

(*N*-Pyrrolyl)B(C₆F₅)₂—A New Organometallic Lewis Acid for the Generation of Group 4 Metallocene Cation Complexes

Gerald Kehr, Roland Fröhlich, Birgit Wibbeling, and Gerhard Erker*^[a]

Abstract: Treatment of the (C₆F₅)₂BF · OEt₂ (**3**) complex with *N*-pyrrolyl lithium gives bis(pentafluorophenyl)(*N*-pyrrolyl)borane (**2**), a strong organometallic Lewis acid, which was characterized by X-ray diffraction (B–N bond length: 1.401(5) Å). It exhibits a columnar superstructure in the crystal and contains π -stacks of pyrrolyl units. Compound **2** readily abstracts alkyl anions from a variety of alkyl Group 4 metallocene-type complexes and leads to the clean formation of the respective metallocene ions or ion pairs. For example, the treatment of Cp₃ZrCH₃ (**9**) with **2**

transfers a methyl anion to yield the ion pair [Cp₃Zr]⁺[(C₄H₄N)B(CH₃)(C₆F₅)₂][−] (**12**). The X-ray crystal structure analysis of **12** shows a close contact between zirconium and the pyrrolyl- β -carbon (2.641(2) Å). The borane **2** adds to (butadiene)zirconocene (**13**) to yield the betaine system [Cp₂Zr]⁺[(C₄H₆)B-(NC₄H₄)(C₆F₅)₂][−] (**15**). Complex **15** contains a distorted η^3 -allyl moiety inside

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the metallacyclic framework and it features an internal Zr⁺... (pyrrolyl)B[−] ion pair interaction with a Zr... pyrrolyl- α -carbon separation of 2.723(3) Å (determined by X-ray diffraction). From the dynamic NMR spectra of **15** the bond strength of the internal ion pair interaction was estimated to be $\Delta G_{\text{diss}}^\ddagger$ (223 K) $\approx$ 15 kcal mol^{−1}. Treatment of dimethylzirconocene (**16**) with **2** yields the metallocene borate salt [Cp₂ZrCH₃]⁺[(C₄H₄N)B(CH₃)(C₆F₅)₂][−] (**17**), which is an active catalyst for the polymerization of ethene.

Introduction

Group 4 metal cations play an important role in organometallic chemistry and in catalysis.^[1] Many of these species are extremely electrophilic and have a pronounced tendency to find electronic stabilization in the absence of external donor ligands by the formation of ion pairs.^[2] Therefore, the nature of the counteranion, and hence the mode of cation generation,^[3] is quite essential for controlling the features of such species.

Among the established methods for the generation of early transition metal cations, the treatment of a suitable precursor, usually a metal-alkyl or -hydride complex, with an electrophilic borane has proven very successful and has found extensive use and application.^[2,4] In the majority of cases, the strong organometallic Lewis acid, tris(pentafluorophenyl)borane (**1**),^[5] was used.^[6] A number of related electrophilic organoboron derivatives were tested for this application; most of them were similar to **1** in that they bore various

fluorine- or fluoroalkyl-substituted arene groups at boron.^[7] We have now used, to our knowledge for the first time, a Lewis acidic abstractor/activator component in this chemistry that bears a halogen-free nitrogen-hetaryl substituent at boron, along with two remaining C₆F₅ substituents. The (*N*-pyrrolyl)bis(pentafluorophenyl)borane system (**2**) appears to make effective use of the electronegative Group 15 heteroatom and at the same time it avoids a pronounced nitrogen–boron π -interaction, so that the boron center in compound **2** is a suitable cation generator in organometallic Group 4 metal chemistry. In this work, we have characterized compound **2** and examples of its application for the effective formation of a variety of Group 4 metal-cation systems are described and discussed.

Results and Discussion

Synthesis and characterization of (*N*-Pyrrolyl)B(C₆F₅)₂ (2**):** The title compound (**2**) was prepared by the reaction of the (C₆F₅)₂BF · OEt₂ complex (**3**)^[8] with *N*-pyrrolyl lithium (**4**) in a 1:1 stoichiometry in diethyl ether (Scheme 1). Crystallization from pentane gave the boron compound **2** in $\approx$ 50 % yield as colorless crystals. (*N*-Pyrrolyl)B(C₆F₅)₂ was characterized by elemental analysis, spectroscopy (see below), and by an X-ray crystal structure analysis.

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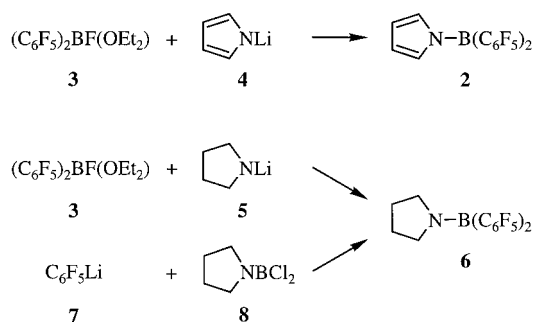
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Scheme 1. Synthesis of **2** and **6**.

In the crystal, the boron atom in **2** is bonded to two C_6F_5 groups and also closely bonded to the NC_4H_4 ring system (see Figure 1). The B–C(aryl) bond length (B–C21/C21*) is 1.582(3) Å. The B–N1 bond is relatively long at 1.401(5) Å (similar to $(\text{Me}_3\text{Si})_2\text{N–B}(\text{C}_6\text{F}_5)_2$: 1.400(3) Å^[9]). Both the boron and the nitrogen center in **2** have trigonal planar coordination [sum of bond angles: 360.0° (B), 360.0° (N)]. The relative spatial arrangement of the $(\text{C}_4\text{H}_4\text{N})\text{B}(\text{C}_6\text{F}_5)_2$ monomeric units of **2** in the crystal is noteworthy—compound **2** adopts a columnar superstructure in the solid state (see Figure 2). This is characterized by a stack of parallel $\text{C}_4\text{H}_4\text{N–[B]}$ rings, from which the $-\text{B}(\text{C}_6\text{F}_5)_2$ substituents laterally protrude. The $-\text{B}(\text{C}_6\text{F}_5)_2$ moieties each exhibit a chiral two-bladed propeller-like conformation. The relative $-\text{B}(\text{C}_6\text{F}_5)_2$ conformations are of the same chiral sense in each individual column; however, they are of opposite relative chirality in adjacent columns. The vertical separation between the pyrrolyl rings in the columns of **2** amounts to ≈ 3.9 Å. The corresponding intermolecular separation between C3/C3* and the next B atom amounts to 3.98 Å.^[10]

The saturated analogue of **2**, (*N*-pyrrolidyl) $\text{B}(\text{C}_6\text{F}_5)_2$ (**6**), was prepared for a structural, spectroscopic, and chemical comparison. The compound was obtained by two different synthetic routes (Scheme 1), namely by treatment of the precursor $(\text{C}_6\text{F}_5)_2\text{BF}(\text{OEt}_2)$ (**3**) with *N*-pyrrolidyl lithium (**5**) or alternatively by the reaction of *N*-pyrrolidylboron dichloride (**8**)^[11] with pentafluorophenyllithium (**7**). Both pathways gave **6** in $\approx 50\%$ yield.

