in >70% yield. A single isomer was obtained. Diffusion of pentane vapor into a toluene solution of **12** gave single crystals. The X-ray crystal structure analysis showed the presence of a *Z* (i.e., cisoid) (1−3-η^3)-C_4H_6−B(C_6F_5)$_3$ ligand bonded to the zirconium atom, which also contained a short Zr−C4 contact (2.542(3) Å) indicating an internal ion pair interaction inside the dipolar structure. The C4−B vector in complex **12** is oriented away from zirconium (θ = C2−C3−C4−B = −121.6(3)°) and the U-shaped C1−C4 framework has its open side oriented toward the Cp sector of the Me_2C(Cp)(fluorenyl) *ansa*-metallocene framework (for structural details see Table 3 and Figure 4).

The X-ray crystal structure analyses of the examples presented above have revealed that two different structural types of the group 4 metallocene [C_4H_6−B(C_6F_5)$_3$] betaines can be formed that are distinguished by exhibiting either an *E* or *Z* configuration of the substituted π-allyl moiety inside the connecting C_4 chain. Both situations result in fundamentally different modes of a supporting stabilization of the positively polarized reactive zirconium center: in the *E* isomers it is geometrically feasible for an (ortho aryl)C−F moiety to reach over to zirconium and form a C−F···Zr bond, whereas such an interaction is spatially precluded in the examples exhibiting (*Z*)-allyl configuration. In these cases an internal Zr−C^{4}H$_2$−[B] ion pair interaction seems to represent the prevailing mode of coordinative

Table 4. ^{1}H NMR Data of the Metallocene [C_4H_6−$B(C_6F_5)_3$] Betaines[a]

compd	metallocene	C2, C3 confign	1-H	1-H′	2-H	3-H	4-H	4-H′
2[b]	Cp_2Zr	*E*	1.85	1.47	5.88	5.23	2.56	2.25
14[c]	Cp_2Zr	*Z*	2.63	0.76	5.05	4.20	−0.28	−2.37
6a[d]	$[Me_2Si(C_5H_4)_2]Zr$	*E*	1.86	1.53	5.92	5.43	2.63	2.31
13[e]	$[Me_2Si(C_5H_4)_2]Zr$	*Z*	2.58	0.86	5.12	4.38	−0.39	−1.90
6b	$[Me_2Si(3\text{-}MeC_5H_3)_2]Zr$	*E*	1.67	1.34	5.90	4.73	2.42	2.15
9	$[Me_2C(Cp)(ind.)]Zr$	*Z*	0.94	0.94	4.52	4.86	−0.57	−0.74
12	$[Me_2C(Cp)(flu.)]Zr$	*Z*	0.96	0.26	4.53	3.93	−0.53	−0.53

[a] In toluene-d_8 at 298 K, if not noted otherwise. [b] At 303 K. [c] At 253 K. [d] In benzene-d_6 at 298 K. [e] 233 K.

Table 5. ^{13}C NMR Data of the Metallocene [C_4H_6−$B(C_6F_5)_3$] Betaines[a]

compd	confign	C1	C2	C3	C4
2[b]	*E*	52.7	131.8	123.8	28.5
14[c]	*Z*	57.5	133.5	109.7	∼23
6a[d]	*E*	52.0	130.4	123.1	28.3
13[e]	*Z*	55.9	132.9	111.0	24.4
6b	*E*	53.0	131.3	123.2	26.7
9	*Z*	62.8	135.2	109.9	∼22
12	*Z*	58.3	136.3	121.4	∼20

[a] In toluene-d_8 at 298 K if not noted otherwise. [b] 303 K. [c] 213 K. [d] In benzene-d_6 at 298 K. [e] 233 K.

saturation of the reactive zirconium center. There is evidence that this structural dichotomy is also found in solution. For some examples of such single-component metallocene betaine Ziegler catalyst systems both types of structural isomers were even observed in solution under specific conditions.

Behavior of the Metallocene Betaines in Solution. In solution we have also found only a single isomer of the Me_2C-bridged *ansa*-metallocene [C_4H_6−$B(C_6F_5)_3$] betaine systems **9** and **12**, respectively. The NMR (^{1}H, ^{13}C, ^{19}F) spectroscopic characterization provided cumulative evidence that both complexes exhibit structures in solution that are analogous to those found for these complexes in the crystal state (see above). This is evident from a comparison of typical chemical shift data of the C_4H_6−$B(C_6F_5)_3$ ligand (for details see Tables 4 and 5 and the Experimental Section) and the result of a series of NOE NMR experiments on both **9** and **12** (and **6b** for a comparison, details are provided with the Supporting Information).

A strong indication of the presence of a (*Z*)-C_4H_6−[B] moiety in **9** is the magnitude of the vicinal coupling constant, ^3J(2-H,3-H) = 11.5 Hz. For the structurally closely related [Me_2C(Cp)(fluorenyl)][C_4H_6−$B(C_6F_5)_3$]Zr complex **12** a coupling constant of ^3J(2-H,3-H) = 10.0 Hz was found. This is in contrast to the parent metallocene [C_4H_6−$B(C_6F_5)_3$] betaine complex **2**, for which a vicinal coupling constant of ^3J(2-H,3-H) = 15.8 Hz was found.[23]

From the ^{1}H and ^{13}C NMR data (see Tables 4 and 5) we deduce that the structure of the *ansa*-metallocene [C_4H_6−$B(C_6F_5)_3$] betaine complexes **6a** and **6b** in solution is characteristically different from those of **9** and **12**. It is likely that **6a** and **6b** exhibit (*E*)-η^3-allyl configurations inside their C_4H_6−$B(C_6F_5)_3$ moieties, just as was observed for these complexes in the solid state. The analogy between the structures in solution and in the crystal state was demonstrated for these complexes by their dynamic ^{19}F NMR spectra. At 298 K complex **6b** (see Figure 5) exhibits a set of three ^{19}F NMR resonances in toluene-d_8 solution at 564 MHz corresponding to rapidly equilibrating ortho, para, and meta C_6F_5 fluorine substituents at δ −132.8, −161.1, and −165.2, respectively. Lowering the temperature gradually to 228 K results in broadening and decoalescence to eventually give rise to a set of 14 separated signals for the 15 fluorine substituents in this complex, corresponding to five *o*-C−F (δ −126.1, −130.5, −131.9, −134.1, −136.0), three *p*-C−F and six *m*-C−F resonances (δ −158.1, −159.7, −161.2, −161.5, −164.5, −164.8, −165.1, −166.3 (double intensity)). At 228 K the remaining (ortho aryl)C−F resonance appears at an extremely negative value of δ −208.8, which indicates the presence of a bridging divalent fluorine atom in complex **6b** in solution.[24] From the *o*-C−F signal exchange in the dynamic ^{19}F NMR spectra a Gibbs activation energy of $\Delta G^{\ddagger}_{CF}(275\ K) = 9.7 \pm 0.5$ kcal mol^{-1} was determined[25] for the thermally induced automerization process of **6b**, which probably involves (aryl)C−F⋯Zr bond breaking in the rate-determining step.[4b] Complex **6a** shows an analogous behavior ($\Delta G^{\ddagger}_{CF}(250\ K) = 8.7 \pm 0.5$ kcal mol^{-1}; for details see the Experimental Section).

