Observing a Homogeneous Ziegler Catalyst Precursor at Work: Insertion Reactions into the Zirconium–Carbon Bond of the (Butadiene)$ZrCp_2/B(C_6F_5)_3$ Addition Product

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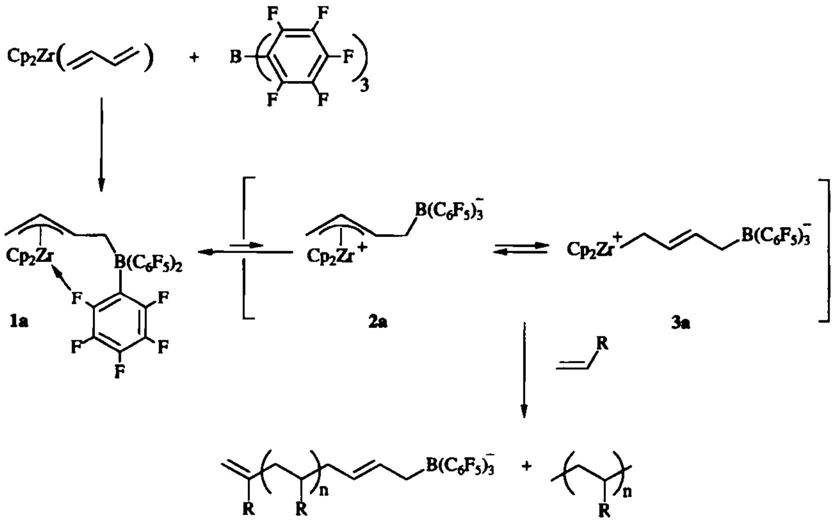
Abstract: (Butadiene)zirconocene adds to $B(C_6F_5)_3$ to form the metallacyclic metallocene–boron betaine system **1**, which contains a C–F → Zr interaction. Addition of *tert*-butylisocyanide or *tert*-butylcyanide leads to cleavage of the zirconium–fluorine linkage and formation of the adducts **4** and **7**, respectively. With additional *tert*-butylisocyanide, **4** reacts further to yield the corresponding η^2-iminoacyl betaines **5** and **6** (2 stereoisomers), whereas **7** inserts additional *tert*-butylcyanide into the Zr–C bond to give a chiral metallacyclic N-zirconaketimine complex that is probably stabilized by an internal borate → Zr interaction. Ethene and propene insertion reactions into the Zr–C bond of **1** follow a similar course: the mono-insertion products **9** and **10**, respectively, generated in situ and characterized by NMR spectroscopy at −35 °C in $[D_8]$toluene solution, are chiral and are also stabilized by internal borate → Zr coordination. Complexes **9** and **10** are likely to be intermediates in the formation of active homogeneous Ziegler polymerization catalysts.

Keywords
homogeneous catalysis · metallocenes · polymerization · Ziegler catalysts · zirconium complexes

Introduction

Homogeneous Ziegler catalyst systems based on the Group 4 metallocenes have become enormously important in recent years,[1] and the generation of single-component catalysts, or their direct precursors, is therefore of great current interest.[2] We have recently described a new system in this context that may potentially exhibit a number of advantages. It is based on the general observation that X–[M] reagents containing sufficiently electrophilic metal centers [M] add to butadiene/Group 4 metallocene complexes to give the heterodimetallic 1:1 adducts of a general composition represented by the example $Cp_2Zr(\mu\text{-}C_4H_6)(\mu\text{-}X)[M]$.[3] Thus, the strong Lewis acid tris(pentafluorophenyl)borane adds to (butadiene)zirconocene to yield the μ-hydrocarbyl–Zr/B system **1a** containing a C–F···Zr bridge (Scheme 1).[4] Complex **1a** is a very active α-olefin polymerization catalyst. From its dynamic behavior we have assumed that there is a rapid equilibration of the isolated cyclic system with the open-chain dipolar forms **2** and **3**. These isomers are likely to constitute active systems for α-olefin insertion. Repeated insertion leads to the formation of the observed $RB(C_6F_5)_3^-$ anions with alkene oligomer substituents, which eventually enter into an α-olefin polymerization cycle.[5]



Scheme 1.

We have now found suitable conditions for the experimental observation of a variety of primary products of the insertion of isonitriles, nitriles, and even simple α-olefins (ethylene and propene) into the zirconium- and hafnium-based systems of equilibrating isomers $1 \rightleftharpoons 2 \rightleftharpoons 3$. In several cases, intramolecular $(C_6F_5)_3B{-}R$ borate group participation is found to play a vital role in the product formation. Typical examples are described in this article.

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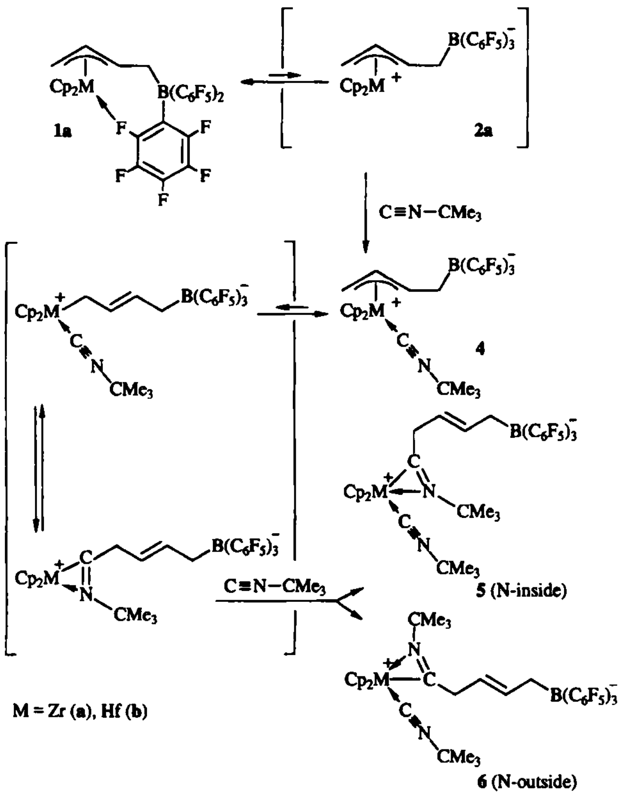
Results and Discussion