In contrast to **2**, the X-ray crystal structure analysis of **6** in the solid state showed isolated molecules (Figure 1). The B–N1 bond in **6** (1.366(3) Å) is markedly shorter than in **2**. The boron atom and the nitrogen center in **6** both have a trigonal planar coordination geometry (sum of bond angles at N1: 359.9°, at B: 360.1°). The five-membered ring in **6** has adopted a twist conformation so that C3 and C4 are located above and below the C2–N1–C5 plane (Figure 1). The observed geometry at N1 and rather short bond lengths indicate a partial double-bond character of the B–N linkage in **6**.^[12] From a structural point of view, the interaction between the nitrogen lone pair and the boron is significantly less pronounced in the pyrrolyl compound **2**.

This interpretation is supported by the different chemical behavior of **2** and **6** (see below) and by differences in some of their spectroscopic properties. Thus, the ^{11}B NMR resonance of **2** occurs at $\delta = 40.8$ (in $[\text{D}_6]\text{benzene}$), that is, at a substantially increased δ value than that found for **6** ($\delta =$

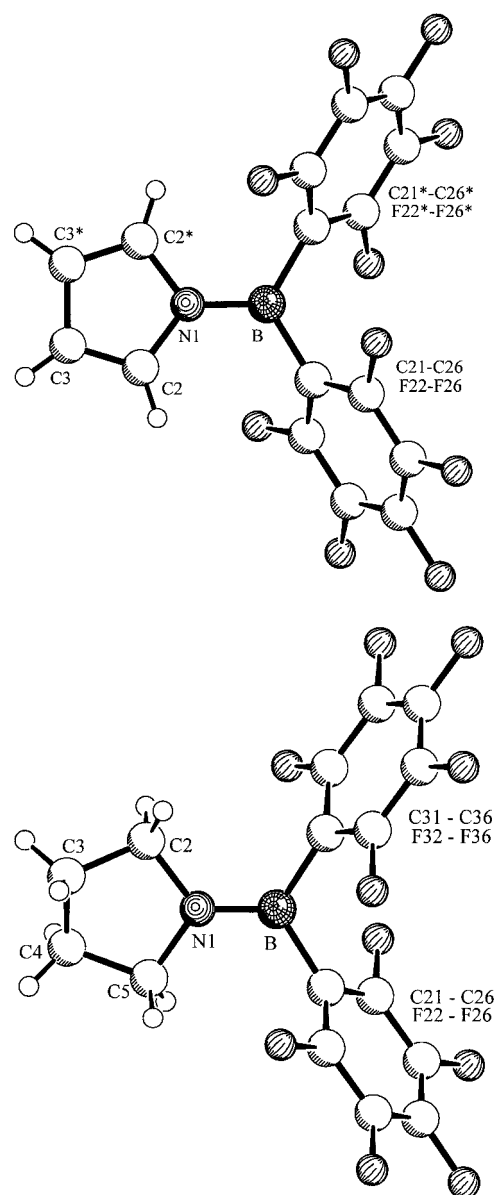


Figure 1. Views of the molecular structures of the compounds (*N*-pyrrolyl) $\text{B}(\text{C}_6\text{F}_5)_2$ (**2**, top) and (*N*-pyrrolidyl) $\text{B}(\text{C}_6\text{F}_5)_2$ (**6**, bottom) with selected bond lengths [Å] and angles [°]. Compound **2**: B–N1 1.401(5), B–C21 1.582(3), N1–C2 1.402(3), C2–C3 1.346(4), C3–C3* 1.433(6), C21–B–C21* 118.3(3), C21–B–N1 120.8(2), B–N1–C2 126.9(2), C2–N1–C2* 106.3(3). Compound **6**: B–N1 1.366(3), B–C21 1.595(3), B–C31 1.586(4), N1–C2 1.479(3), C2–C3 1.509(4), C3–C4 1.505(6), C4–C5 1.508(4), N1–C5 1.488(3), C21–B–C31 116.4(2), C21–B–N1 121.3(2), C31–B–N1 122.4(2), B–N1–C2 125.7(2), B1–N1–C5 124.8(2), C2–N1–C5 109.4(2).

32.5). This probably indicates a marked increase in the electrophilic character of the boron center in **2** [the strong organometallic Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ (**1**) shows a ^{11}B NMR resonance at $\delta = 60$ in $[\text{D}_6]\text{benzene}$, while in $[\text{D}_8]\text{tetrahydrofuran}$ (i.e., as the coordinatively saturated THF adduct) it is $\delta = 2.5$]. The ^{15}N NMR spectra of **2** ($\delta = -188$) and **6** ($\delta = -238$) are also very different.^[13]

Reactions with zirconocene complexes: $\text{B}(\text{C}_6\text{F}_5)_3$ (**1**) readily abstracts alkyl anion equivalents from zirconocene complexes and related compounds.^[2, 4] We started with the treatment of

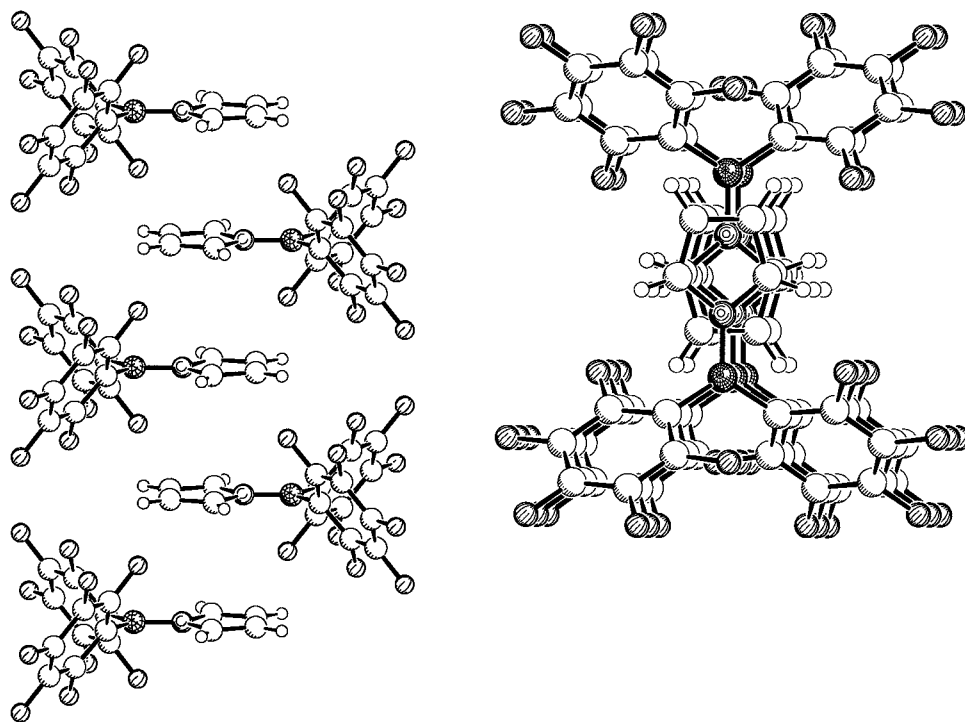


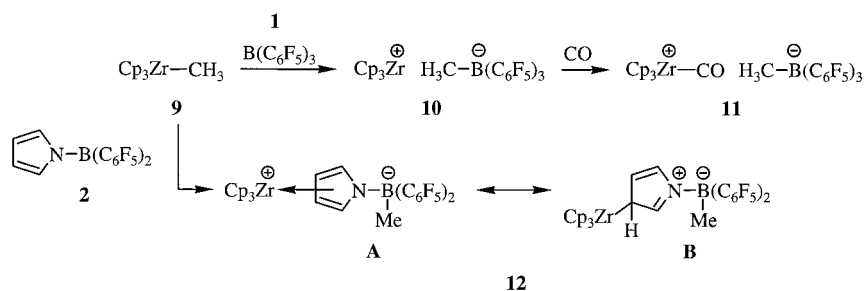
Figure 2. Two projections of the columnar arrangement of the molecules of **2** in the crystal.