A low-temperature NMR study has revealed that a structurally different isomeric metallocene [(*Z*)-C_4H_6−$B(C_6F_5)_3$] betaine is involved in the [$Me_2Si(C_5H_4)_2$](butadiene)Zr/$B(C_6F_5)_3$ chemistry as a primary product formed under kinetic control. The reaction of the butadiene *ansa*-metallocene complex **5a** with tris(pentafluorophenyl)borane in toluene-d_8 at 233 K selectively yields a single addition product (**13**) that is markedly different from the previously isolated metallocene [(*E*)-C_4H_6−$B(C_6F_5)_3$] betaine **6a** (see Figure 6). The spectroscopic analysis revealed the typical features of the presence of a (1−3-η^3)-(*Z*)-C_4H_6−$B(C_6F_5)_3$ moiety at the *ansa*-metallocene, similar to that observed for the topologically related complexes **9** and **12** (see Tables 4 and 5 for a comparison of data). Typically, the kinetic product **13** shows the 4-H/4-H′ resonances at negative δ values (−0.39, −1.90) shifted by $\Delta\delta$ −3.02 and −4.21 ppm relative to the corresponding resonances of **6a**. This typically indicates a close interaction of the $H_2C(4)$ methylene group with the zirconium metal center.[26]

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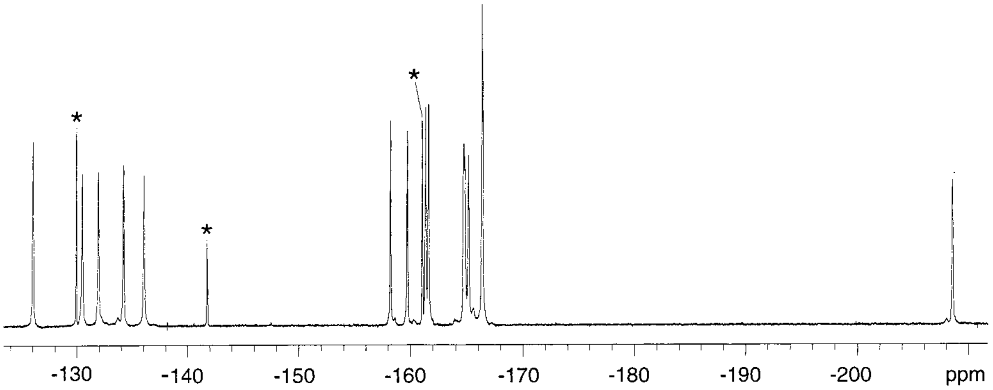


Figure 5. ^{19}F NMR spectrum of **6b** at 228 K, obtained from an in situ generated sample in toluene-d_8. The asterisks mark excess $B(C_6F_5)_3$ present in the solution.

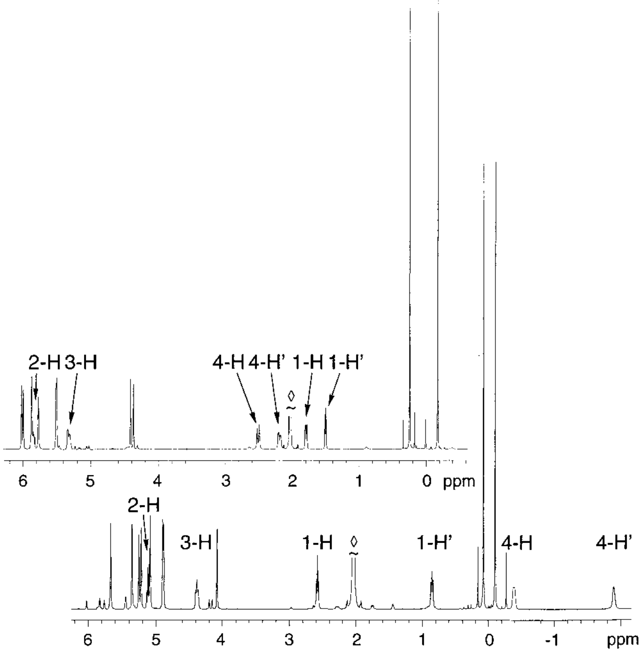
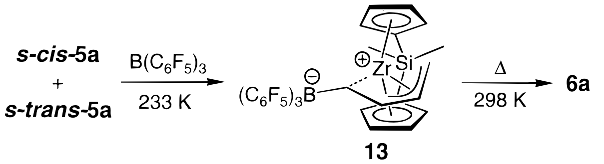


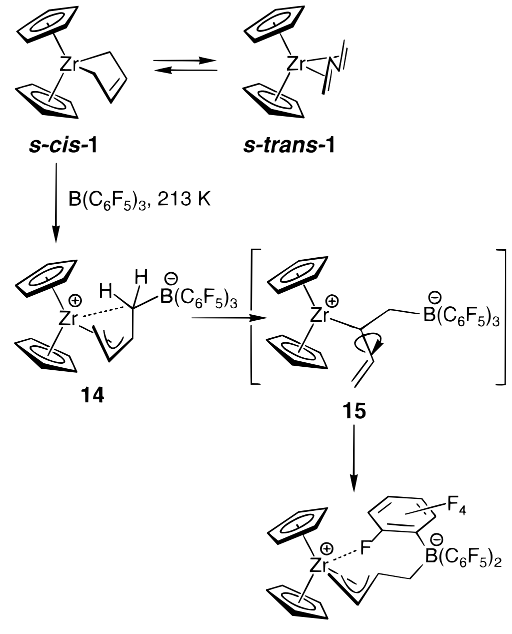
Figure 6. ^{1}H NMR spectra of the $[Me_2Si(C_5H_4)_2]Zr[C_4H_6-B(C_6F_5)_3]$ betaine isomers **6a** (*E* isomer, 233 K, top) and **13** (*Z* isomer, 198 K, bottom) in toluene-d_8.

Scheme 4



Consequently, the C4 ^{13}C NMR resonance in **13** is also shifted to a smaller δ value (24.4) relative to **6a** (28.3), although here this effect is not so pronounced.[4a] Warming a solution of **13** in toluene-d_8 to 298 K results in a clean conversion to the thermodynamic product **6a** (Scheme 4). The activation barrier of the thermally induced **13** → **6a** isomerization was determined as $\Delta G^{\ddagger}_{\mathrm{isom}}(298\ \mathrm{K}) = 21.5 \pm 0.5$ kcal mol^{-1}.

Scheme 5



The reaction of butadiene zirconocene (**1**) with $B(C_6F_5)_3$ was also investigated under conditions of kinetic control. At −60 °C the clean formation of the $Cp_2Zr[(Z)\text{-}C_4H_6-B(C_6F_5)_3]$ betaine **14** was observed, which was quantitatively rearranged to the thermodynamically favored (*E*)-betaine isomer **2** at −20 °C. The (*Z*)-betaine complex is again characterized by a drastic shift of the ^{1}H NMR 4-H/4-H′ resonances to smaller δ values ($\Delta\delta$ −2.84 and −4.62 ppm). In the cases of **14** and **2** the structure-sensitive vicinal coupling constant of the 2-H and 3-H protons at the substituted η^3-allyl units could be determined. The (*Z*)-η^3-allyl complex **14** shows ^3J(2-H,3-H) = 10.6 Hz, whereas ^3J(2-H,3-H) = 15.8 Hz was found for the *E* isomer **2**.[27] We assume that the *Z*/*E* isomerization in these cases proceeds via a (σ-allyl)metallocene betaine intermediate (e.g., **15**) that is reversibly formed from the respective, more stable (π-allyl)metallocene betaine systems (see Scheme 5).[28] It must be noted that the $Cp_2Zr[(Z)\text{-}C_4H_6-B(C_6F_5)_3]$betaine isomer **14** is generated almost quantitatively from the 1:1 mixture of the *s-trans-/s-cis*-η^4-butadiene zirconocene isomers at −60

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(27) The $^1J_{CH}$ (H_2C^4-) coupling constants are quite different for **2** (122, 115 Hz) and **14** (141, 89 Hz); the latter situation indicates a single agostic Zr···H−CH interaction.[26]

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Table 6. Ethene Polymerization with the *ansa*-Metallocene [C_4H_6−$B(C_6F_5)_3$] Betaines and Related *ansa*-Metallocene Dichloride/MAO Catalyst Systems[a]

precursor	metallocene	activator	betaine	B/Zr (Al/Zr)	cat. activity[b]
5a	[$Me_2Si(C_5H_4)_2$]$Zr(C_4H_6)$	$B(C_6F_5)_3$	**6a**	1.05	1550
5b	[$Me_2Si(3\text{-}Me\text{-}C_5H_4)_2$]$Zr(C_4H_6)$	$B(C_6F_5)_3$	**6b**	1.03	3360
8	[$Me_2C(C_5H_4)$(ind.)]$Zr(C_4H_6)$	$B(C_6F_5)_3$	**9**	1.21	340
7	[$Me_2C(C_5H_4)$(ind.)]$ZrCl_2$	MAO		(1065)	410
11	[$Me_2C(C_5H_4)$(flu.)]$Zr(C_4H_6)$	$B(C_6F_5)_3$	**12**	1.10	114
10	[$Me_2C(C_5H_4)$(flu.)]$ZrCl_2$	MAO		(1117)	147

[a] Polymerization reactions in toluene at 40 °C, 2 bar ethene. [b] In units of (g of polymer)/((mmol of Zr) h bar).