The heterodimetallic complex **1a** (and its hafnocene analogue **1b**) was readily prepared by treatment of the (butadiene)metallocene with $B(C_6F_5)_3$ at room temperature in a 1:1 ratio. Complex **1a** was isolated in high yield and characterized by X-ray crystal structure analysis.[4] It has a fluorine-bridged metallacyclic structure analogous to that observed in solution by variable temperature NMR spectroscopy. Generally, the solubility of **1a** in noncoordinating solvents is rather low, but, when it is generated in situ from its components in toluene, oversaturated solutions tend to be formed (even at low temperature). Therefore, for studying the chemical properties of **1**, solutions were first generated by the addition reaction of the (butadiene)metallocene and tris(pentafluorophenyl)borane. An aliquot of the solution was used to check that the reaction was complete and that a clean product had been obtained in solution. The remainder of the **1a** or **1b** solution was then employed in subsequent reactions. This procedure allowed a variety of interesting reactions to be observed, starting from these rather sensitive mixed-metal organometallic systems, and, in some cases, the respective primary and secondary products could even be isolated.

Isonitrile Insertion: From the dynamic behavior and the catalytic properties one must assume that a rapid reversible dissociative cleavage of the fluorine bridge is taking place in **1**. Therefore, we expected that the open form **2** would be trapped and stabilized by the addition of a suitable donor ligand. This was indeed observed. Treatment of a toluene solution of the zirconium–boron betaine **1a** with excess *tert*-butylisonitrile at room temperature for 1 h resulted in the formation of a precipitate (86% isolated yield), which was identified as the isonitrile addition product **4a** (Scheme 2).



Scheme 2.

Complex **4a** shows $^1H/^{13}C$ NMR signals for diastereotopic Cp ligands at zirconium (in $[D_8]THF$: $\delta = 5.84$, 5.70/106.5, 105.4) and a monosubstituted π-allyl unit (see Experimental Section). The $-N{\equiv}C$ carbon resonance of the coordinated isonitrile unit is observed at $\delta = 156.1$. The $\tilde{\nu}_{-N\equiv C}$ IR band is at 2193 cm^{-1}. By analogy with the structurally related $Cp_2Hf[C_4H_6 \cdot B(C_6F_5)_3] \cdot CO$ adduct,[4] we assign the structure **4a** to the addition product $Cp_2Zr[C_4H_6 \cdot B(C_6F_5)_3] \cdot CNCMe_3$.[6, 7a]

It is likely that complex **4a** undergoes a (potentially reversible) π-allyl$\rightleftharpoons$σ-allyl rearrangement that is sufficiently fast on the "chemical timescale" at ambient temperature to allow a slow isonitrile insertion reaction into the Zr–C σ-bond to take place.[7] This reaction was indeed observed when the zirconium–boron betaine system **1a** was stirred for four days at ambient temperature in neat *tert*-butylisonitrile. Workup and washing with pentane gave an analytically pure reaction product, isolated in 90% yield, which contained two *tert*-butylisonitrile-derived units. Apparently, one *tert*-butylisonitrile moiety was inserted into a terminal Zr–C bond to give a η^2-iminoacyl functional group (^{13}C NMR of the iminoacyl carbon atom at $\delta = 234.3$ in $[D_8]THF$; IR $\tilde{\nu}_{-C=N}$ band (in KBr) at 1641 cm^{-1}). The reactive (η^2-iminoacyl)zirconocene(μ-C_4H_6)$B(C_6F_5)_3$ betaine structure was then stabilized by coordination of a second *tert*-butylisonitrile ligand to zirconium (^{13}C NMR: $\delta_{-N\equiv C} = 154.3$; IR: $\tilde{\nu}_{-N\equiv C} = 2202\ cm^{-1}$).

The isonitrile donor ligand occupies the third available coordination site in the bent metallocene σ-ligand plane.[8] Consequently, two stereoisomers are possible, one with the RNC donor oriented *cis* to the η^2-iminoacyl nitrogen and one with the donor *cis* to the η^2-iminoacyl carbon.[9] Both isomers are found here, in a ratio of approximately 9:1. On the basis of the selected spectroscopic data cited above, we tentatively assign the major isomer to the structure with the iminoacyl nitrogen atom in the central position (**5a**, "N-inside").

Analogously, the reaction of the hafnium–boron betaine with *tert*-butylisonitrile (neat) gave a mixture of the isonitrile-stabilized (η^2-iminoacyl)zirconium–boron betaine isomers **5b** and **6b** in a ratio of approximately 9:1.

Nitrile Insertion: We conclude that isonitrile insertion into **1** follows the expected course. Starting from **1a** and *tert*-butylisonitrile a mixture of two achiral (η^2-iminoacyl)zirconocene stereoisomers are obtained, each of which shows only a single Cp singlet in the ^1H and ^{13}C NMR spectra. Nitrile addition to zirconium cations is often related to the analogous reaction with isonitriles: simple addition of the $RC{\equiv}N$ reagent serving as a donor ligand is often followed by CC coupling with formation of an N-metalated imine system (see below).[10] The reaction of **1a** with *tert*-butylcyanide basically follows this expected pattern, but a product exhibiting interesting structural features is also formed.

The zirconium–boron betaine **1a** was treated with an approximately fivefold excess of *tert*-butylcyanide in toluene solution at room temperature for 1 h. During this time a precipitate of the 1:1 addition product was formed (Scheme 3). The nitrile-stabilized betaine complex **7** shows the typical NMR pattern of a substituted π-allyl group bound to zirconium[11] [in $[D_8]THF$, ^1H NMR: $\delta = 4.70$, 4.41, 2.19, 1.85 (4×1H); ^{13}C NMR: $\delta = 130.7$, 115.3, 43.7]. The $-CH_2-[B]$ $^1H/^{13}C$ NMR resonances appear at $\delta = 2.67/35.0$, and the NMR signals of the diastereotopic Cp ligands are at $\delta = 5.96$, 5.86 (^1H) and 108.9, 108.3 (^{13}C). The ^{13}C NMR resonance of the coordinated $Me_3CC{\equiv}N$ ligand appears at $\delta = 145.4$. The IR $\tilde{\nu}_{-C\equiv N}$ feature is found at 2267 cm^{-1} (in KBr), which is some 35 wavenumbers