(*N*-pyrrolidinyl) $\text{B}(\text{C}_6\text{F}_5)_2$ (**6**) with a variety of these Group 4 metal compounds. At room temperature, no reaction was observed with the examples selected (see below), while unspecific decomposition reactions took place at elevated temperatures. This was very different when the hetarene analogue (*N*-pyrrolyl) $\text{B}(\text{C}_6\text{F}_5)_2$ (**2**) was employed. Here a very similar behavior to compound **1** was observed. Clean methyl abstractions or related $(\text{C}_4\text{H}_4\text{N})\text{B}(\text{C}_6\text{F}_5)_2$ addition reactions were found. A series of representative examples is described below.

We have already reported that $\text{B}(\text{C}_6\text{F}_5)_3$ abstracts a methyl anion from $[\text{Cp}_3\text{ZrCH}_3]$ (**9**) to yield the $[\text{Cp}_3\text{Zr}]^+$ cation system (**10**), which readily reacts with added monodentate two-electron donors to form a variety of adducts, such as the d^0 -metal carbonyl cation in **11** (see Scheme 2).^[14] Complex **9** reacts quite similarly with **2**: at room temperature a rapid reaction occurs between **9** and **2** in a 1:1 stoichiometry to afford **12** (isolated yield > 70 %). Crystallization from benzene gave single crystals of **12** that were suitable for an X-ray crystal structure analysis.

The X-ray crystal structure analysis of **12** (Figure 3) shows that a methyl group was transferred from zirconium to boron during the reaction ($\text{B}-\text{C}41$ 1.621(2) Å). This results in the formation of a $[(\text{C}_4\text{H}_4\text{N})\text{B}(\text{C}_6\text{F}_5)_2(\text{CH}_3)]^-$ anion moiety [$\text{B}-\text{C}(\text{aryl}) = 1.662(2)$ Å and 1.651(2) Å; boron-centered bond angles between 102.8(2) and 115.0(2)°] and a $[\text{Cp}_3\text{Zr}]^+$ cation unit [with the three $\text{Cp}(\text{centroid})-\text{Zr}-\text{Cp}(\text{centroid})$ angles amounting to 118.0, 118.1, and 116.4°]. In the solid state these two subunits of **12** combine to form a tight ion pair (schematically depicted by the resonance forms **A** and **B** shown in Scheme 2).

The closest contact between the two parts occurs between Zr and the pyrrolyl carbon atom C13 (2.641(2) Å, while $\text{Zr} \cdots \text{C}14 = 3.418(2)$ Å and $\text{Zr} \cdots \text{C}15 = 4.303(2)$ Å). This is ≈ 0.2 – 0.3 Å greater than a true $\text{Zr}-\text{C}$ σ -bond;^[15] however, this interaction is quite strong—the $\text{Zr}-\text{C}(\text{Cp})$ bond lengths, which were found to be between 2.549(2) and 2.660(2) Å in complex **12**. It is not unexpected that the internal pyrrolyl bonding features in **12** are quite different from those usually found in a pyrrolyl moiety.^[16] For instance, the pyrrolyl bond lengths alternate in the starting material **2**: $\text{N}1-\text{C}2$ 1.402(3) Å, $\text{C}2-\text{C}3$ 1.346(4), and $\text{C}3-\text{C}3^*$ 1.433(6) (Figure 1), whereas the sequence of bond lengths inside the $(\text{C}_4\text{H}_4\text{N})$ ring of **12** is quite different: $\text{N}11-\text{C}12$ 1.336(2) Å, $\text{C}12-\text{C}13$ 1.418(2), $\text{C}13-\text{C}14$ 1.443(2), $\text{C}14-\text{C}15$ 1.356(2), and $\text{C}15-\text{N}11$ 1.398(2). The



Scheme 2. Reaction of **9** with $\text{B}(\text{C}_6\text{F}_5)_3$ (**1**) and (*N*-pyrrolyl) $\text{B}(\text{C}_6\text{F}_5)_2$ (**2**).

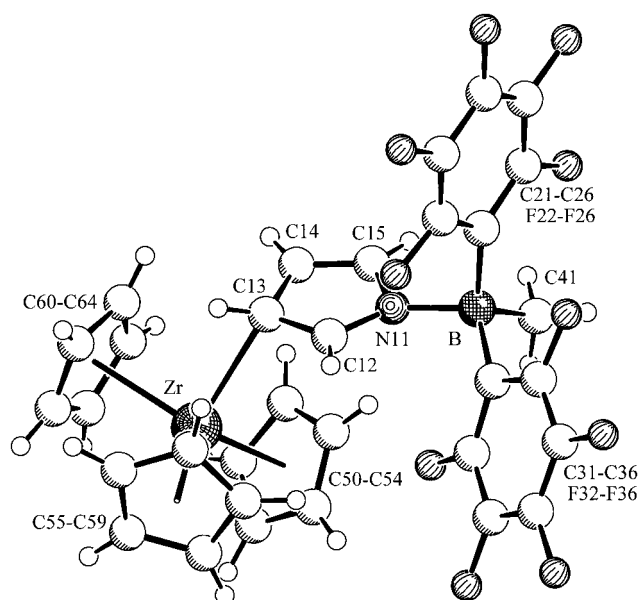


Figure 3. Molecular structure of **12** with an unsystematic atom numbering scheme. Selected bond lengths [Å] and angles [°]: Zr–C13 2.641(2), Zr–C14 3.418(2), Zr–C15 4.303(2), N11–B 1.605(2), N11–C12 1.336(2), N11–C15 1.398(2), C12–C13 1.418(2), C13–C14 1.443(2), C14–C15 1.356(2), B–C21 1.662(2), B–C31 1.651(2), B–C41 1.621(2); N11–B–C21 102.8(1), N11–B–C31 112.1(1), N11–B–C41 109.8(1), C21–B–C31 111.9(1), C21–B–C41 115.0(1), C31–B–C41 105.6(1), B–N11–C12 130.3(1), B–N11–C15 121.8(1), C15–N11–C12 107.3(1), N11–C12–C13 110.9(1), C12–C13–Zr 113.1(1), C12–C13–C14 104.3(1), Zr–C13–C14 110.2(1), C13–C14–C15 107.4(2), C14–C15–N11 110.1(2).

N–B bond length in **12** is much longer than that in the precursor **2**. The nitrogen coordination sphere is again trigonal planar (sum of bond angles at N11: 359.4°). These features indicate some iminium ion character of the B–pyrrolyl moiety of the ion pair **12**, as illustrated by the mesomeric formula **B** in Scheme 2.