Table 7. Propene Polymerization Reaction, Employing the *ansa*-Metallocene [C_4H_6−$B(C_6F_5)_3$] Betaines and Related *ansa*-Metallocene Dichloride/MAO Catalysts[a]

precursor	activator	betaine	B/Zr (Al/Zr)	cat. activity[b]	% *mmmm*
5a	$B(C_6F_5)_3$	**6a**	1.05	38	2.5
5b	$B(C_6F_5)_3$	**6b**	1.03	238	85
8	$B(C_6F_5)_3$	**9**	1.21	446	10
7	MAO		(1065)	222	10
11	$B(C_6F_5)_3$	**12**	1.10	298	73[c]
10	MAO		(1117)	420	82[c]

[a] Polymerization reactions in toluene at 40 °C and 2 bar of propene. [b] Catalyst activities in units of (g of polymer)/((mmol of Zr) h bar). [c] Percentage of *rrrr* pentad (values from ^{13}C NMR methyl pentad analysis).[32]

°C. This implies that the *s-trans*-**1** ⇌ *s-cis*-**1** isomerization is effectively catalyzed under the actually applied reaction conditions. The mechanism of this interesting organometallic catalytic process is not known at present; a bimetallic pathway seems likely.[29]

α-Olefin Polymerization Reactions. We have used the *ansa*-metallocene [C_4H_6−$B(C_6F_5)_3$] betaine complexes **6a**,**b**, **9**, and **12** as single-component Ziegler catalysts in ethene and propene polymerization reactions. In two cases a comparison was made with the respective conventional homogeneous metallocene Ziegler catalysts that were generated by treatment of the corresponding *ansa*-metallocene dichlorides (**4a**,**b**, **7**, or **10**) with a ca. 1000-fold molar excess of methylalumoxane in toluene solution.[30] The metallocene betaine catalysts were also generated in situ in these experiments by treatment of the respective butadiene *ansa*-metallocene precursors with ca. 1.2 molar equiv of $B(C_6F_5)_3$ (for details see Tables 6 and 7). Both the ethene and the propene polymerization reactions were carried out in toluene solution at 40 °C under a 2 bar pressure of the monomer. It can be seen from the results listed in Table 6 that the *ansa*-metallocene [C_4H_6−$B(C_6F_5)_3$] betaine complexes prepared and described in this study represent active homogeneous single-component Ziegler catalysts for polyethylene formation. The systems seem to be as active in ethene polymerization as the usually employed metallocene dichloride/MAO catalyst systems.[30,31] The same *ansa*-metallocene-derived betaines are also active propene polymerization catalysts (see Table 7), again as suited for the rapid and active production of the respective polypropylene variant as their related methylalumoxane activated *ansa*-metallocene catalyst systems.[12]

We must note that excellent catalyst activities are obtained from both structural betaine types found in this study, the C−F- and the [B]−CH_2-protected metallocene [C_4H_6−$B(C_6F_5)_3$] betaines. The (aryl)-C−F···Zr interaction is energetically located in a bond dissociation energy range of 8−10 kcal mol^{-1},[4b] which must be regarded as ideal for the purpose of protecting the electron-deficient positively polarized zirconium center but also weak enough to be rapidly cleaved by an added 1-alkene to initiate the reaction sequence leading to the catalytic polymerization cycle. Zirconocene cation/alkyl−$B(C_6F_5)_3^-$ anion ion pair dissociation energies in simple acyclic systems are markedly above these values at ca. 15−19 kcal mol^{-1},[8] but incorporation of the related intramolecular ion pair interaction in a metallacyclic metallocene betaine system, such as that represented by the examples discussed in this study, seems to result in an overall favorable situation, probably due to energetic compensation effects. These make the C−F···Zr (**6a**,**b**) and the [B]−CH_2···Zr (**9**, **12**) bridged metallocene [C_4H_6−$B(C_6F_5)_3$] betaine systems equally well suited as readily available, very active, homogeneous single-component Ziegler catalyst systems for α-olefin polymerization processes.

Experimental Section

General Remarks. All manipulations involving air-sensitive compounds were carried out under argon in a glovebox or using Schlenk type glassware. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. Tris(pentafluorophenyl)borane[2] (*caution* is advised in the preparation of $B(C_6F_5)_3$, since the LiC_6F_5 intermediate is potentially explosive if brought to too high temperatures), [dimethylsilylenebis(cyclopentadienyl)]dichlorozirconium (**4a**), [isopropylidene(cyclopentadienyl)(1-indenyl)]dichlorozirconium (**7**), and [isopropylidene(cyclopentadienyl)(9-fluorenyl)]-dichlorozirconium (**10**) were prepared according to literature procedures.[12] The synthesis of *rac*-[dimethylsilylenebis(3-methylcyclopentadienyl)](butadiene)zirconium (**5b**) was described previously by us.[18] NMR experiments were performed on a Varian Unity Plus 600 NMR spectrometer (^1H, 600 MHz; ^{13}C, 150 MHz; ^{19}F, 564 MHz). Assignments in ^1H and ^{13}C NMR spectra were confirmed through GCOSY (gradient ^1H−^1H COSY), 1D-TOCSY (^1H total correlation spectroscopy), GHSQC (^1H−^{13}C gradient heteronuclear single bond quantum coherence), and GHMBC (^1H−^{13}C gradient heteronuclear multiple bond correlation) spectra; in some cases further information

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was obtained from NOE difference and 1D-ROESY (rotating frame Overhauser enhancement spectroscopy) spectra.[33] IR spectra were recorded on a Nicolet 5 DXC Fourier transform IR spectrometer. Melting points were obtained by differential scanning calorimetry (DuPont 910); elemental analyses were determined on a Foss-Heraeus CHN-Rapid elemental analyzer.

Preparation of Butadiene Zirconocene Complexes. General Procedure. Toluene (100 mL) was slowly added at −78 °C to a solid mixture of ca. 10 mmol of the respective dichlorometallocene and 1.1 molar equiv of "butadiene magnesium". The mixture was warmed to room temperature with stirring over 6 h and was then stirred for an additional 6 h at ambient temperature. The precipitate of magnesium chloride was removed by filtration and washed with toluene (2 × 20 mL). The combined organic solutions were concentrated under reduced pressure until precipitation of the butadiene zirconium product set in. The solid was redissolved by warming the mixture to 45 °C for ca. 30 min. The product was then precipitated at −20 °C. It was collected by filtration, washed with pentane (10 mL), and dried in vacuo. Concentration of the mother liquor under reduced pressure and repetition of the crystallization process furnished additional clean product fractions.