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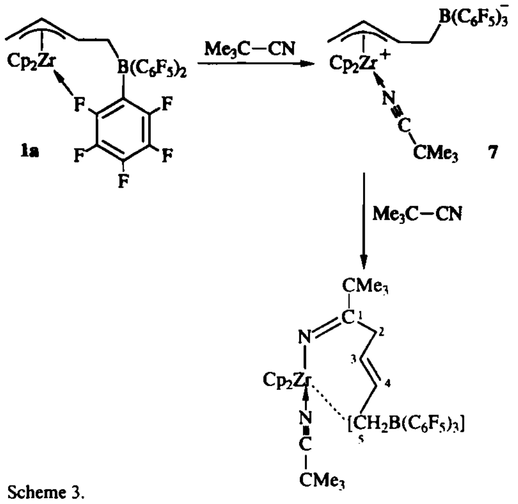


Scheme 3.

above the $\tilde{\nu}_{-C\equiv N}$ vibration (2230 cm^{-1}, neat) of the free *tert*-butylcyanide. Within the limits of detection (NMR), only one stereoisomer is obtained. We assume that it has the structure 7.

The betaine complex **1a** was suspended in neat *tert*-butylcyanide and stirred for one week at ambient temperature. The resulting solid was free of the starting material and contained the pure reaction product **8**. The product contains a metalated ketimine moiety[10] formed by insertion of a RC≡N unit into the Zr–C bond of the starting material. The presence of the Zr–N=*C*(R)– moiety is evident from the IR (KBr, $\tilde{\nu}_{-C=N-}$ = 1644 cm^{-1}) and ^{13}C NMR spectra [in [D$_8$]THF, δ = 145.4 (–C=N–), *tert*-butyl signals at δ = 27.2 (C) and 27.3 (CH$_3$)]. Complex **8** contains an additional Me$_3$C–C≡N ligand that is loosely coordinated to the electrophilic zirconium center. This is evident from the observation of a 1:1 pair of ^{1}H NMR *tert*-butyl resonances [δ = 1.58, 1.33; –(C*H*$_3$)$_3$CC(R)=N– and (C*H*$_3$)$_3$CC≡N] and a typical $\tilde{\nu}_{-C\equiv N}$ IR band at 2269 cm^{-1} (in KBr).

The insertion takes place by means of completely regioselective carbon–carbon coupling at the free CH$_2$ terminus of the butadiene ligand. The overall reaction can be described as a completely 1,4-selective sequential coupling of the strong Lewis acid B(C$_6$F$_5$)$_3$ and *tert*-butylcyanide to the conjugated diene attached to the zirconocene template. This is the expected pattern for the reaction of a "zirconated" butadiene dianion equivalent (i.e., (butadiene)zirconocene) with two equivalents of electrophilic reagents.[12]

This regiochemical outcome of the reaction of **1a** with *tert*-butylcyanide is therefore as expected, but, quite surprisingly, complex **8** is found to be chiral. This follows from the ^{1}H/^{13}C NMR resonances corresponding to diastereotopic cyclopentadienyl ligands at zirconium (δ = 5.96, 5.86/109.2, 108.7). Also, the methylene groups of the butadiene-derived part of the [Zr]–N=C(R)–C*H*$_2$–CH=CH–C*H*$_2$–[B] structural unit each contain diastereotopic hydrogens. Thus, six separate signals are observed for the six C$_4$H$_6$ hydrogen atoms in complex **8** (2-H to 5-H: δ = 2.19, 1.84, 4.41, 4.73, 1.54, 2.66).

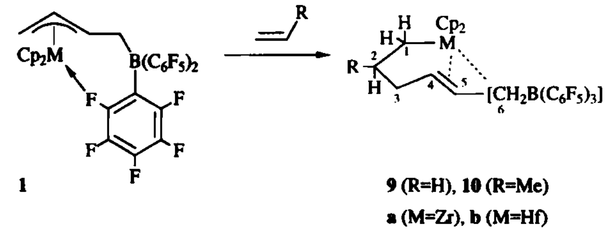
Clearly, an open-chain betaine structure [Zr]–N=C(R)–CH$_2$–CH=CH–CH$_2$–[B] cannot contain an element of chirality. Therefore, a ring structure in the *tert*-butylcyanide insertion product **8** containing a *trans*-C=C double bond must be assumed. It is likely that the –CH=CHCH$_2$B(C$_6$F$_5$)$_3$ group is internally coordinated to the very electrophilic zirconium center.[13–15]

There is increasing evidence that RB(C$_6$F$_5$)$_3$ coordination is very effective at stabilizing electron-deficient, bent Group 4 metallocene cations.[4, 13] Such coordination to cationic zirconium centers sometimes seems to be extremely favorable, and it is almost certainly present even in cases of four-coordinate pseudotetrahedral zirconocene cations. Here, internal RB(C$_6$F$_5$)$_3$ coordination to zirconium in the σ-ligand plane is very likely, since this completes the coordination sphere and leads to very stable five-coordinate zirconocene cation moieties,[14] just as found here in the case of the betaine complex **8**. This tendency towards internal borate coordination must be assumed to be an essential feature in Group 4 metallocene betaine systems. Furthermore, this concept is probably of great importance for understanding the chemistry taking place in the initial phase of α-olefin polymerization reactions catalyzed by homogeneous metallocene Ziegler systems based on zirconium–boron betaines. This can indeed be demonstrated by treating the Cp$_2$Zr(butadiene)·B(C$_6$F$_5$)$_3$ addition product **1a** with ethene or propene under carefully controlled conditions.

α-Olefin Insertion Reactions: The zirconium–boron betaine complex **1a** was generated in a [D$_8$]toluene solution by treating (butadiene)zirconocene with B(C$_6$F$_5$)$_3$ in equimolar amounts at ambient temperature. The solution was then cooled to −35 °C and some ethene slowly introduced to the solution by means of a capillary. An instantaneous reaction ensued that led to a single organometallic 1:1 reaction product. A slight excess of ethene was consumed only very slowly under these specifically chosen conditions.