In solution, complex **12** shows the expected NMR features (^{11}B NMR signal at $\delta = -6.8$ in $[\text{D}_6]$ benzene at ambient temperature). Sharp $^1\text{H}/^{13}\text{C}$ NMR resonances of the three symmetry-equivalent Cp ligands are observed at $\delta = 4.94$ and 113.5, whereas the corresponding $\text{C}_4\text{H}_4\text{N}$ resonances at $\delta(^1\text{H}) = 7.65$ (2-/3-H) and 5.58 (3-/4-H) as well as $\delta(^{13}\text{C}) = 142.5$ and 113.4 are broadened. This probably indicates the beginning of an exchange of the respective signals on the NMR timescale, which is probably caused by a dissociation/recombination process of the ion pair structure in solution.^[2, 17] Unfortunately, as the monitoring temperature is lowered, the solubility of **12** rapidly decreased in the various solvents tested and has thus precluded the investigation of this process

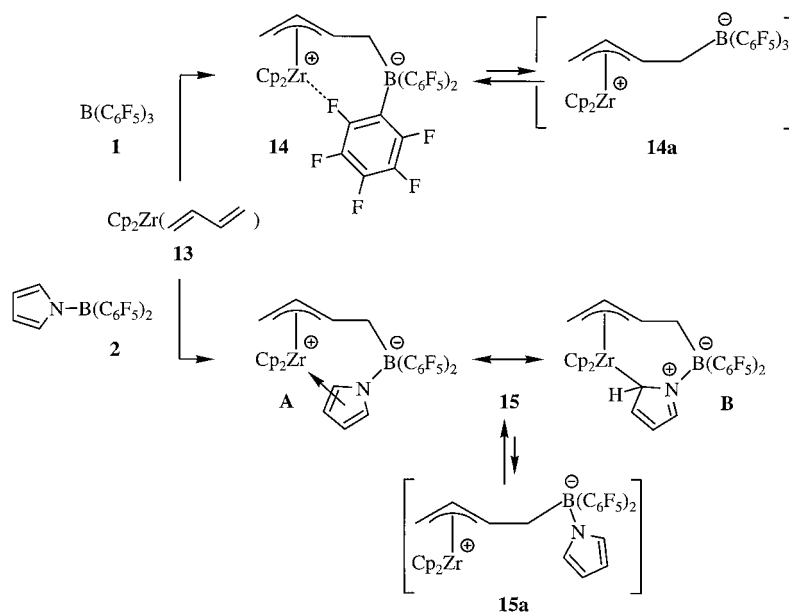
by dynamic NMR spectroscopy. The ^{15}N NMR resonance of **12** was observed at $\delta = -159$ (in $[\text{D}_8]$ toluene at 298 K; GHMBC, by polarization transfer from both the B–CH₃ and the pyrrolyl–C²H resonances).

We have recently reported that **1** adds to (butadiene)zirconocene (**13**) to yield the metallocene-hydrocarbyl betaine system **14**.^[18] The dipolar product has served as a single-component Ziegler catalyst.^[19] In complex **14** a lateral coordination site at the bent metallocene wedge is used to coordinate a fluorine atom from one of the *o*-C–F bonds of the C₆F₅ group at the boron center. The Zr...F–C(aryl) coordination was shown by X-ray diffraction and by variable-temperature ^{19}F NMR spectroscopy. From the latter, a bond dissociation energy ($\Delta G_{\text{diss}}^\ddagger$) of $\approx 8 \text{ kcal mol}^{-1}$ was deduced.^[20]

Compound **2** shows an analogous reaction pattern with [(butadiene)ZrCp₂] (**13**).^[21] They react rapidly at ambient temperature in toluene solution to give the dipolar 1:1 addition product **15** (isolated in 65 % yield, Scheme 3).

Single crystals of **15** were obtained from benzene/pentane. The X-ray crystal structure analysis shows that the borane **2** has cleanly added to a terminal carbon atom of the butadiene ligand of **13** to form the betaine complex **15** (B–C6 1.620(4) Å; Figure 4). The remaining former butadiene carbon atoms form a η^3 -allyl ligand moiety at zirconium (*syn*-substituted at C7). Its bonding to Zr is distorted toward a σ – π coordination, as often observed for [Cp₂Zr(allyl)] groups.^[22] This is evident from the observed C–C and C–Zr bond lengths [C8–C9 1.411(5), C7–C8 1.359(4), C6–C7 1.496(4), C9–Zr 2.402(3), C8–Zr 2.525(3), and C7–Zr 2.682(3) Å] and angles [C7–C8–C9 122.7(3), C6–C7–C8 125.6(3), B–C6–C7 110.7(2)°]. Since complex **15** is chiral because of the π -allyl coordination, two diastereotopic C₆F₅ substituents are present at boron [B–C21 1.651(4) Å, B–C31 1.657(4) Å, and bond angles at boron between 106.1(2)° and 115.2(2)°].

The pyrrolyl group is the fourth substituent at the boron atom in **15**. It is again coordinated weakly to the electron-



Scheme 3. Reaction of [Cp₂Zr(butadiene)] with B(C₆F₅)₃ (**1**) and (N-pyrrolyl)B(C₆F₅)₂ (**2**).

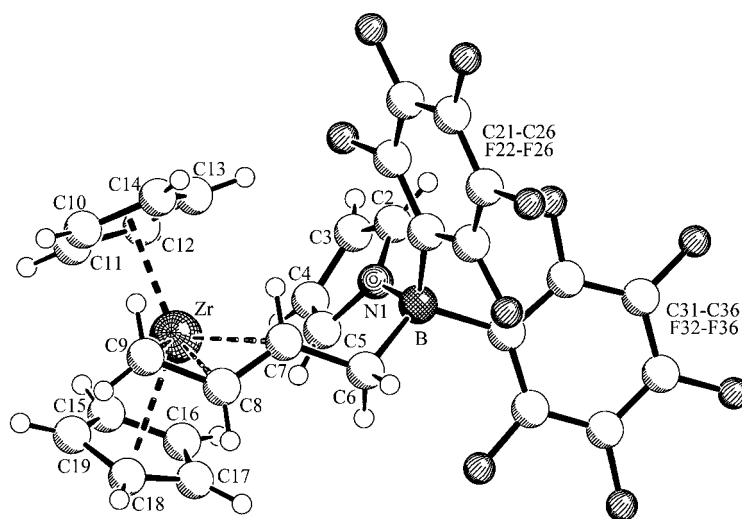


Figure 4. Molecular structure of **15**. Selected bond lengths [Å] and angles [°]: Zr–C9 2.402(3), Zr–C8 2.525(3), Zr–C7 2.682(3), Zr–C5 2.723(3), C9–C8 1.411(5), C8–C7 1.359(4), C7–C6 1.496(4), C6–B 1.620(4), B–N1 1.574(4), N1–C2 1.342(4), C2–C3 1.381(5), C3–C4 1.375(5), C4–C5 1.393(4), C5–N1 1.395(4), B–C21 1.651(4), B–C31 1.657(4); C9–Zr–C8 33.2(1), C9–Zr–C7 56.8(1), C9–Zr–C5 124.9(1), C8–Zr–C7 30.1(1), C8–Zr–C5 93.5(1), C7–Zr–C5 68.3(1), C9–C8–C7 122.7(3), C8–C7–C6 125.6(3), C7–C6–B 110.7(2), C6–B–N1 107.5(2), C6–B–C21 106.5(2), C6–B–C31 115.2(2), N1–B–C21 114.0(2), N1–B–C31 106.1(2), C21–B–C31 107.9(2), B–N1–C2 128.4(3), B–N1–C5 123.6(2), N1–C2–C3 110.9(3), C2–C3–C4 106.7(3), C3–C4–C5 107.7(3), C4–C5–N1 108.0(3), C4–C5–Zr 103.3(2), N1–C5–Zr 116.8(2).

deficient zirconium center to form a (here internal) ion pair. However, a comparison of the characteristic bonding features reveals that the $\text{Zr}/(\text{C}_4\text{H}_4\text{N})\text{--}[\text{B}]$ interaction in **15** is probably slightly less pronounced than in **12** (see above). In **15** the N1–B bond length is 1.574(4) Å. Again, the nitrogen center exhibits trigonal planar coordination (sum of bond angles at N1: 358.6°).