[Dimethylsilylenebis(cyclopentadienyl)](butadiene)zirconium (5a). Reaction of [dimethylsilylenebis(cyclopentadienyl)]dichlorozirconium (**4a**; 5.00 g, 14.3 mmol) with "butadiene magnesium" (3.52 g, 15.8 mmol) gave the orange butadiene complex **5a** in three product fractions (total yield 3.40 g, 72%; mp 159 °C). In C_6D_6 solution an equilibrium mixture of *s-trans*-**5a** and *s-cis*-**5a** in a 1:1 ratio was observed by ^{1}H NMR spectroscopy at 298 K. *s-trans*-**5a**: ^{1}H NMR (599.9 MHz, C_6D_6, 298 K) δ 5.51, 5.48, 4.52, 4.38 (each m, each 2H, C_5H_4), 3.12 (m, 2H, H_{syn}), 2.92 (m, 2H, H_{meso}), 1.34 (m, 2H, H_{anti}), 0.35 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (150.8 MHz, C_6D_6, 298 K) δ 113.0, 109.3, 96.8, 96.6 (each CH, α- and β-C_5H_4), 95.8 (CH, butadiene CH), 90.4 (C, ipso-C_5H_4), 59.5 (CH_2, butadiene CH_2), −5.2 (CH_3, $Si(CH_3)_2$). *s-cis*-**5a**: ^{1}H NMR (599.9 MHz, C_6D_6, 298 K) δ 5.89, 5.21, 5.19, 5.00 (each m, each 2H, C_5H_4), 4.79 (m, 2H, H_{meso}), 3.44 (m, 2H, H_{syn}), 0.39 (s, 6H, $Si(CH_3)_2$), −0.83 (m, 2H, H_{anti}); ^{13}C NMR (150.8 MHz, C_6D_6, 298 K) δ 112.7 (CH, α- or β-C_5H_4), 111.6 (CH, butadiene CH), 106.8, 105.5, 100.0 (each CH, α- and β-C_5H_4), 94.1 (C, 2 × ipso-C_5H_4), 50.5 (CH_2, butadiene CH_2), −4.9 (CH_3, $Si(CH_3)_2$). IR (KBr): $\tilde{\nu}$ 3102 (w), 3064 (w), 2954 (m), 1501 (m), 1440 (w), 1416 (m), 1398 (m), 1370 (m), 1359 (m), 1317 (m), 1253 (s), 1175 (s), 1166 (s), 1049 (s), 1040 (s), 901 (m), 808 (vs), 677 (s), 635 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{20}SiZr$ (331.6): C, 57.95; H, 6.08. Found: C, 57.39; H, 5.90.

[Isopropylidene(cyclopentadienyl)(1-indenyl)](butadiene)zirconium (8). Reaction of [isopropylidene(cyclopentadienyl)(1-indenyl)]dichlorozirconium (**7**; 3.00 g, 7.84 mmol) with "butadiene magnesium" (1.92 g, 8.63 mmol) yielded the red butadiene complex **8** (1.29 g, 45%; mp 150.8 °C). ^{1}H NMR (599.9 MHz, toluene-d_8, 298 K): δ 7.46 (dddd, $^3J = 8.7$ Hz, $^4J = 1.0$ Hz, 2 × $^5J = 1.0$ Hz, 1H, indenyl 7-H), 6.67 (ddd, $^3J = 8.3$ Hz, $^4J = 1.0$ Hz, $^5J = 1.0$ Hz, 1H, indenyl 4-H), 6.63 (ddd, $^3J = 8.7$ Hz, $^3J = 6.6$ Hz, $^4J = 1.0$ Hz, 1H, indenyl 6-H), 6.56 (ddd, $^3J = 8.3$ Hz, $^3J = 6.6$ Hz, $^4J = 1.0$ Hz, 1H, indenyl 5-H), 5.82, 5.60 (each ddd, 2 × $^3J = 2.3$ Hz, $^4J = 0.9$ Hz, each 1H, C_5H_4), 5.38 (d, $^3J = 3.6$ Hz, 1H, indenyl 2-H), 5.20 (m, 1H, internal butadiene H), 5.18 (dd, $^3J = 3.6$ Hz, $^5J = 1.0$ Hz, 1H, indenyl 3-H), 4.66 (m, 2H, C_5H_4), 4.10 (m, 1H, internal butadiene H), 3.14 (dd, $^2J = 8.7$ Hz, $^3J = 9.6$ Hz, 1H, terminal butadiene H), 2.03 (m, 1H, terminal butadiene H), 1.75, 1.52 (each s, each 3H, $C(CH_3)_2$), −0.82 (ddd, $^2J = 12.2$ Hz, $^3J = 8.4$ Hz, $^4J = 1.7$ Hz, 1H, terminal butadiene H), −1.31 (ddd, $^2J = 8.7$ Hz, $^3J = 12.2$ Hz, $^4J = 1.7$ Hz, 1H, terminal butadiene H). ^{13}C NMR (150.8 MHz, toluene-d_8, 298 K): δ 125.1 (CH, indenyl C-7), 123.9 (CH, indenyl C-4), 122.6 (CH, indenyl C-6), 121.3 (CH, indenyl C-5), 119.2 (C, indenyl C-8 or indenyl C-9), 117.7 (CH, butadiene CH), 117.1 (C, indenyl C-8 or indenyl C-9), 112.6 (CH, butadiene CH), 108.7, 108.4 (each CH, α- or β-C_5H_4), 107.2 (CH, indenyl C-2), 99.2, 95.2 (each C, indenyl C-1 and ipso-C_5H_4), 94.7 (CH, indenyl C-3), 89.6, 88.8 (each CH, α- or β-C_5H_4), 56.7, 49.6 (each CH_2, butadiene CH_2), 37.5 (C, $C(CH_3)_2$), 26.6, 25.8 (each CH_3, $C(CH_3)_2$). IR (KBr): $\tilde{\nu}$ 3085 (w), 3028 (w), 2977 (m), 1497 (m), 1475 (m), 1454 (m), 1445 (m), 1412 (m), 1385 (m), 1367 (m), 1340 (m), 1320 (m), 1249 (m), 1213 (m), 1160 (m), 1055 (m), 1041 (m), 853 (m), 793 (vs), 779 (s), 747 (vs), 732 (s), 726 (s), 701 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{22}Zr$ (365.6): C, 68.99; H, 6.07. Found: C, 68.49; H, 6.31.

X-ray Crystal Structure Analysis of 8. Crystals suitable for an X-ray structural analysis were obtained from a concentrated solution of **8** in toluene at room temperature. Crystal data: formula $C_{21}H_{22}Zr$, $M_r = 365.61$, red crystal, 0.60 × 0.45 × 0.30 mm, $a = 14.864(1)$ Å, $b = 12.287(1)$ Å, $c = 18.123(1)$ Å, $\beta = 102.84(1)°$, $V = 3227.1(4)°$, $\rho_{calcd} = 1.505$ g cm^{-3}, $\mu = 6.76$ cm^{-1}, no absorption correction ($0.687 \leq T \leq 0.823$), $Z = 8$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.710\ 73$ Å, $T = 198$ K, ω and φ scans, 21 117 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.59$ Å^{-1}, 5513 independent ($R_{int} = 0.156$) and 3035 observed reflections ($I \geq 2\sigma(I)$), 401 refined parameters, R1 = 0.098, wR2 = 0.216, maximum (minimum) residual electron density 1.91 (−1.09) e Å^{-3}, crystals are always twinned (double peaks in the ω scans on the diffractometer), contains two almost identical molecules in the asymmetric unit, hydrogens calculated and refined as riding atoms.

[Isopropylidene(cyclopentadienyl)(9-fluorenyl)](butadiene)zirconium (11). Treatment of [isopropylidene(cyclopentadienyl)(9-fluorenyl)]dichlorozirconium (**10**; 5.27 g, 12.19 mmol) with "butadiene magnesium" (2.98 g, 13.40 mmol) yielded the brownish red butadiene complex **11** in three product fractions (total yield 2.59 g, 51%; mp 162.3 °C). ^{1}H NMR (599.9 MHz, toluene-d_8, 288 K): δ 7.59 (ddd, $^3J = 8.6$ Hz, $^4J = 1.0$ Hz, $^5J = 1.0$ Hz, 2H, $C_{13}H_8$), 7.33 (ddd, $^3J = 8.1$ Hz, $^4J = 1.0$ Hz, $^5J = 1.0$ Hz, 2H, $C_{13}H_8$), 6.92 (ddd, $^3J = 8.6$ Hz, $^3J = 6.7$ Hz, $^4J = 1.0$ Hz, 2H, $C_{13}H_8$), 6.85 (ddd, $^3J = 8.1$ Hz, $^3J = 6.7$ Hz, $^4J = 1.0$ Hz, 2H, $C_{13}H_8$), 5.96, 4.55 (each m, each 2H, C_5H_4), 3.90 (m, 2H, internal butadiene H), 1.88 (s, 6H, $C(CH_3)_2$), 1.67, −0.97 (each m, each 2H, terminal butadiene H). ^{13}C NMR (150.8 MHz, toluene-d_8, 288 K): δ 125.0, 123.7 (each CH, $C_{13}H_8$), 122.5 (CH, butadiene CH), 121.4, 120.3 (each CH, $C_{13}H_8$), 119.7, 119.6 (each C, $C_{13}H_8$), 114.7 (C, ipso-C_5H_4), 108.3, 89.9 (each CH, α- and β-C_5H_4), 80.9 (C, ipso-$C_{13}H_8$), 52.7 (CH_2, butadiene CH_2), 39.0 (C, $C(CH_3)_2$), 28.6 (CH_3, $C(CH_3)_2$). IR (KBr): $\tilde{\nu}$ 3020 (w), 2967 (w), 2930 (w), 1589 (w), 1496 (m), 1473 (m), 1465 (m), 1442 (m), 1434 (m), 1409 (m), 1212 (m), 1045 (m), 811 (m), 783 (s), 754 (s), 744 (vs), 723 (s), 712 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{24}Zr$ (415.7): C, 72.24; H, 5.82. Found: C, 71.70; H, 5.88.