The ethene molecule was inserted into the Zr–C bond of **1a** to give a product containing a linear C$_6$ hydrocarbon chain connecting zirconium and boron (Scheme 4). The presence of a single regioisomeric coupling product with an unbranched [Zr]–CH$_2$–CH$_2$–CH$_2$–CH=CH–CH$_2$–[B] substructure is evident from the typical ^{13}C NMR resonances of this fragment (C1–C5: δ = 49.2, 42.6, 34.7, 146.4, 123.6 in [D$_8$]toluene, carbon atom C6, adjacent to boron, not observed), and is supported by the ^{1}H NMR spectrum. In addition, the ^{1}H NMR spectrum clearly shows that the ethylene insertion product **9a** is chiral. It exhibits a pair of singlets in the ^{1}H NMR spectrum at δ = 5.12 and 5.08 (^{13}C NMR Cp resonances at δ = 110.8 and 110.0) corrresponding to diastereotopic cyclopentadienyl groups. Most characteristically, all four methylene groups exhibit diastereotopic hydrogens. Separate ^{1}H NMR signals for the ten hydrogen atoms of the bridging (CH$_2$)$_3$CH=CH–CH$_2$– chain are observed (1-H to 6-H in [D$_8$]toluene: δ = −0.42, 0.96, 1.60, 1.91, 0.96, 1.37, 5.90, 5.63, 0.19, 0.36).

The very characteristic appearance of the NMR spectra led us to assume that complex **9a** also contains a cyclic structure with the medium-sized ring system containing a *trans*-C=C double



Scheme 4.

bond,[15] closed by formation of the favorable intramolecular borate → Zr interaction.[13] The corresponding (butadiene)-hafnocene/B(C$_6$F$_5$)$_3$ addition product **1b** also selectively inserts one equivalent of ethene at low temperature to form the analogously structured betaine metallacycle **9b**. The ^{1}H NMR spectrum of **9b** is depicted in Figure 1. The mono-insertion products **9a,b** are rather sensitive compounds, which rapidly decompose to mixtures of as yet unidentified materials upon raising the temperature. In the presence of excess ethene polymerization reactions ensue.

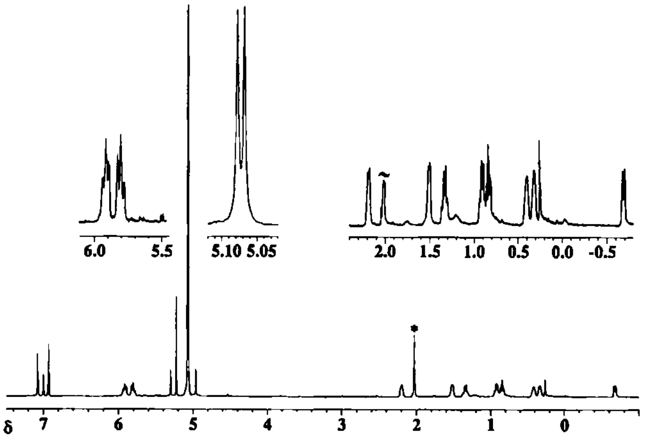


Fig. 1. ^{1}H NMR spectrum of **9b** ([D$_8$]toluene; 600 MHz, −35°C).

In a similar way, one molar equivalent of propene is inserted into the terminal zirconium-to-C$_4$H$_6$B(C$_6$F$_3$)$_3$ linkage of **1a** at low temperature. The a priori analysis reveals that four diastereomeric products could in principle be formed in this reaction: two regiochemical insertion modes are possible, positioning the propene-derived methyl substituent α or β to zirconium. In each case, a chirality center is introduced in the product in addition to the topochemical chirality element based on the organometallic ring structure that is already present. In this case, the α-olefin insertion reaction is very selective. Only one of the four possible isomers is formed under the applied conditions of kinetic control. According to the characteristic NMR spectra (see Experimental Section) the methyl substituent originating from the propene reagent ends up at the β-position. We assume that in the favored stereoisomer formed the CH$_3$ substituent is in a pseudoequatorial position in the rather rigid organometallic ring system of the metallocene–borate betaine complex **10** (see Scheme 4).

Again, the hafnium system **1b** reacts analogously with propene, giving the single organometallic mono-insertion product **10b**. Increasing the temperature of the reaction mixtures above 0 °C in both cases **10a** and **10b** results in a rapid unspecific decomposition. In the presence of excess propene polypropylene is formed.

Conclusions

A major structural feature of the zirconium–boron betaine complex **1a** is the presence of an (sp^2)C–F → Zr interaction.[4, 13] In the resulting metallacyclic system this pronounced fluorine-to-metal coordination effectively serves to kinetically protect and thermodynamically stabilize the very electrophilic metallocene center. Catalytic activity of **1a** requires opening of the zirconium–fluorine linkage; for the catalyst precursor to persist in the absence of monomers, the Zr–F bond cleavage must be reversible. These requirements are ideally fulfilled in the case of these metallocene betaine catalyst precursors. We have found, and recently qualitatively described, two dynamic processes of **1a** related to reversible zirconium–fluorine bond cleavage.[4] Equilibration of the six *ortho* C$_6$F$_5$ fluorine atoms takes place very rapidly on the ^{19}F NMR timescale. This process could be "frozen" at very low temperature in the case of **1a**, as shown by the inequivalency of all 15 fluorines present in this specific molecule.

In the case of the betaine complex **1** the second barrier, involving formal π-allyl inversion and thus resulting in an enantiomerization of the starting material, is higher. Consequently, trapping of the intermediate **2** by the *tert*-butylcyanide and *tert*-butylisocyanide donor reagents, which just requires C–F → Zr bond fission, takes place instantaneously, whereas the subsequent insertion reactions, which require π-allyl$\rightleftharpoons$σ-allyl interconversion, are markedly slower. The final products show a tendency to acquire maximum coordinative saturation in the metallocene σ-ligand plane. In the case of isonitrile insertion, this is readily achieved by formation of an η^2-iminoacyl complex and additional alkylisonitrile coordination, whereas in the case of **8** an additional borate coordination appears to be the most favorable mode of stabilization.