There is a close contact between the pyrrolyl C5 and Zr [2.723(3) Å; compare with $\text{Zr}\cdots\text{C4}$ 3.332(3) Å and $\text{Zr}\cdots\text{N1}$ 3.576(3) Å]. Again, the C–C and C–N bond order inside the five-membered heterocycle is very different from a normal pyrrol unit. It is also distorted towards an iminium-type mesomeric structure, albeit less pronounced than in complex **12** (see above and Figure 3), and it has a different relative arrangement because of the close Zr–C5 (i.e., α -carbon) contact in **15**. The pertinent bond lengths are 1.395(4) Å (N1–C5), 1.393(4) Å (C4–C5), 1.375(3) Å (C3–C4), 1.381(5) Å (C2–C3), and 1.342(4) Å (N1–C2). The internal ion-pair character is supported by the obtained bond angles at the pyrrolyl-carbon center C5 [116.8(2)° (N1–C5–Zr), 103.3(2)° (C4–C5–Zr), and 108.0(3)° (N1–C5–C4)], these appear to be typical for a dominating electrostatic interaction^[14, 23] without a pronounced rehybridization at the ring carbon center. A resonance hybrid description with the formulations **A** and **B** (see Scheme 3) may serve as an approach to illustrate the bonding features found for complex **15**.

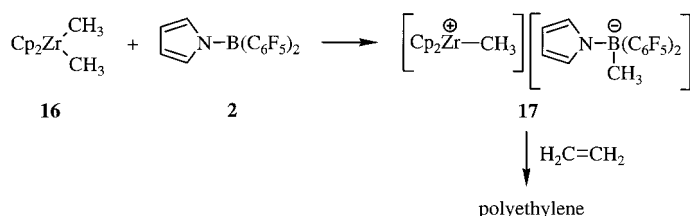
The low-temperature NMR spectra indicate a similar structure of complex **15** in solution. It shows a ^{11}B NMR signal at $\delta = -7.3$ and a ^{15}N NMR signal at $\delta = -165$ (for details see the Experimental Section). Complex **15** is chiral. It exhibits the signals of a pair of diastereotopic Cp ligands (^1H : $\delta = 4.70, 4.45$; ^{13}C : $\delta = 109.8, 107.0$, both in $[\text{D}_8]\text{toluene}$). The ^{19}F NMR spectrum exhibits a total of ten C_6F_5 signals of

equal intensity at 193 K in $[\text{D}_8]\text{toluene}$, namely a set of four *o*-F ($\delta = -163.2, -162.9, -162.6, -161.9$), two *p*-F ($\delta = -158.4, -157.7$), and four *m*-F signals ($\delta = -134.1, -133.9, -131.3$ and -128.6).

This observed pattern indicates that the rotation about the B–C(aryl) vectors is frozen at 193 K on the 282 MHz ^{19}F NMR timescale, and that there are two diastereotopic C_6F_5 groups at boron. Raising the temperature leads to coalescence of the respective *m*-F and *o*-F pairs of resonances of each individual C_6F_5 group, while the pair of *p*-F resonances remains unchanged by the onset of the B–C(aryl) rotational process. A Gibbs activation energy of $\Delta G_{\text{rot}}^\ddagger$ (223 K) = $9.0 \pm 0.5 \text{ kcal mol}^{-1}$ was obtained for the B– C_6F_5 rotational process of complex **15**.^[24]

The $^1\text{H}/^{13}\text{C}$ NMR signals of the $[(\pi\text{-allyl})\text{Zr}]$ group in **15** were observed at $\delta = 1.30, 1.92$ (9-H/H')/47.0 (C9), 4.85 (8-H)/121.0 (C8), and 4.14 (7-H)/110.0 (C7) (at 298 K in $[\text{D}_8]\text{toluene}$, atom numbering as in Figure 4; C(6) H_2 signals at $\delta = 2.85, 2.34/28.3$). These signals are almost temperature-invariant in the applied temperature range. At low temperature [^1H NMR: 213 K (600 MHz), ^{13}C NMR: 233 K (150 MHz), both in $[\text{D}_8]\text{toluene}$] the pyrrolyl group exhibits four $^1\text{H}/^{13}\text{C}$ NMR methine resonances of the $\text{C}_4\text{H}_4\text{N}$ nucleus of equal intensity at $\delta = 7.70, 5.22/145.0, 134.1$ (α -CH), and 6.24, 5.98/110.1, 92.0 (β -CH), as expected from the internal ion pair structure of **15** (Figure 4). Raising of the temperature results in the broadening and pairwise coalescence of the respective resonances. This dynamic behavior is most likely caused by a reversible cleavage of the internal ion pair combined with a rotation of the pyrrolyl ring around the B–N vector (via **15a**, analogous to that observed for **14**, see Scheme 3). The activation barrier of this internal pyrrolyl equilibration process may, to a first approximation, be used to obtain an estimate of the strength of the interaction between the pyrrolyl-borate anion/zirconocene cation ion-pair.^[2, 17] From the dynamic NMR spectra of **15** a value of $\Delta G_{\text{diss}}^\ddagger$ (223 K) = $15.0 \pm 0.3 \text{ kcal mol}^{-1}$ was obtained.

The reaction of dimethylzirconocene (**16**) with (*N*-pyrrolyl) $\text{B}(\text{C}_6\text{F}_5)_2$ (**2**) proceeded rapidly at room temperature (Scheme 4). A methyl group is transferred from the transition metal to the boron to yield the organometallic salt $[\text{Cp}_2\text{Zr}(\text{CH}_3)]^+[(\text{C}_4\text{H}_4\text{N})\text{B}(\text{CH}_3)(\text{C}_6\text{F}_5)_2]^-$ (**17**; isolated yield: >60%). The product shows broad $^1\text{H}/^{13}\text{C}$ NMR $\text{CH}_3[\text{B}]$ resonances at $\delta = 1.10/10.9$. The (*N*-pyrrolyl) B group exhibits ^1H NMR signals at $\delta = 7.20$ and 5.05 for the 2-/5-H and 3-/4-H pairs of hydrogens (corresponding ^{13}C NMR signals at $\delta = 139.2$ and 99.4). We have no experimental information about



Scheme 4. Synthesis of **17**, a catalyst for the polymerization of ethene.

the ion pairing in **17**.^[25] The ¹¹B NMR spectra of **17** shows signals at $\delta = -6.7$; the ¹⁵N NMR signal is also in the expected range at $\delta = -159$.

The salt **17** is, as expected, an active catalyst for alkene polymerization. Polyethylene is formed at the catalyst **17** in toluene solution at 60 °C and 2 bar ethene pressure with a moderate activity ($\approx 18 \text{ kg mol}[\text{Zr}]^{-1} \text{ h}^{-1} \text{ bar}^{-1}$).