Reaction of Butadiene Zirconocenes with $B(C_6F_5)_3$ at Room Temperature. General Procedure. For their NMR spectroscopic characterization the zirconocene $[C_4H_6-B(C_6F_5)_3]$ betaines were prepared in situ by the addition of a solution of $B(C_6F_5)_3$ (ca. 60 μmol) in C_6D_6 or toluene-d_8 (0.4 mL) to a solution of the respective butadiene complex (ca. 0.98 molar equiv) in C_6D_6 or toluene-d_8 (0.8 mL) at room temperature. After mixing, the resulting solution of the betaine complex was allowed to stand at ambient temperature for ca. 30 min prior to its spectroscopic characterization.

The synthesis of the butadiene zirconocene/$B(C_6F_5)_3$ adducts on a preparative scale was performed by the slow addition of a solution of $B(C_6F_5)_3$ (ca. 100−200 μmol) in toluene (1−3 mL) to a solution of the respective butadiene complex (ca. 0.95 molar equiv) in toluene (3−6 mL) at room temperature. The reaction mixture was stirred for 30 min and then kept at −40 °C for 1−3 days. During this time the product precipitated and was collected by filtration, washed with toluene (2 × 2 mL), and dried in vacuo.

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[33] Braun, S.; Kalinowski, H.; Berger, S. *150 and More Basic NMR Experiments*; Wiley-VCH: Weinheim, Germany, 1998.

Reaction of [$Me_2Si(C_5H_4)_2$]Zr(butadiene) (5a) with $B(C_6F_5)_3$: Formation of 6a. According to the general procedure, betaine complex **6a** was generated in situ from 31 mg (60.5 μmol) of $B(C_6F_5)_3$ and 20 mg (60.3 μmol) of butadiene complex **5a**. Complex **6a** was obtained in a preparative synthesis from 117 mg (229 μmol) of $B(C_6F_5)_3$ and 69 mg (208 μmol) of **5a** as a yellow crystalline solid (146 mg, 82%; mp 119 °C dec). ^{1}H NMR (599.9 MHz, C_6D_6, 298 K): δ 6.11, 6.00 (each m, each 1H, C_5H_4), 5.92 (m, 2H, C_5H_4 and 2-H), 5.78 (1H), 5.55 (2H) (each m, C_5H_4), 5.43 (m, 1H, 3-H), 4.40 (m, 2H, C_5H_4), 2.63 (broad d, ^{2}J = 18.2 Hz, 1H, 4-H), 2.31 (broad dd, ^{2}J = 18.2 Hz, ^{3}J = 6.0 Hz, 1H, 4-H′), 1.86 (dd, ^{2}J = 5.0 Hz, ^{3}J = 17.9 Hz, 1H, 1-H), 1.53 (dd, ^{2}J = 5.0 Hz, ^{3}J = 8.3 Hz, 1H, 1-H′), 0.24, −0.17 (each s, each 3H, $Si(CH_3)_2$). ^{13}C NMR (150.8 MHz, C_6D_6, 298 K): δ 149.5 (d, $^{1}J_{CF}$ = 240 Hz, *o*-$B(C_6F_5)_3$), 138.9 (d, $^{1}J_{CF}$ = 250 Hz, *p*-$B(C_6F_5)_3$), 137.3 (d, $^{1}J_{CF}$ = 250 Hz, *m*-$B(C_6F_5)_3$), 130.4 (CH_2, broad, C-2), 125.8 (C, broad, ipso-$B(C_6F_5)_3$), 125.1, 123.7 (each CH, α- or β-C_5H_4), 123.1 (CH, broad, C-3), 121.9, 121.2, 109.9, 107.2 (double intensity), 106.6 (each CH, α- or β-C_5H_4), 106.1, 102.7 (each C, ipso-C_5H_4), 52.0 (CH_2, C-1), 28.3 (CH_2, broad, C-4), −5.7, −7.1 (each CH_3, $Si(CH_3)_2$). ^{19}F NMR (564.3 MHz, toluene-d_8, 298 K): δ −165.0 (broad, 6F, *m*-F), −161.1 (broad t, $^{3}J_{FF}$ = 21 Hz, 3F, *p*-F) ppm, signals of the *o*-F not detected at 298 K. ^{19}F NMR (564.3 MHz, toluene-d_8, 238 K): δ −211.6 (broad, 1F, *o*-F (coordinated)), −165.4, −163 to −157 (each broad m, 9F, *m*-F and *p*-F), −125.8 (1F), −132.7 (4F) (each broad, *o*-F). Coalescence of the *o*-F is reached at ca. 250 K, $\Delta\nu$(238 K) ≈ 45 500 Hz, $\Delta G^{\ddagger}$(250 K) = 8.7 ± 0.8 kcal/mol. IR (KBr): $\tilde{\nu}$ 2966 (w), 1645 (s), 1518 (s), 1466 (vs), 1402 (m), 1375 (m), 1261 (s), 1172 (m), 1091 (s), 919 (s), 828 (m), 812 (m), 800 (m), 680 (m) cm^{-1}. Anal. Calcd for $C_{34}H_{20}BF_{15}SiZr$ (843.6): C, 48.41; H, 2.39. Found: C, 47.41; H, 2.44.

X-ray Crystal Structure Analysis of 6a. Crystals suitable for an X-ray structural analysis were obtained within 4 days from a solution of the in situ generated betaine complex in toluene-d_8 at room temperature. Crystal data: formula $C_{34}H_{20}BF_{15}SiZr\cdot 1.5C_7H_8$, M_r = 981.82, colorless crystal, 0.25 × 0.15 × 0.10 mm, a = 16.446(1) Å, b = 12.088(1) Å, c = 22.062(1) Å, β = 99.54(1)°, V = 4325.3(5) Å^3, ρ_{calcd} = 1.508 g cm^{-3}, μ = 3.78 cm^{-1}, empirical absorption correction via SORTAV (0.911 ≤ T ≤ 0.963), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 17 835 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.59 Å^{-1}, 7294 independent (R_{int} = 0.063) and 4835 observed reflections ($I \geq 2\sigma(I)$), 532 refined parameters, R1 = 0.070, wR2 = 0.172, maximum (minimum) residual electron density 1.13 (−0.75) e Å^{-3}, positional, unrefined disorder in the methyl groups at Si, disordered solvent molecules refined as rigid rings, the half-molecule also with one common isotropic thermal displacement parameter, hydrogens calculated and refined as riding atoms.