Internal stabilizing borate coordination to zirconium seems to be an important and rather general feature observed in this area of chemistry. We have recently noticed that even Cp$_2$Zr(acac) cations favor borate C–F coordination in the σ-ligand plane.[13b] In the olefin insertion into the C–Zr bond of **1a**, some internal borate coordination appears to be the essential feature that allows the system to "rest" at the stage of the mono-insertion product. This has enabled us to experimentally study the primary process of olefin coupling in the initial phase of the homogeneous Ziegler–Natta process. This very special feature will probably make this general system one of the models best suited for studying in detail the essential features of carbon–carbon bond formation in these enormously important new catalyst systems. The outcome of the preliminary studies on the system described above makes us hopeful that we will learn much about the intrinsic properties of single initial carbon–carbon bond-forming steps in such catalyst systems. Furthermore, the effect of variations in the bent metallocene and the nature of the "chain end" on the regio- and stereochemical preferrences can be investigated. The scope of such catalyst systems and what combinations of olefinic and acetylenic substrates can be employed, given the fact that there are no complications brought about by specific modes of catalyst activation, is also of interest. Studies along these lines are presently being actively pursued in our laboratory.

Experimental Section

General information: All reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. (Butadiene)zirconocene and -hafnocene were prepared as described in the literature [16]. Tris(pentafluorophenyl)borane was prepared by treatment of BCl$_3$ with three molar equivalents of pentafluorophenyllithium [17]. It was recrystallized from pentane prior to use. In general, the (butadiene)metallocene/B(C$_6$F$_5$)$_3$ adducts used in this study were generated in situ in a suitable solvent. Only in a few cases did we use the isolated compounds **1a** and **1b** that were synthesized as recently described [4]. The following instruments were used for physical characterization: Varian Unity plus600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 150 MHz, ^{19}F NMR: 564 MHz) and Bruker AM360 NMR spectrometer (^{1}H NMR: 360 MHz, ^{13}C NMR: 90 MHz); Nicolet5 DXC FT-IR spectrometer. DuPont2910 DSC, STA Instruments.

Preparation of 4: Complex **1a** was generated by treatment of (butadiene)zirconocene (100 mg, 0.36 mmol) with $B(C_6F_5)_3$ (190 mg, 0.36 mmol) in toluene (20 mL) at ambient temperature. To this solution was added *tert*-butylisocyanide (0.2 mL, 1.8 mmol). The mixture was stirred for 1 h at room temperature, and the resulting precipitate collected by filtration. The product was washed with pentane (10 mL) and dried in vacuo to yield **4** (300 mg, ca. 85%) containing ca. 1 equiv of toluene as judged by ^{1}H NMR, m.p. 93 °C (DSC). ^{1}H NMR ([D$_8$]THF): $\delta = 6.32$ (m, 1 H, =CH−), 5.84, 5.70 (each s, 10 H, Cp), 5.80 (m, 1 H, =CH−), 3.95 (br s, 2 H, CH_2), 3.13 (m, 1 H, CH_2), 2.44 (m, 1 H, CH_2), 1.73 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR ([D$_8$]THF): $\delta = 156.1$ (C≡N−), 149.0 ($^1J_{CF} = 234$ Hz, *o*-$B(C_6F_5)_3$), 138.2 ($^1J_{CF} = 244$ Hz, *p*-$B(C_6F_5)_3$), 137.3 ($^1J_{CF} = 246$ Hz, *m*-$B(C_6F_5)_3$), 128.0 (*ipso*-$B(C_6F_5)_3$), 119.1 ($^1J_{CH} = 149$ Hz, CH), 114.1 ($^1J_{CH} = 153$ Hz, CH), 106.5, 105.4 (Cp), 60.6 ($C(CH_3)_3$), 41.8 ($^1J_{CH} = 150$ Hz, CH_2), 35.0 (br s, B-CH_2), 30.8 ($C(CH_3)_3$). IR (KBr): $\tilde{\nu} = 3126$, 2990, 2909, 2193 (C≡N), 1641, 1514, 1458, 1375, 1271, 1194, 1082, 978, 818, 733, 681 cm^{-1}; $C_{37}H_{25}BF_{15}NZr \cdot C_7H_8$ (962.76): calcd C 54.89, H 3.45; found C 53.12, H 3.50.

Preparation of the mixture of 5a and 6a: (Butadiene)zirconocene (3.15 g, 11.4 mmol) was treated with $B(C_6F_5)_3$ (6.20 g, 12.1 mmol) in toluene (100 mL). The mixture was stirred for 1 d at room temperature. The resulting precipitate was collected by filtration, washed with pentane and dried to give 7.60 g (84%). 194 mg (0.25 mmol) of the thus prepared zirconium–boron betaine **1a** was dissolved in *tert*-butylisocyanide (2 mL, 18 mmol). The mixture was stirred for 4 d at room temperature. Volatiles were then removed in vacuo and the precipitate washed with pentane (2 × 10 mL) and dried in vacuo to give 215 mg (90%) of a ca. 90:10 mixture of the stereoisomers **5a** and **6a**, m.p. 167 °C (DSC, decomp.); IR (KBr): $\tilde{\nu} = 2202$ (−N≡C), 1641 (C=N) cm^{-1}.

5a: ^{1}H NMR (600 MHz, 303 K, [D$_6$]benzene/[D$_8$]THF 2:1): $\delta = 5.98$ (m, 1 H, 4-H), 5.42 (s, 10 H, Cp), 5.28 (m, 1 H, 3-H), 3.31 (d, $^3J_{HH} = 7.0$ Hz, 2 H, 2-H), 2.73 (br d, $^3J_{HH} = 7.1$ Hz, 2 H, 5-H), 1.16, 0.87 (s, each 9 H, *tert*-butyl). ^{13}C NMR (90 MHz, 293 K, [D$_8$]THF): $\delta = 234.3$ (C-1), 154.3 (RN*C*), 153.9 ($^1J_{CF} = 242.1$ Hz, *o*-$B(C_6F_5)_3$), 146.9 (C-4), 143.0 ($^1J_{CF} = 243.3$ Hz, *p*-$B(C_6F_5)_3$), 141.8 ($^1J_{CF} = 245$ Hz, *m*-$B(C_6F_5)_3$), 119.4 (C-3), 111.5 (Cp), 65.3, 65.8 (*C*Me$_3$), 45.5 (C-2), 33.6, 33.9 (*C*H$_3$), C5 and *ipso*-C of $B(C_6F_5)_3$ not observed. ^{19}F NMR (564 MHz, 303 K, [D$_6$]benzene/[D$_8$]THF 2:1): $\delta = -174.4$ ($^3J_{FF} = 19$ Hz, 6 F, *m*-F), −171.6 ($^3J_{FF} = 21$ Hz, 3 F, *p*-F), −138.4 ($^3J_{FF} = 23$ Hz, 6 F, *o*-F).