Conclusions

We conclude that boron Lewis acids that contain electro-negative substituents, which are different from the usually used fluoro- or fluoroalkyl-substituted trisarylboranes, have an interesting application potential in metallocene cation chemistry. In the example described here (**2**), the pyrrol aromaticity keeps the electron pair at nitrogen electronically occupied and thus prevents an effective intramolecular neutralization of the borane Lewis acidity. The remaining electron-withdrawing inductive effect of the nitrogen center seems to assist in making the trivalent boron atom in **2** an effective Lewis acid that features the typical anion abstraction activity towards carbon centers bound to Group 4 metallocenes. The resulting salts, ion pairs, and addition products show properties similar to those of their often used B(C₆F₅)₃ analogues, although the pyrrolyl-borate moiety appears to lead to slightly increased ion-pairing energies. This study indicates that borane derivatives of the aromatic heterocycle pyrrol, and probably of a great variety of other related heterocyclic systems as well, have a marked potential as Lewis acidic compounds for the generation of electrophilic, early transition metal cations and of active catalyst systems derived thereof.^[26]

Experimental Section

All reactions were carried out in an inert atmosphere (Ar) with Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under Ar prior to use. NMR experiments were carried out on a Varian Unity plus 600, Bruker AC200P, or Bruker ARX 300 spectrometer. Chemical shifts of the heteronuclei are given relative to BF₃·OEt₂ [$\delta(^{11}\text{B})=0$ for $\Xi(^{11}\text{B})=32.084 \text{ MHz}$], to neat nitromethane [$\delta(^{15}\text{N})=0$ for $\Xi(^{15}\text{N})=10.133 \text{ MHz}$], and to neat CFCl₃ [$\delta(^{19}\text{F})=0$ for $\Xi(^{19}\text{F})=94.077 \text{ MHz}$]. The spectral assignments were mostly based on the results of a combination of APT (attached proton test), COSY 45 (¹H, ¹H COSY), HETCOR (¹H, ¹³C heteronuclear shift correlation), GCOSY, 1D-TOCSY, GHSQC, and/or GHMBC experiments.^[27] IR spectra were recorded on a Nicolet 5DXC FT-IR spectrometer; melting points were measured by DSC (DSC 2010, TA

Instruments). Pyrrolidinyborondichloride (**8**),^[11] the bis(pentafluorophenyl)boronfluoride–diethyl ether complex (**3**),^[8] bis(η^5 -cyclopentadienyl)dimethylzirconium (**16**),^[28] tris(η^5 -cyclopentadienyl)methylzirconium (**9**),^[15] and (butadiene)zirconocene (**13**)^[29] were prepared according to literature procedures.

Preparation of bis(pentafluorophenyl)(*N*-pyrrolyl)borane (2**):** A suspension of *N*-pyrrolyllithium (**4**, 5.3 g, 73 mmol) prepared by deprotonation of pyrrol with *n*-butyllithium in diethyl ether (50 mL) was added in small portions with stirring to a freshly prepared 0.52 M solution of complex **3** (140 mL, 73 mmol) at -78°C . The reaction mixture was allowed to warm to room temperature and stirring was continued for 14 h. The solvent was then changed from diethyl ether to pentane. The precipitate was removed by filtration and washed with pentane ($2 \times 20 \text{ mL}$). The pale yellow pentane phases were combined, and their volume reduced in vacuo until the first precipitate was observed and then stored at 8°C . The product was obtained as pale yellow crystals by fractional crystallization from pentane. Yield: 15.6 g (52 %); m.p. 126°C ; ¹H NMR (200.13 MHz, [D₆]benzene, 300 K): $\delta = 6.59$ (m, 2H; 2-/5-H), 6.23 (m, 2H; 3-/4-H); ¹³C NMR (75.47 MHz, [D₆]benzene, 300 K): $\delta = 147.1$ (dm, ¹J(C,F) = 257 Hz, *o*-C₆F₅), 143.4 (dm, ¹J(C,F) = 240 Hz, *p*-C₆F₅), 138.1 (dm, ¹J(C,F) = 254 Hz, *m*-C₆F₅), 127.7 (C2/5), 118.3 (C3/4), 110.0 (br, *ipso*-C of C₆F₅); ¹¹B NMR (64.21 MHz, [D₆]benzene, 300 K): $\delta = 40.8$ ($\nu_{1/2} = 480 \text{ Hz}$); ¹⁵N NMR (50.74 MHz, [D₆]benzene, 298 K): $\delta = -187.5$; ¹⁹F NMR (282.41 MHz, [D₆]benzene, 300 K): $\delta = -130.5$ (m, 2F, *o*-F), -148.4 (t, 1F, *p*-F), -160.0 (m, 2F, *m*-F); C₁₆H₄NBF₁₀ (411.0): calcd C 46.76, H 0.98, N 3.41; found C 46.58, H 1.25, N 3.30.

X-ray crystal structure analysis of **2:** Formula C₁₆H₄NBF₁₀, $M = 411.01$, $0.6 \times 0.6 \times 0.1 \text{ mm}$, $a = 17.112(1)$, $b = 11.791(1)$, $c = 7.677(1) \text{ \AA}$, $\beta = 91.75(1)^\circ$, $V = 1548.2(3) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.763 \text{ g cm}^{-3}$, $\mu = 17.14 \text{ cm}^{-1}$, empirical absorption correction with ψ -scan data ($0.589 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group *C2/c* (No. 15), $\lambda = 1.54178 \text{ \AA}$, $T = 223 \text{ K}$, $\omega/2\theta$ scans, 2440 reflections collected ($\pm h$, $\pm k$, $-l$), $[\sin \theta/\lambda] = 0.53 \text{ \AA}^{-1}$, 1155 independent and 1064 observed reflections [$I \geq 2\sigma(I)$], 129 parameters, $R = 0.067$, $wR^2 = 0.191$, max./min. residual electron density: $0.32/-0.44 \text{ e \AA}^{-3}$, hydrogens calculated and riding.

Preparation of bis(pentafluorophenyl)(*N*-pyrrolidinyllithium)borane (**6**)

Method 1: A freshly prepared suspension of pentafluorophenyllithium (80.0 mmol) [**Caution:** C₆F₅Li is potentially explosive and should always be handled with particular care, and only at low temperature] in pentane (50 mL) was stirred at -78°C , and a solution of compound **8** (6.07 g, 40.0 mmol) in pentane (20 mL) was added over a period of 15 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for 14 h. All insoluble material was filtered off, and the solid material was washed with pentane (50 mL). The combined yellowish pentane phases were reduced to one half of their original volume and were stored at 8°C . The product was obtained as yellowish crystals by fractional crystallization from pentane. Yield: 9.1 g (55 %).

Method 2: A freshly prepared solution of complex **3** (0.48 M, 150 mL, 72.0 mmol) in diethyl ether was stirred at -78°C , and a suspension of *N*-pyrrolidinyllithium (**5**, 5.55 g, 72.0 mmol) in diethyl ether (50 mL) was added carefully in small portions. The reaction mixture was allowed to warm to room temperature and stirring was continued for 14 h. The solvent was changed from diethyl ether to pentane. All insoluble material was filtered off, and the solid was washed with pentane ($2 \times 20 \text{ mL}$). The combined clear pentane phases were reduced in volume in vacuo until the first precipitate was observed and were stored at 8°C . The product was obtained as yellowish crystals by fractional crystallization from pentane. Yield: 14.3 g (34.4 mmol, 48 %); m.p. 98°C ; ¹H NMR (200.13 MHz, [D₆]benzene, 300 K): $\delta = 2.88$ (m, 4H; 2-/5-H), 1.30 (m, 4H; 3-/4-H); ¹³C NMR (50.5 MHz, [D₆]benzene, 300 K): $\delta = 146.4$ (dm, ¹J(C,F) = 242 Hz, *o*-C₆F₅), 141.9 (dm, ¹J(C,F) = 232 Hz, *p*-C₆F₅), 137.7 (dm, ¹J(C,F) = 253 Hz, *m*-C₆F₅), 122.2 (br, *ipso*-C of C₆F₅), 50.1 (C2/5), 25.6 (C3/4); ¹¹B NMR (64.21 MHz, [D₆]benzene, 300 K): $\delta = 32.5$ ($\nu_{1/2} = 240 \text{ Hz}$); ¹⁵N NMR (50.74 MHz, [D₆]benzene, 298 K): $\delta = -238$; ¹⁹F NMR (282.41 MHz, [D₆]benzene, 300 K): $\delta = -133.0$ (m, 2F, *o*-F), -153.4 (t, 1F, *m*-F), -162.1 (m, 2F, *m*-F); C₁₆H₈NBF₁₀ (415.0): calcd C 46.30, H 1.94, N 3.37; found C 45.96, H 1.98, N 3.25.