Reaction of *rac*-[$Me_2Si(3\text{-}Me\text{-}C_5H_3)_2$]Zr(butadiene) (5b) with $B(C_6F_5)_3$: Formation of 6b. Betaine **6b** was generated in situ by the reaction of 22 mg (41.9 μmol) of $B(C_6F_5)_3$ and 15 mg (41.7 μmol) of butadiene complex **5b**. Reaction of 97 mg (189 μmol) of $B(C_6F_5)_3$ and 65 mg (181 μmol) of **5b** on a preparative scale yielded betaine **6b** as a yellow solid (150 mg, 86%; mp 174 °C). ^{1}H NMR (599.9 MHz, toluene-d_8, 298 K): δ 5.90 (m, 1H, 2-H), 5.78, 5.70, 5.53, 5.25 (each m, each 1H, C_5H_3), 4.73 (dd, ^{3}J = 16.3 Hz, ^{3}J = 6.0 Hz, 1H, 3-H), 4.40, 4.12 (each m, each 1H, C_5H_3), 2.42 (broad d, ^{2}J = 18.6 Hz, 1H, 4-H), 2.15 (dd, ^{2}J = 18.6 Hz, ^{3}J = 6.0 Hz, 1H, 4-H′), 1.76 (s, 3H, $C_5H_3{-}CH_3$), 1.67 (dd, ^{2}J = 5.3 Hz, ^{3}J = 8.5 Hz, 1H, 1-H), 1.59 (s, 3H, $C_5H_3{-}CH_3$), 1.34 (ddd, ^{2}J = 5.3 Hz, ^{3}J = 12.5 Hz, ^{3}J = 1.3 Hz, 1H, 1-H′), 0.25, −0.19 (each s, each 3H, $Si(CH_3)_2$). ^{13}C NMR (150.8 MHz, toluene-d_8, 298 K): δ 149.4 (d, $^{1}J_{CF}$ = 240 Hz, *o*-$B(C_6F_5)_3$), 138.9 (d, $^{1}J_{CF}$ = 250 Hz, *p*-$B(C_6F_5)_3$), 137.3 (d, $^{1}J_{CF}$ = 250 Hz, *m*-$B(C_6F_5)_3$), 136.0, 135.4 (each C, cyclopentadienyl $C{-}CH_3$), 131.3 (CH, C-2), 123.2 (CH, C-3), 122.1, 121.6, 110.1, 107.7, 106.4, 106.2 (each CH, cyclopentadienyl CH), 103.9, 101.3 (each C, cyclopentadienyl $C{-}Si$), 53.0 (CH_2, C-1), 26.7 (CH_2, broad, C-4), 14.6, 13.6 (each CH_3, $C_5H_3{-}CH_3$), −5.4, −7.2 (each CH_3, $Si(CH_3)_2$), resonance of the ipso-C of $B(C_6F_5)_3$ not detected. ^{19}F NMR (564.3 MHz, toluene-d_8, 298 K): δ −165.2 (broad, 6F, *m*-F), −161.1 (broad, 3F, *p*-F), −132.8 (broad, 6F, *o*-F). ^{19}F NMR (564.3 MHz, toluene-d_8, 218 K): δ −208.8 (d, $^{3}J_{FF}$ ≈ 30 Hz, 1H, *o*-F (coordinated)), −166.3 (2F), −165.1, −164.8, −164.5, −161.5, −161.2, −159.7, −158.1 (each 1F) (each broad m, *m*-F and *p*-F), −136.0, −134.1, −131.9, −130.5, −126.1 (each broad m, each 1F, *o*-F). IR (KBr): $\tilde{\nu}$ 2999 (w), 2964 (w), 2945 (m), 2900 (w), 1645 (s), 1513 (s), 1467 (s), 1458 (s), 1350 (m), 1274 (s), 1261 (s), 1258 (s), 983 (s), 970 (s), 930 (s), 850 (s), 816 (s), 808 (s), 761 (s), 679 (s), 546 (m) cm^{-1}. Anal. Calcd for $C_{36}H_{24}BF_{15}SiZr\cdot C_6D_6$ (949.793): C, 53.11; H, 3.18. Found: C, 52.92; H, 3.04.

X-ray Crystal Structure Analysis of 6b. Crystals suitable for an X-ray structural analysis were obtained within 4 days from a solution of the in situ generated betaine complex in C_6D_6 at room temperature. Crystal data: formula $C_{36}H_{24}BF_{15}SiZr\cdot 2C_6H_6$, M_r = 1027.89, yellow crystal, 0.25 × 0.20 × 0.20 mm, a = 15.307(1) Å, b = 13.304(1) Å, c = 21.597(1) Å, β = 93.95(1)°, V = 4387.7(5) Å^3, ρ_{calcd} = 1.556 g cm^{-3}, μ = 3.77 cm^{-1}, empirical absorption correction via SORTAV (0.912 ≤ T ≤ 0.928), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 43 066 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.65 Å^{-1}, 10 066 independent (R_{int} = 0.049) and 7919 observed reflections ($I \geq 2\sigma(I)$), 599 refined parameters, R1 = 0.036, wR2 = 0.084, maximum (minimum) residual electron density 0.46 (−0.59) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Reaction of [$Me_2C(C_5H_4)$(1-indenyl)]Zr(butadiene) (8) with $B(C_6F_5)_3$: Formation of 9. Betaine complex **9** was generated in situ from 29 mg (56.6 μmol) of $B(C_6F_5)_3$ and 20 mg (54.7 μmol) of butadiene complex **8**. On a preparative scale **9** was obtained from 123 mg (240 μmol) of $B(C_6F_5)_3$ and 80 mg (219 μmol) of butadiene complex **8** as a red crystalline solid (172 mg, 81%; mp 127 °C). ^{1}H NMR (599.9 MHz, toluene-d_8, 298 K): δ 6.67 (dddd, ^{3}J = 8.8 Hz, ^{4}J = 1.0 Hz, 2 × ^{5}J = 1.0 Hz, 1H, indenyl 7-H), 6.40 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.0 Hz, 1H, indenyl 5-H), 6.32 (ddd, ^{3}J = 8.8 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.0 Hz, 1H, indenyl 6-H), 6.28 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 1.0 Hz, ^{5}J = 1.0 Hz, 1H, indenyl 4-H), 5.77 (d, ^{3}J = 3.7 Hz, 1H, indenyl 2-H or indenyl 3-H), 5.54 (m, 1H, C_5H_4), 5.49 (d, ^{3}J = 3.7 Hz, 1H, indenyl 2-H or indenyl 3-H), 5.09 (m, 1H, C_5H_4), 4.93 (ddd, 3 × J = 2.4 Hz, 1H, C_5H_4), 4.86 (dd, 2 × ^{3}J = 11.5 Hz, 1H, 3-H), 4.78 (m, 1H, C_5H_4), 4.52 (ddd, 3 × ^{3}J = 10.6 Hz, 1H, 2-H), 1.32, 1.17 (each s, each 3H, $C(CH_3)_2$), 0.94 (broad d, ^{3}J = 10.6 Hz, 2H, 1-H and 1-H′), −0.57, −0.74 (each broad, 1H, 4-H and 4-H′). ^{13}C NMR (150.8 MHz, toluene-d_8, 298 K): δ 148.6 (d, $^{1}J_{CF}$ = 240 Hz, *o*-$B(C_6F_5)_3$), 139.4 (d, $^{1}J_{CF}$ = 250 Hz, *p*-$B(C_6F_5)_3$), 137.5 (d, $^{1}J_{CF}$ = 250 Hz, *m*-$B(C_6F_5)_3$), 135.2 (CH, C-2), 125.9 (CH, indenyl C-7), 125.7 (CH, indenyl C-4), 125.2 (CH, indenyl C-6), 124.3 (CH, indenyl C-5), 116.1, 110.8 (each CH, C_5H_4), 109.9 (CH, C-3), 109.8, 100.4 (each CH, indenyl C-2 and indenyl C-3), 95.2, 93.7 (each CH, C_5H_4), 62.8 (CH_2, C-1), 25.5, 24.5 (each CH_3, $C(CH_3)_2$), ∼22 (CH_2, C-4), resonances of the ipso-C of $B(C_6F_5)_3$ and of the quaternary carbon atoms of the isopropylidene(cyclopentadienyl)(1-indenyl) ligand not detected, signal of C-4 only detected in the GHSQC NMR spectrum. IR (KBr): $\tilde{\nu}$ 2986 (w), 2974 (w), 2965 (w), 1644 (m), 1515 (s), 1463 (vs), 1381 (m), 1370 (m), 1276 (m), 1090 (s), 976 (s), 962 (m), 820 (m), 814 (m), 804 (m), 754 (m), 736 (m), 684 (m) cm^{-1}. Anal. Calcd for $C_{39}H_{22}BF_{15}Zr\cdot C_7H_8$ (969.8): C, 56.97; H, 3.12. Found: C, 57.22; H, 3.01.