6a: ^{1}H NMR (600 MHz, 303 K, [D$_6$]benzene/[D$_8$]THF 2:1): $\delta = 5.61$ (m, 1 H, 4-H), 5.46 (s, 10 H, Cp), 5.06 (m, 1 H, 3-H), 3.26 (d, $^3J_{HH} = 5.8$ Hz, 2 H, 2-H), 2.56 (br d, $^3J_{HH} = 7.1$ Hz, 2 H, 5-H), 1.18, 0.96 (s, each 9 H, *tert*-butyl); $C_{42}H_{34}N_2BF_{15}Zr$ (953.75): calcd C 52.98, H 3.59, N 2.94; found C 52.08, H 3.78, N 2.87.

Preparation of the 5b/6b mixture: **1b** (475 mg, 0.54 mmol) was suspended in *tert*-butylisocyanide (1 mL, 9 mmol). The mixture was stirred for 1 week. Volatiles were removed in vacuo. The residue was washed with pentane (2 × 10 mL) and dried in vacuo to yield 500 mg (88%) of the **5b/6b** mixture (ca. 90:10 ratio), m.p. 170 °C (DSC, decomp.); IR (KBr): $\tilde{\nu} = 2201$ (−N≡C), 1644 (C=N) cm^{-1}.

5b: ^{1}H NMR (600 MHz, 303 K, [D$_6$]benzene/[D$_8$]THF 2:1): $\delta = 5.89$ (m, 1 H, 4-H), 5.26 (s, 10 H, Cp), 5.25 (m, 1 H, 3-H), 3.29 (d, $^3J_{HH} = 6.9$ Hz, 2 H, 2-H), 2.66 (br d, $^3J_{HH} = 7.6$ Hz, 2 H, 5-H), 1.06, 0.76 (s, each 9 H, *tert*-butyl). ^{1}H NMR (600 MHz, 303 K, [D$_2$]dichloromethane): $\delta = 5.66$ (m, 1 H, 4-H), 5.64 (s, 10 H, Cp), 5.31 (m, 1 H, 3-H), 3.58 (d, $^3J_{HH} = 6.4$ Hz, 2 H, 2-H), 2.31 (br s, 2 H, 5-H), 1.68, 1.21 (s, each 9 H, *tert*-butyl). ^{13}C NMR (150.8 MHz, 303 K, [D$_2$]dichloromethane): $\delta = 237.0$ (C-1), 148.7 ($^1J_{CF} = 267$ Hz, *o*-$B(C_6F_5)_3$), 141.9 (C-4), 138.1 ($^1J_{CF} = 243$ Hz, *p*-$B(C_6F_5)_3$), 136.9 ($^1J_{CF} = 245$ Hz, *m*-$B(C_6F_5)_3$), 127.3 (br, *ipso*-C, $B(C_6F_5)_3$), 118.5 (C-3), 105.1 (Cp), 61.5, 60.6 (each C, C-6, C-9), 41.1 (CH_2, C-2), 29.7, 29.1 (CH_3, C-7, C-10), C5 and −N≡*C* not observed. ^{19}F NMR (282 MHz, 303 K, [D$_2$]dichloromethane): $\delta = -169.9$ ($^3J_{FF} = 19$ Hz, 6 F, *m*-F), −162.9 ($^3J_{FF} = 21$ Hz, 3 F, *p*-F), −130.5 ($^3J_{FF} = 23$ Hz, 6 F, *o*-F).

6b: ^{1}H NMR (600 MHz, 303 K, [D$_6$]benzene/[D$_8$]THF 2:1): $\delta = 5.29$ (m, 1 H, 4-H), 5.29 (s, 10 H, Cp), 3.22 (d, $^3J_{HH} = 6.4$ Hz, 2 H, 2-H), 2.48 (br d, $^3J_{HH} = 5.8$ Hz, 2 H, 5-H), 0.99, 0.81 (s, each 9 H, *tert*-butyl), 3-H, 4-H not observed; $C_{42}H_{34}N_2BF_{15}Zr$ (953.75): calcd C 48.46, H 3.29; found C 47.89, H 3.79.

Preparation of 7: The zirconium–boron betaine **1a**, generated from (butadiene)zirconocene (100 mg, 0.36 mmol) and tris(pentafluorophenyl)borane (190 mg, 0.36 mmol) in toluene (20 mL), was treated with *tert*-butylcyanide (0.2 ml, 0.15 g, 1.8 mmol). After 1 h of stirring at ambient temperature, the resulting precipitate was collected by filtration, washed with pentane (10 mL), and dried in vacuo to yield **7** (250 mg, 80%), m.p. 141 °C (DSC, decomp.); IR (KBr): $\tilde{\nu} = 2267$ cm^{-1}. ^{1}H NMR ([D$_8$]THF): $\delta = 5.96$, 5.86 (s, each 5 H, Cp), 4.70 (m, 1 H, =CH−), 4.41 (m, 1 H, =CH−), 2.67 (br s, 2 H, CH_2), 2.19 (m, 1 H, CH_2), 1.85 (m, 1 H, CH_2), 1.58 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR ([D$_8$]THF): $\delta = 149.2$ ($^1J_{CF} = 234$ Hz, *o*-$B(C_6F_5)_3$), 145.4 (CN), 138.2 ($^1J_{CF} = 244$ Hz, *p*-$B(C_6F_5)_3$), 137.3 ($^1J_{CF} = 246$ Hz, *m*-$B(C_6F_5)_3$), 130.7 ($^1J_{CH} = 154$ Hz, CH), 126.0 (*ipso*-C, $B(C_6F_5)_3$), 115.3 ($^1J_{CH} = 150$ Hz, CH), 108.9, 108.3 (Cp), 43.7 ($^1J_{CH} = 150$ Hz, CH_2), 35.0 (br s, B-CH_2), 31.0 ($C(CH_3)_3$), 27.2 ($C(CH_3)_3$); $C_{37}H_{25}BF_{15}NZr$ (870.62): calcd C 51.04, H 2.89, N 1.61; found C 51.09, H 3.09, N 1.55.