X-ray crystal structure analysis of **6:** Formula C₁₆H₈NBF₁₀, $M = 415.04$, $0.3 \times 0.2 \times 0.2 \text{ mm}$, $a = 9.766(1)$, $b = 17.707(2)$, $c = 10.456(1) \text{ \AA}$, $\beta = 115.86(1)^\circ$, $V = 1627.1(3) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.694 \text{ g cm}^{-3}$, $\mu = 16.32 \text{ cm}^{-1}$, empirical

absorption correction with ψ -scan data ($0.948 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178 \text{ \AA}$, $T = 223 \text{ K}$, $\omega/2\theta$ scans, 3502 reflections collected ($-h, +k, \pm l$), $[(\sin \theta)/\lambda] = 0.62 \text{ \AA}^{-1}$, 3309 independent and 2512 observed reflections [$I \geq 2\sigma(I)$], 254 parameters, $R = 0.058$, $wR^2 = 0.172$, max./min. residual electron density $0.31/-0.36 \text{ e \AA}^{-3}$, hydrogens calculated and riding.

Reaction of (N-pyrrolyl)B(C₆F₅)₂ (2) with Cp₃ZrCH₃ (9)—preparation of complex 12: A mixture of compounds **9** (0.13 g, 0.44 mmol) and **2** (0.18 g, 0.44 mmol) was dissolved in toluene (10 mL) at room temperature and stirred for 1.5 h. Then the solvent was removed in vacuo. Pentane (50 mL) was added to the remaining solid, and the mixture stirred for 3 h. The solid product was collected by filtration, washed with pentane ($2 \times 10 \text{ mL}$), and dried in vacuo to afford **12** as a yellow solid. Yield: 0.22 g (71 %); ¹H NMR (200.13 MHz, [D₆]benzene, 300 K): $\delta = 7.65$ (m, 2H; 2-/5-H), 5.58 (m, 2H; 3-/4-H), 4.94 (s, 15H; Cp), 1.28 (brm, 3H; [B]CH₃); ¹³C NMR (125.9 MHz, [D₆]benzene, 298 K): $\delta = 148.7$ (dm, ¹J(C,F) = 236 Hz, *o*-C₆F₅), 142.5 (br, C2/5), 139.3 (dm, ¹J(C,F) = 239 Hz, *p*-C₆F₅), 137.6 (dm, ¹J(C,F) = 249 Hz, *m*-C₆F₅), 113.5 (Cp), 113.4 (C3/4), 10.9 (br, [B]CH₃), *ipso*-C of C₆F₅ not observed; ¹¹B NMR (64.21 MHz, [D₆]benzene, 300 K): $\delta = -6.8$ ($\nu_{1/2} = 188 \text{ Hz}$); ¹⁵N NMR (50.74 MHz, [D₈]toluene, 298 K): $\delta = -159.5$; ¹⁹F NMR (282.41 MHz, [D₆]benzene, 300 K): $\delta = -132.4$ (m, 4F, *o*-F), -159.9 (t, 2F, *p*-F), -164.1 (m, 4F, *m*-F); C₃₂H₂₂NBF₁₀Zr (711.0): calcd C 53.94, H 3.11, N 1.97; found C 52.81, H 3.18, N 2.04.

X-ray crystal structure analysis of 12: Formula C₃₂H₂₂NBF₁₀Zr · 2/2 C₆H₆, $M = 790.64$, $0.45 \times 0.15 \times 0.10 \text{ mm}$, $a = 8.301(1)$, $b = 12.125(1)$, $c = 16.632(1) \text{ \AA}$, $\alpha = 91.73(1)$, $\beta = 100.46(1)$, $\gamma = 97.24(1)^\circ$, $V = 1630.6(3) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.610 \text{ g cm}^{-3}$, $\mu = 4.25 \text{ cm}^{-1}$, absorption correction with SORTAV ($0.832 \leq T \leq 0.959$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073 \text{ \AA}$, $T = 198 \text{ K}$, ω and ψ scans, 16865 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.67 \text{ \AA}^{-1}$, 7991 independent and 6895 observed reflections [$I \geq 2\sigma(I)$], 527 parameters, $R = 0.030$, $wR^2 = 0.072$, max./min. residual electron density $0.36/-0.50 \text{ e \AA}^{-3}$, hydrogens calculated and riding. The asymmetric unit contains two half molecules of benzene.

Reaction of (butadiene)zirconocene (13) with (C₄H₆N)B(C₆F₅)₂ (2)—preparation of 15: A $\approx 1:1$ mixture of *s-cis*- and *s-trans* **13** (0.12 g, 0.44 mmol) and **2** (0.18 g, 0.44 mmol) were dissolved in toluene (10 mL) at room temperature and the mixture was stirred for 1 h. The solvent was removed in vacuo, pentane (50 mL) was added to the remaining solid, and the mixture stirred for 3 h. The product **15** was collected by filtration, washed with pentane ($2 \times 10 \text{ mL}$), and dried in vacuo to give **15** as a yellow solid. Yield: 0.20 g (65 %); m.p. 176°C (decomp); ¹H NMR (599.2 MHz, [D₈]toluene, 213 K, atom numbering as in Figure 4): $\delta = 7.70$ (s, 1H; 2-H), 6.24 (d, 1H; 3-H), 5.98 (m, 1H; 4-H), 5.22 (s, 1H; 5-H), 4.75 (m, 1H; 8-H), 4.70 (s, 5H; Cp), 4.45 (s, 5H; Cp'), 4.01 (dd, ³J(H,H) = 15.2 Hz, 11.3 Hz, 1H; 7-H), 2.90 (d, ²J(H,H) = 16.2 Hz, 1H; 6-H), 2.52 (dd, ²J(H,H) = 16.2 Hz, ³J(H,H) = 11.3 Hz, 1H; 6-H'), 1.87 (dd, ²J(H,H) = 4.2 Hz, ³J(H,H) = 7.2 Hz, 1H; 9-H), 1.22 (dd, ²J(H,H) = 4.2 Hz, ³J(H,H) = 13.3 Hz, 1H; 9-H'); ¹³C NMR (150.7 MHz, [D₈]toluene, 233 K): $\delta = 148.0$ (dm, ¹J(C,F) = 234 Hz, *o*-C₆F₅), 145.0 (C2), 138.9 (dm, ¹J(C,F) = 235 Hz, *p*-C₆F₅), 137.2 (dm, ¹J(C,F) = 254 Hz, *m*-C₆F₅), 134.1 (C5), 121.0 (C8), 111.0 (C7), 110.1 (C3), 109.8 (Cp), 107.0 (Cp'), 92.0 (C4), 47.2 (C9), 27.8 (br, C6), *ipso*-C of C₆F₅ not observed; ¹¹B NMR (64.21 MHz, [D₆]benzene, 300 K): $\delta = -7.3$ ($\nu_{1/2} = 185 \text{ Hz}$); ¹⁵N NMR (50.74 MHz, [D₆]benzene, 298 K): $\delta = -165.6$; ¹⁹F NMR (282.41 MHz, [D₈]toluene, 193 K): $\delta = -128.6$ (1F, *o*-F), -131.3 (1F, *o*-F), -133.9 (1F, *o*-F), -134.1 (1F, *o*-F), -157.7 (1F, *p*-F), -158.4 (1F, *p*-F), -161.9 (1F, *m*-F), -162.6 (1F, *m*-F), -162.9 (1F, *m*-F), -163.2 (1F, *m*-F); C₃₀H₂₀NBF₁₀Zr (686.5): calcd C 52.49, H 2.94, N 2.04; found C 51.84, H 3.27, N 2.16.