X-ray Crystal Structure Analysis of 9. Crystals suitable for an X-ray structural analysis were obtained within 6 days from a solution of the in situ generated betaine complex in C_6D_6 at room temperature. Crystal data: formula $C_{39}H_{22}BF_{15}Zr\cdot C_6H_6$, M_r = 955.70, yellow-orange crystal, 0.50 × 0.35 × 0.20 mm, a = 10.641(1) Å, b = 12.944(1) Å, c = 14.650(1) Å, α = 92.99(1)°, β = 104.91(1)°, γ = 95.32(1)°, V = 1935.4(3) Å^3, ρ_{calcd} = 1.640 g cm^{-3}, μ = 3.91 cm^{-1}, empirical absorption correction via ψ scan data (0.829 ≤ T ≤ 0.926), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\ 73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 8179 reflections collected ($\pm h$, $\pm k$, $-l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 7858 independent ($R_{\text{int}} = 0.032$) and 6345 observed reflections ($I \geq 2\sigma(I)$), 561 refined parameters, R1 = 0.032, wR2 = 0.084, maximum (minimum) residual electron density 0.43 (−0.69) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Reaction of [$Me_2C(C_5H_4)$(9-fluorenyl)]Zr(butadiene) (11) with $B(C_6F_5)_3$: Formation of 12. Betaine complex **12** was generated by the reaction of 13 mg (25.4 μmol) of $B(C_6F_5)_3$ and 10 mg (24.6 μmol) of butadiene complex **11**. On a preparative scale betaine **12** was obtained from 31 mg (60.9 μmol) of $B(C_6F_5)_3$ and 23 mg (55.3 μmol) of butadiene complex **11** as a red solid (36 mg, 71%; mp 121 °C dec). ^{1}H NMR (599.9 MHz, toluene-d_8, 298 K): δ 7.16 (m, 2H, $C_{13}H_8$), 7.08 (d, $^3J = 8.3$ Hz, 1H, $C_{13}H_8$), 7.03, 6.94 (each m, each 1H, $C_{13}H_8$), 6.79 (d, $^3J = 8.7$ Hz, 1H, $C_{13}H_8$), 6.73 (m, 1H, $C_{13}H_8$), 6.59 (ddd, $^3J = 8.7$ Hz, $^3J = 6.9$ Hz, $^4J = 1.0$ Hz, 1H, $C_{13}H_8$), 5.70, 5.23, 4.97, 4.85 (each ddd, $3 \times J = 3.0$ Hz, each 1H, C_5H_4), 4.53 (ddd, $3 \times {}^3J = 10.0$ Hz, 1H, 2-H), 3.93 (dd, $^3J = 15.3$ Hz, $^3J = 10.0$ Hz, 1H, 3-H), 1.55, 1.44 (each s, each 3H, $C(CH_3)_2$), 0.96 (dd, $^2J = 10.0$ Hz, $^3J = 10.0$ Hz, 1H, 1-H), 0.26 (dd, $^2J = 10.0$ Hz, $^3J = 10.0$ Hz, 1H, 1-H′), −0.53 (broad, 2H, 4-H and 4-H′). ^{13}C NMR (150.8 MHz, toluene-d_8, 298 K): δ 148.5 (d, $^1J_{\text{CF}} = 240$ Hz, *o*-$B(C_6F_5)_3$), 137.3 (d, $^1J_{\text{CF}} = 250$ Hz, *p*-$B(C_6F_5)_3$), 139.4 (d, $^1J_{\text{CF}} = 250$ Hz, *m*-$B(C_6F_5)_3$), 136.3 (CH, C-2), 129.8, 126.8, 126.4, 124.6, 124.2, 123.7 (each CH, $C_{13}H_8$), 122.6, 122.0 (each C, $C_{13}H_8$), 121.8, 121.7 (each CH, $C_{13}H_8$), 121.5 (C, $C_{13}H_8$), 121.4 (CH, C-3), 119.7, 118.4 (each C, $C_{13}H_8$ and ipso-C_5H_4), 115.0, 111.9, 95.9, 92.9 (each CH, C_5H_4), 96.0 (C, ipso-$C_{13}H_8$), 58.3 (CH_2, C-1), 38.7 (C, $\mathit{C}(CH_3)_2$), 27.5 (double intensity, $2 \times CH_3$, $C(\mathit{C}H_3)_2$), ~20 (CH_2, C-4), resonance of the ipso-C of $B(C_6F_5)_3$ not detected, signal of C-4 only detected in the GHSQC NMR spectrum. ^{19}F NMR (599.9 MHz, toluene-d_8, 298 K): δ −165.8 (dd, $2 \times {}^3J_{\text{FF}} = 21$ Hz, 6F, *m*-F), −161.0 (t, $^3J_{\text{FF}} = 21$ Hz, 3F, *p*-F), −132.9 (d, $^3J_{\text{FF}} = 21$ Hz, 6F, *o*-F). IR (KBr): $\tilde{\nu}$ 2967 (w), 2927 (w), 1645 (m), 1517 (s), 1385 (m), 1370 (m), 1092 (s), 975 (s), 808 (m), 757 (s), 745 (s), 685 (m) cm^{-1}. Anal. Calcd for $C_{43}H_{24}BF_{15}Zr$ (927.7): C, 55.67; H, 2.61. Found: C, 54.82; H, 2.78.

X-ray Crystal Structure Analysis of 12. Crystals suitable for an X-ray structural analysis were obtained by the slow diffusion of pentane via the gas phase into a solution of the in situ generated betaine complex in toluene at 5 °C. Crystal data: formula $C_{43}H_{24}BF_{15}Zr \cdot 0.5C_7H_8$, $M_r = 973.72$, yellow crystal, $0.20 \times 0.20 \times 0.05$ mm, $a = 13.731(1)$ Å, $b = 16.727(1)$ Å, $c = 17.779(1)$ Å, $\beta = 109.15(1)°$, $V = 3857.5(4)$ Å^3, $\rho_{\text{calcd}} = 1.677$ g cm^{-3}, $\mu = 3.94$ cm^{-1}, no absorption correction ($0.925 \leq T \leq 0.981$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\ 73$ Å, $T = 198$ K, ω and φ scans, 21 315 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 7820 independent ($R_{\text{int}} = 0.054$) and 5313 observed reflections ($I \geq 2\sigma(I)$), 580 refined parameters, R1 = 0.043, wR2 = 0.102, maximum (minimum) residual electron density 0.47 (−0.51) e Å^{-3}, asymmetric unit contains a disordered half-molecule of solvent, hydrogens calculated and refined as riding atoms.

Data sets were collected with Nonius MACH3 and KappaCCD diffractometers, equipped with a rotating anode generator (Nonius FR591). Programs used: data collection EXPRESS (Nonius BV, 1994) and COLLECT (Nonius BV, 1998), data reduction MolEN (K. Fair, Enraf-Nonius BV, 1990) and Denzo-SMN,[34] absorption correction for CCD data SORTAV,[35] structure solution SHELXS-97,[36] structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics DIAMOND (K. Brandenburg, Universität Bonn, 1997) and SCHAKAL (E. Keller, Universität Freiburg, 1997).