Preparation of 8: A sample of **1a** (380 mg, 0.43 mmol) was suspended in *tert*-butylcyanide (2 mL, 18 mmol) and stirred for 1 week at ambient temperature. The liquid was then decanted from the resulting residue. The remaining solid was washed with pentane (2 × 10 mL) and dried in vacuo to give **8** (300 mg, 65%), m.p. 116 °C (DSC, decomp.); IR (KBr): $\tilde{\nu} = 2269$ (R−C≡N), 1644 (C=N) cm^{-1}. ^{1}H NMR (600 MHz, 303 K, [D$_2$]dichloromethane): $\delta = 5.87$, 5.74 (s, each 5 H, Cp), 4.73 (m, 1 H, 4-H), 4.32 (m, 1 H, 3-H), 2.60 (br, 1 H, 5′-H), 2.14 (dd, $^3J_{HH} = 5.5$, 7.8 Hz, 1 H, 2′-H), 1.77 (dd, $^3J_{HH} = 5.5$, 12.4 Hz, 1 H, 2-H), 1.55, 1.37 (s, each 9 H, *tert*-butyl), 5-H hidden unter *tert*-butyl signal. ^{1}H NMR (600 MHz, 303 K, [D$_8$]THF): $\delta = 5.96$, 5.86 (s, each 5 H, Cp), 4.73 (m, 1 H, 4-H), 4.41 (m, 1 H, 3-H), 2.66 (br d, $^3J_{HH} = 8.8$ Hz, 1 H, 5′-H), 2.19 (dd, $^3J_{HH} = 5.5$, 8.1 Hz, 1 H, 2′-H), 1.84 (dd, $^3J_{HH} = 5.5$, 12.4 Hz, 1 H, 2-H), 1.54 m, 1 H, 5-H), 1.58, 1.33 (s, each 9 H, *tert*-butyl). ^{13}C NMR (150.8 MHz, 303 K, [D$_8$]THF): $\delta = 149.2$ ($^1J_{CF} = 235.1$ Hz, *o*-$B(C_6F_5)_3$), 145.4 (C-1), 138.8 ($^1J_{CF} = 242.9$ Hz, *p*-$B(C_6F_5)_3$), 137.4 ($^1J_{CF} = 247.5$ Hz, *m*-$B(C_6F_5)_3$), 129.7 (C-4), 127.2 (br, *ipso*-C, $B(C_6F_5)_3$), 115.5 (C-3), 109.2, 108.7 (Cp), 43.9 (C-2), 28.5 (br, N≡C−*C*H$_3$), 27.3 (CH_3), 27.2 (C-6). ^{19}F NMR (564.3 MHz, 303 K, [D$_8$]THF): $\delta = -169.7$ ($^3J_{FF} = 21$ Hz, 6 F, *m*-F), −166.5 ($^3J_{FF} = 21$ Hz, 3 F, *p*-F), −134.0 ($^3J_{FF} = 24$ Hz, 6 F, *o*-F); $C_{42}H_{34}N_2BF_{15}Zr$ (953.75): calcd C 52.98, H 3.59, N 2.94; found C 52.24, H 3.51, N 2.85.

Generation of 9a: A solution of (butadiene)zirconocene (25 mg, 0.091 mmol) in [D$_8$]toluene (2 mL) was combined with a solution containing $B(C_6F_5)_3$ (52 mg, 0.102 mmol) in [D$_8$]toluene (2 mL) at ambient temperature. The resulting solution of **1a** was transferred to a 5 mm NMR tube and cooled to −35 °C. Ethene (2 to 3 mL, ca. 0.9–1.3 mmol) was then slowly introduced into the solution by means of a capillary. The NMR spectroscopic analysis of the resulting mixture at low temperature revealed the rather clean formation of **9a**. ^{1}H NMR (600 MHz, 238 K, [D$_8$]toluene): $\delta = 5.90$ (m, 1 H, 4-H), 5.63 (m, 1 H, 5-H), 5.12 (s, 5 H, Cp), 5.08 (s, 5 H, Cp) 1.91 (m, 1 H, 2′-H), 1.60 (m, 1 H, 2-H), 1.37 (m, 1 H, 3′-H), 0.96 (m, 2 H, 3-H, 1′-H), 0.36 (br, 1 H, 6′-H), 0.19 (br, 1 H, 6-H), −0.42 (m, 1 H, 1-H). ^{13}C NMR (150.8 MHz, 238 K, [D$_8$]toluene): $\delta = 148.4$ ($^1J_{CF} = 255$ Hz, *o*-$B(C_6F_5)_3$), 146.4 ($^1J_{CF} = 156$ Hz, C-4), 139.2 ($^1J_{CF} = 241$ Hz, *p*-$B(C_6F_5)_3$), 137.4 ($^1J_{CF} = 248$ Hz, *m*-$B(C_6F_5)_3$), 123.6 ($^1J_{CH} = 159$ Hz, C-5), 110.8 ($^1J_{CH} = 175$ Hz, Cp), 110.0 ($^1J_{CH} = 175$ Hz, Cp), 49.2 ($^1J_{CH} = 125$ Hz, C-1), 42.6 ($^1J_{CH} = 127$ Hz, C-2), 34.7 ($^1J_{CH} = 129$ Hz, C-3), C6 and *ipso*-C, $B(C_6F_5)_3$ not observed. ^{19}F NMR (564.3 MHz, 238 K, [D$_8$]toluene): $\delta = -165.8$ ($^3J_{FF} = 22$ Hz, 6 F, *m*-F), −160.7 ($^3J_{FF} = 21$ Hz, 3 F, *p*-F), −133.8 ($^3J_{FF} = 22$ Hz, 6 F, *o*-F).