X-ray crystal structure analysis of 15: Formula C₃₀H₂₀NBF₁₀Zr, $M = 686.5$, $0.2 \times 0.2 \times 0.05 \text{ mm}$, $a = 13.757(1)$, $b = 11.905(1)$, $c = 16.126(1) \text{ \AA}$, $\beta = 93.27(1)^\circ$, $V = 2636.8(3) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.729 \text{ g cm}^{-3}$, $\mu = 5.11 \text{ cm}^{-1}$, absorption correction with SORTAV ($0.905 \leq T \leq 0.975$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073 \text{ \AA}$, $T = 198 \text{ K}$, ω and ψ scans, 19770 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.71 \text{ \AA}^{-1}$, 7975 independent and 5063 observed reflections [$I \geq 2\sigma(I)$], 388 parameters, $R = 0.055$, $wR^2 = 0.102$, max./min. residual electron density $0.54/-0.48 \text{ e \AA}^{-3}$, hydrogens calculated and riding.

All data sets were collected with Enraf Nonius CAD4 or KappaCCD diffractometers, equipped with sealed-tube or rotating-anode generators. Programs used: data collection EXPRESS or COLLECT, data reduction

MoLEN or Denzo-SMN, absorption correction for CCD data SORTAV, structure solution SHELXS-86 and SHELXS-97, structure refinement SHELXL-97, and graphics SCHAKAL-92.^[50] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-120975 (**2**), CCDC-120976 (**6**), CCDC-120977 (**12**), and CCDC-120978 (**15**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

Reaction of the bis(η^5 -methylcyclopentadienyl)dimethylzirconium with compound 2:^[25] Bis(η^5 -methylcyclopentadienyl)dimethylzirconium (32.4 mg, 115.9 μmol) and compound **2** (47.7 mg, 116.1 μmol) were dissolved in toluene (2 mL) at room temperature and stirred for 5 min. The solvent was removed in vacuo, pentane (5 mL) was added to the remaining precipitate, and the mixture was stirred for 10 min. The yellow suspension was filtered and the solid washed with pentane ($2 \times 5 \text{ mL}$) to give the product as a yellow powder. ¹H NMR (599.9 MHz, C₇D₈, 298 K): $\delta = 7.14$ (m, 2H; pyrrolyl H(2,5)), 5.23/4.64 (m, each 2H; Cp(2,5)), 5.20 (m, 2H; pyrrolyl H(3,4)), 4.99/4.89 (m, each 2H; Cp(3,4)), 1.46 (s, 6H; Me), 1.01 (brm, 3H; BMe), -0.15 (s, 3H; ZrMe).

Reaction of the bis(η^5 -methylcyclopentadienyl)dimethylzirconium with compound 1:^[25] Bis(η^5 -methylcyclopentadienyl)dimethylzirconium (20.0 mg, 71.5 μmol) and compound **1** (36.7 mg, 71.7 μmol) were dissolved in toluene (2 mL) at room temperature and stirred for 5 min. The solvent was removed in vacuo, pentane (5 mL) was added to the remaining precipitate, and the mixture was stirred for 10 min. The suspension was filtered, and the solid washed with pentane ($2 \times 5 \text{ mL}$) to give the product as a yellowish powder. ¹H NMR (599.9 MHz, C₇D₈, 298 K): $\delta = 5.47/5.04$ (m, each 2H; Cp(2,5)), 5.33/5.22 (m, each 2H; Cp(3,4)), 1.44 (s, 6H; Me), 0.20 (s, 3H; ZrMe), 0.06 (brm, 3H; BMe).

Reaction of dimethylzirconocene (16) with (C₄H₆N)B(C₆F₅)₂ (2)—preparation of 17: A mixture of compounds **16** (0.13 g, 0.53 mmol) and **2** (0.24 g, 0.53 mmol) was dissolved in toluene (10 mL) at room temperature and the mixture was stirred for 5 min. The solvent was removed in vacuo, pentane (20 mL) was added to the residue, and the mixture was stirred for 10 min. The solid product was collected by filtration, washed with pentane ($2 \times 5 \text{ mL}$), and dried in vacuo. Yield: 0.22 g (62 %); m.p. 195°C (decomp); ¹H NMR (599.9 MHz, [D₈]toluene, 298 K): $\delta = 7.15$ (m, 2H; 2-/5-H), 5.14 (m, 2H; 3-/4-H), 5.14 (s, 10H; Cp), 0.99 (brm, 3H; [B]CH₃), -0.10 (s, 3H; [Zr]CH₃); ¹³C NMR (125.9 MHz, [D₈]toluene, 298 K): $\delta = 148.6$ (dm, ¹J(C,F) = 248 Hz, *o*-C₆F₅), 139.3 (dm, ¹J(C,F) = 250 Hz, *p*-C₆F₅), 139.2 (C2/5), 137.7 (dm, ¹J(C,F) = 246 Hz, *m*-C₆F₅), 112.5 (Cp), 99.4 (C3/4), 37.3 ([Zr]CH₃), 10.5 (br, [B]CH₃), *ipso*-C₆F₅ not observed; ¹¹B NMR (64.21 MHz, [D₆]benzene, 300 K): $\delta = -6.7$ ($\nu_{1/2} = 192 \text{ Hz}$); ¹⁵N NMR (50.74 MHz, [D₈]toluene, 298 K): $\delta = -158.5$; ¹⁹F NMR (282.41 MHz, [D₆]benzene, 300 K): $\delta = -132.5$ (m, 4F, *o*-F), -159.6 (t, 2F, *p*-F), -163.9 (m, 4F, *m*-F); C₂₈H₂₀NBF₁₀Zr (661.0): calcd C 50.76, H 3.04, N 2.11; found C 49.68, H 3.14, N 1.96.

Ethene polymerization: A Büchi glass autoclave (1 L) was charged with toluene (300 mL) and triisobutylaluminum (3 mL). The mixture was thermostated at 60°C and then saturated with ethene at 2 bar for 1 h. The catalyst **17** (78 μmol) was freshly prepared in toluene (3 mL), and this solution was then injected by syringe into the reaction chamber. The reaction was allowed to proceed for 1 h, and then it was quenched by the addition of aqueous HCl/methanol (1:1 per volume, 15 mL). The resulting polyethylene was collected by filtration, washed with HCl, methanol, and acetone, and then dried in vacuo to give 2.9 g of polyethylene, which corresponds to a catalyst activity of $a = 18.6 \text{ kg PE mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$. In a second experiment, under otherwise analogous conditions, 1.0 g of polyethylene was formed at 61 μmol of **17** over a period of 30 min ($a = 16.4$).

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