Reaction of [$Me_2Si(C_5H_4)_2$]Zr(butadiene) (5a) with $B(C_6F_5)_3$ at 233 K: Formation of 13. A solution of butadiene complex **5a** (15 mg, 45.2 μmol) in toluene-d_8 (0.4 mL) was placed in an NMR tube which was sealed with a septum and cooled to −60 °C. A solution of $B(C_6F_5)_3$ (24 mg, 46.9 μmol) in toluene-d_8 (0.2 mL) was slowly injected by syringe. The tube was shaken vigorously to ensure homogeneity of the reaction mixture. The NMR spectra were recorded instantaneously at −40 °C. The formation of betaine **13**, along with small amounts of **6a**, could be observed. At temperatures above 10 °C the rearrangement of **13** to **6a** sets in. **13**: ^{1}H NMR (599.9 MHz, toluene-d_8, 233 K) δ 5.67, 5.36, 5.26, 5.22 (each m, each 1H, C_5H_4), 5.12 (m, $^3J = 11.8$ Hz, $^3J = 10.3$ Hz, $^3J = 9.0$ Hz, 1H, 2-H), 5.09, 4.90, 4.88 (each m, each 1H, C_5H_4), 4.38 (m, $2 \times {}^3J = 10.3$ Hz, 1H, 3-H), 4.08 (m, 1H, C_5H_4), 2.58 (dd, $^2J = 9.0$ Hz, $^3J = 9.0$ Hz, 1H, 1-H), 0.86 (dd, $^2J = 9.0$ Hz, $^3J = 11.8$ Hz, 1H, 1-H′), 0.08, −0.10 (each s, each 3H, $Si(CH_3)_2$), −0.39 (broad d, $^3J = 10.3$ Hz, 1H, 4-H), −1.90 (broad s, 1H, 4-H′); ^{13}C NMR (GATED, 150.8 MHz, toluene-d_8, 233 K) δ 148.4 (d, $^1J_{\text{CF}} = 240$ Hz, *o*-$B(C_6F_5)_3$), 139.3 (d, $^1J_{\text{CF}} = 250$ Hz, *p*-$B(C_6F_5)_3$), 137.3 (d, $^1J_{\text{CF}} = 250$ Hz, *m*-$B(C_6F_5)_3$), 132.9 (d, $^1J_{\text{CH}} = 154$ Hz, CH, C-2), 122.3 (broad, C, ipso-$B(C_6F_5)_3$), 118.8, 116.6, 115.6, 112.6 (each d, $^1J_{\text{CH}} = 175$ Hz, CH, α- or β-C_5H_4), 111.0 (d, $^1J_{\text{CH}} = 135$ Hz, CH, C-3), 110.8, 109.7, 105.8, 105.0 (each d, $^1J_{\text{CH}} = 175$ Hz, CH, α- or β-C_5H_4), 100.9 (s, C, $2 \times$ ipso-C_5H_4), 55.9 (dd, $^1J_{\text{CH}} = 164$ Hz, $^1J_{\text{CH}} = 139$ Hz, CH_2, C-1), 24.4 (broad, CH_2, C-4), −6.2 (d, $^1J_{\text{CH}} = 123$ Hz, CH_3, $Si(CH_3)_2$), −6.6 (d, $^1J_{\text{CH}} = 120$ Hz, CH_3, $Si(CH_3)_2$); ^{19}F NMR (564.3 MHz, toluene-d_8, 253 K) δ −163.4 (broad, 6F, *m*-F), −158.1 (broad t, $^3J_{\text{FF}} = 21$ Hz, 3F, *p*-F), −132.1 (broad, 6F, *o*-F); ^{19}F NMR (564.3 MHz, toluene-d_8, 203 K) δ −165 to −162 (5F), −160.9 (1F) (each broad, *m*-F), −157.9 (1F), −157.2 (2F) (each broad, *p*-F), −133.7, −131.2, −129.2 (each broad, each 2F, *o*-F).

Quantitative Monitoring of the Rearrangement Reaction of 13 to 6a. A solution of **13** was prepared in toluene-d_8 at −60 °C as described above. The reaction mixture was brought to 25 °C inside the probe of an NMR spectrometer. The decay in the concentration of **13** was followed by recording one scan (^{1}H) per minute and integration of the $Si(C\mathit{H}_3)_2$ signals of **13** (δ 0.16 and −0.01 ppm at 298 K). Exponential regression yielded the first-order rate constant $k = 1.145 \times 10^{-3}$ s^{-1}; $\Delta G^{\ddagger}(298\ \text{K}) = (21.5 \pm 0.5)$ kcal/mol.

Reaction of Cp_2Zr(butadiene) (1) with $B(C_6F_5)_3$ at 213 K: Formation of 14. A solution of butadiene complex **1** (8 mg, 29.0 μmol) in toluene-d_8 (0.4 mL) was placed in an NMR tube which was sealed with a septum and cooled to −60 °C. A solution of $B(C_6F_5)_3$ (15 mg, 29.3 μmol) in toluene-d_8 (0.2 mL) was slowly injected by syringe. The tube was shaken vigorously to ensure homogeneity of the reaction mixture. The NMR spectra were recorded instantaneously at −60 °C. The formation of betaine **14**, along with small amounts of **2**, could be observed. At temperatures above −20 °C the rearrangement of **14** to **2** sets in. **14**: ^{1}H NMR (599.9 MHz, toluene-d_8, 213 K) δ 5.17 (s, 5H, C_5H_5), 5.05 (ddd, $^3J = 11.9$ Hz, $2 \times {}^3J = 10.6$ Hz, 1H, 2-H), 4.60 (s, 5H, C_5H_5), 4.20 (dd, $2 \times {}^3J = 10.6$ Hz, 1H, 3-H), 2.63 (m, 1H, 1-H), 0.76 (m, 1H, 1-H′), −0.28, −2.37 (each broad s, each 1H, 4-H, 4-H′); ^{1}H NMR (599.9 MHz, toluene-d_8, 213 K) δ 5.12 (s, 5H, C_5H_5), 5.05 (m, 1H, 2-H), 4.51 (s, 5H, C_5H_5), 4.14 (m, 1H, 3-H), 2.63, 0.73 (each m, each 1H, 1-H, 1-H′), −0.27, −2.48 (each broad s, each 1H, 4-H, 4-H′); ^{13}C NMR (GATED, 150.8 MHz, toluene-d_8, 213 K) δ 148.3 (d, $^1J_{\text{CF}} = 240$ Hz, *o*-$B(C_6F_5)_3$), 139.1 (d, $^1J_{\text{CF}} = 250$ Hz, *p*-$B(C_6F_5)_3$), 137.2 (d, $^1J_{\text{CF}} = 250$ Hz, *m*-$B(C_6F_5)_3$), 133.5 (d, $^1J_{\text{CH}} = 157$ Hz, CH, C-2), 109.7 (d, $^1J_{\text{CH}} = 160$ Hz, CH, C-3), 108.9, 105.9 (each d, $^1J_{\text{CH}} = 178$ Hz, CH, C_5H_5), 57.5 (t, $^1J_{\text{CH}} = 145$ Hz, CH_2, C-1), ~23 (CH_2, C-4), resonance of the ipso-C of $B(C_6F_5)_3$ not detected, signal of C-4 only observed in the GHSQC NMR spectrum. GHSQC (no proton decoupling, 599.9 MHz, toluene-d_8, 213 K): δ −0.27/~23 (d, $^1J_{\text{CH}} = 141$ Hz, 4-H/C-4), −2.48/~23 (d, $^1J_{\text{CH}} = 89$ Hz, 4-H′/C-4).

Polymerization Reactions. A 1 L glass autoclave was charged with toluene (300 mL) and triisobutylaluminum (0.5

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mL). The mixture was stirred (800 rpm), thermostated at 40 °C, and saturated with the gaseous monomer. The polymerization reaction was started by the injection of a toluene solution of the respective betaine complex (ca. 35 μmol), generated in situ as described above. After a given time the reaction was stopped by the addition of methanol (15 mL) and the mixture acidified with HCl (aqueous, 2 N, 15 mL). Polyethylene and stereoregular polypropylene was precipitated by further addition of aqueous HCl (6 N, 100 mL), collected by filtration, washed with 6 N HCl (50 mL), water (200 mL), and acetone (30 mL), and dried in vacuo to constant weight. For the isolation of atactic polypropylene the phases were separated and the aqueous layer was extracted with toluene (50 mL). The combined organic layers were washed with 2 N HCl (2 × 50 mL) and water (2 × 100 mL), dried over $MgSO_4$, and evaporated to dryness in vacuo. Melting points were determined by differential scanning calorimetry using a heating rate of 10 °C/min. The results of the second scan after complete melting and cooling of the samples are reported. ^{13}C NMR spectra of the polypropylene samples were recorded on a Bruker AC 200 P spectrometer (^{13}C, 50.3 MHz) with proton decoupling at 350 K in a solvent mixture of 1,2,4-trichlorobenzene and C_6D_6 (5:1).

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Supporting Information Available: Additional NMR data and detailed information about the X-ray crystal structure analyses of compounds **6a**,**b**, **8**, **9**, and **12** and the polymerization reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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