Generation of 9b: Analogously as described above, (butadiene)hafnocene (20 mg, 0.055 mmol) was treated with $B(C_6F_5)_3$ (32 mg, 0.063 mmol) in toluene (2 mL). Then ethene (2–3 mL) was introduced at −35 °C and the resulting product **9b** characterized by NMR. ^{1}H NMR (600 MHz, 238 K, [D$_8$]toluene): $\delta = 5.92$ (m, 1 H, 4-H), 5.81 (m, 1 H, 5-H), 5.08 (s, 5 H, Cp), 5.07 (s, 5 H, Cp), 2.19 (dd, $^3J_{HH} = 4.8$, 9.4 Hz, 1 H, 2′-H), 1.51 (d, $^3J_{HH} = 9.4$ Hz, 1 H, 3′-H), 1.33 (m, 1 H, 2-H), 0.92 (m, 1 H, 3-H), 0.85 (m, 1 H, 1′-H), 0.41 (br, 1 H, 6′-H), 0.33 (br, 1 H, 6-H), −0.67 (d, $^3J_{HH} = 14.3$ Hz, 1 H, 1-H). ^{13}C NMR (150.8 MHz, 238 K, [D$_8$]toluene): $\delta = 148.3$ ($^1J_{CF} = 239$ Hz, *o*-$B(C_6F_5)_3$), 145.1 (C-4), 139.0 ($^1J_{CF} = 249$ Hz, *p*-$B(C_6F_5)_3$), 137.3 ($^1J_{CF} = 243$ Hz, *m*-$B(C_6F_5)_3$), 125.7 (C-5), 110.7 (Cp), 109.7 (Cp), 50.1 (C-1), 36.0 (C-2), 35.8 (C-3), C6 and *ipso*-C of $B(C_6F_5)_3$ not observed. ^{19}F NMR (564.3 MHz, 238 K, [D$_8$]toluene): $\delta = -165.5$ ($^3J_{FF} = 21$ Hz, 6 F, *m*-F), −160.5 ($^3J_{FF} = 21$ Hz, 3 F, *p*-F), −133.1 ($^3J_{FF} = 20$ Hz, 6 F, *o*-F).

Generation of 10a: **1a** was prepared in situ by allowing (butadiene)zirconocene (25 mg, 0.091 mmol) to react with $B(C_6F_5)_3$ (52 mg, 0.102 mmol) in [D$_8$]toluene (4 mL). At −35 °C propene (2–3 mL) was introduced and the resulting product **10a** characterized by NMR spectroscopy. ^{1}H NMR (600 MHz, 238 K, [D$_8$]toluene): $\delta = 5.72$ (m, 1 H, 4-H), 5.54 (m, 1 H, 5-H), 5.12 (s, 5 H, Cp), 5.11 (s, 5 H, Cp), 1.73 (m, 1 H, 2-H), 1.35 (m, 1 H, 3′-H), 0.98 (dd, $^3J_{HH} = 6.6$, 13.2 Hz, 1 H, 1′-H), 0.62 (d, $^3J_{HH} = 6.6$ Hz, 3 H, 7-H), 0.61 (m, 1 H, 3-H), 0.27 (br, 2 H, 6-H), −0.71 (d, $^3J_{HH} = 13.2$ Hz, 1 H, 1-H). ^{13}C NMR (150.8 MHz, 238 K, [D$_8$]toluene): $\delta = 148.3$ ($^1J_{CF} = 248$ Hz, *o*-$B(C_6F_5)_3$), 143.2 (C-4), 139.0 ($^1J_{CF} = 254$ Hz, *p*-$B(C_6F_5)_3$), 137.4 ($^1J_{CF} = 254$ Hz, *m*-$B(C_6F_5)_3$), 122.1 (C-5), 121.9 (br, *ipso*-C, $B(C_6F_5)_3$), 111.0 (Cp), 109.9 (Cp), 58.8 (C-1), 50.0 (C-2), 42.6 (C-3), 27.6 (CH_3), ≈4 (br, C-6). ^{19}F NMR (564.3 MHz, 238 K, [D$_8$]toluene): $\delta = -165.4$ ($^3J_{FF} = 22$ Hz, 6 F, *m*-F), −161.3 ($^3J_{FF} = 22$ Hz, 3 F, *p*-F), −133.3 ($^3J_{FF} = 21$ Hz, 6 F, *o*-F).

Generation of 10b: Analogously as described above, **1b** was prepared by treatment of (butadiene)hafnocene (20 mg, 0.055 mmol) with $B(C_6F_5)_3$ (32 mg, 0.063 mmol) in [D$_8$]toluene (2 mL). Propene (2–3 mL) was introduced at −35 °C and the resulting product **10b** directly analyzed by NMR spectroscopy. ^{1}H NMR (600 MHz, 238 K, [D$_8$]toluene): $\delta = 5.81$ (m, 1 H, 4-H), 5.72 (m, 1 H, 5-H), 5.08 (s, 5 H, Cp), 5.07 (s, 5 H, Cp), 1.48 (m, 2 H, 2-H, 3′-H), 0.73 (dd, $^3J_{HH} = 6.1$, 12.3 Hz, 1 H, 1′-H), 0.64 (d, $^3J_{HH} = 6.1$ Hz, 3 H, 7-H), 0.62 (m, 1 H, 3-H), 0.34 (br, 1 H, 6′-H), 0.29 (br s, 1 H, 6-H), −0.83 (d, $^3J_{HH} = 14.4$ Hz, 1 H, 1-H). ^{13}C NMR (150.8 MHz, 238 K, [D$_8$]toluene): $\delta = 148.3$ ($^1J_{CF} = 239$ Hz, *o*-$B(C_6F_5)_3$), 143.0 (C-4), 139.1 ($^1J_{CF} = 243$ Hz, *p*-$B(C_6F_5)_3$), 137.3 ($^1J_{CF} = 246$ Hz, *m*-$B(C_6F_5)_3$), 124.4 (C-5), 110.7 (Cp), 109.5 (Cp), 59.8 (C-1), 44.2 (C-2), 43.3 (C-3), 28.0 (CH_3), ≈10 (br, C-6), *ipso*-C of $B(C_6F_5)_3$ not observed. ^{19}F NMR (564.3 MHz, 238 K, [D$_8$]toluene): $\delta = -165.5$ ($^3J_{FF} = 22$ Hz, 6 F, *m*-F), −160.4 ($^3J_{FF} = 21$ Hz, 3 F, *p*-F), −133.1 ($^3J_{FF} = 19$ Hz, 6 F, *o*-F).

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