Reactions of Functional Groups at the Periphery of Group 4 Metallocene Frameworks: Selective Formation of a Cp-Bonded Azaboretidine Derivative by a Hydroboration Route

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Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

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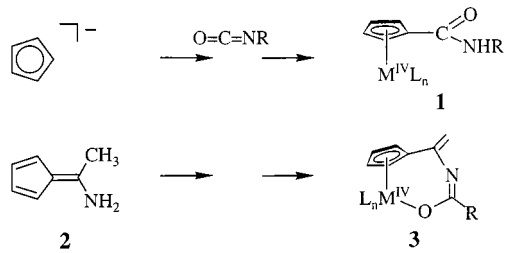
6-Amino-6-methylfulvene has been coupled with benzoic acid by treatment with 7-azahydroxybenzotriazole and DCC. Subsequent two-fold deprotonation, at the NH and 6-methyl groups, generated the vinylidene-bridged Cp/benzoylamido ligand **5**. Treatment of **5** with $ZrCl_4(THF)_2$ gave the *spiro*-metallocene complex **3a** (characterized by X-ray crystal structure analysis), while reaction of **5** with $(Et_2N)_2ZrCl_2(THF)_2$ yielded the bridged half-sandwich complex **3b**. Treatment of **3a** with two molar equivalents of the strongly electrophilic borane $HB(C_6F_5)_2$ resulted in hydroboration of the exocyclic C=C double bond with concomitant intramolecular N–B adduct formation to yield the azaboretidine-type systems **7** (three diastereoisomers, one of which has been characterized by X-ray diffraction analysis). Similarly, hydroboration of **3b** with $HB(C_6F_5)_2$ yielded the azaboretidine derivative **9**. Activation of the complexes **7** and **9** with methylalumoxane led to active homogeneous Ziegler-type propene polymerization catalysts.

Introduction

The chemistry of functional groups attached to Group 4 metallocene frameworks is important, e.g. for extending the structural scope of the "constrained geometry" Ziegler catalysts,[1] but as yet remains little developed. The introduction of functionalities typically used in organic chemistry is often difficult to accomplish by the conventional methods employed in organic synthesis due to the sensitivity of the organometallic Group 4 metal systems to hydrolytic conditions as well as to acidic or basic reaction environments. However, that increased efforts are being made to find suitable conditions and methods to overcome this apparent deficiency in the organic chemistry of Group 4 metallocenes is evident from recent literature.[2,3]



Scheme 1. Syntheses of functionalized Group 4 metal Cp-complexes

We have recently described several ways of introducing carboxamide-derived functional groups at the Cp rings of zirconocene or titanocene complexes (see Scheme 1).[4] A fulvene route has made functionalized systems such as **3** readily available.[5] It was conceivable that the azadiene moiety in **3**, the framework of which is perpendicularly oriented with respect to the metallocene backbone, could be used as a target for a hydrometallation reaction.[6] This posed the question as to whether the two parts of this conjugated metallocene side-chain would react independently or jointly with a suitable H–[M] reagent. Examples of zirconium complexes incorporating this ligand system have now been treated with the strongly electrophilic borane $HB(C_6F_5)_2$ (**6**, "Piers' borane"),[7] which has opened a simple route to novel organometallic azaboretidine derivatives exhibiting interesting structural and stereochemical properties as well as useful features in catalysis.

Results and Discussion

The synthesis of the ligand system used in this study started from 6-amino-6-methylfulvene (**2**), which, in turn, was prepared by amine exchange of 6-dimethylamino-6-methylfulvene by treatment with NH_3.[8] The aminofulvene **2** was then *N*-benzoylated. This was cleanly achieved by employing a coupling method used in peptide chemistry.[9] In a series of experiments it was found that benzoic acid was best activated for this purpose by treatment with 7-aza-hydroxybenzotriazole with subsequent addition of dicyclohexylcarbodiimide.[9b] The resulting active ester was then treated with 6-amino-6-methylfulvene **2** and triethylamine to cleanly afford the benzoylated product **4** in $> 60\%$ isolated yield. Double deprotonation of **4**, at the NH group and at the 6-CH_3 substituent,[5,10] was achieved by reaction with two molar equivalents of LDA in diethyl ether. The corresponding dianionic reagent **5** was not isolated but was

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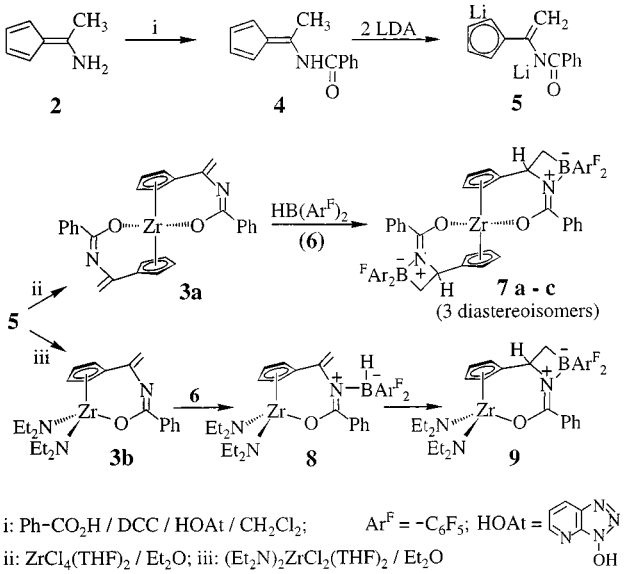
generated in situ and used directly for the preparation of the respective zirconium complexes.

Treatment of the dianion **5** with zirconium tetrachloride resulted in replacement of all four chloride ligands at the metal center with the formation of the *spiro*-metallocene product **3a**. In solution, complex **3a** shows the spectroscopic features of a C_2-symmetric, and hence chiral, framework. This leads to the observation of signals due to four pairs of diastereotopic cyclopentadienyl CH units in the ^{1}H- and ^{13}C-NMR spectra ([D$_6$]benzene, ^{1}H: δ = 5.74, 5.65, 5.61, 5.47; ^{13}C: δ = 120.9, 112.7, 108.3, 105.4). The ^{1}H-NMR signals of the *exo*-methylene group (C=CH$_2$) appear at δ = 5.38 and 5.00 (^2J = 1.1 Hz).

The organometallic *spiro*-complex **3a** was characterized by X-ray crystal structure analysis. It shows an approximately C_2-symmetric framework. Two monosubstituted η^5-Cp ligands and two imidato oxygen atoms are coordinated to zirconium in a pseudo-tetrahedral arrangement. The Zr–O bonds are rather long at 2.032(2) Å (Zr–O9) and 2.047(2) Å (Zr–O19). It would seem that the cyclic structure effectively prevents any pronounced metal–oxygen π-interaction.[11] The corresponding Zr–O9–C8 and Zr–O19–C19 angles are thus rather small [132.2(2)° and 134.2(2)°, respectively] for such a situation.[12] The adjacent C8–N7 bond length [1.277(5) Å] is in the appropriate range for a nitrogen–carbon double bond [C18–N17: 1.281(5) Å], while the adjacent C–O linkages [C8–O9: 1.327(4) Å; C18–O19: 1.335(4) Å] are in the typical C(sp^2)–O σ-bond range.[13] Characterization of **3a** as an *O*-bonded Zr-iminocarboxylate thus seems warranted (see Scheme 2 and Figure 1).



Scheme 2. Synthesis of the hydroboration compounds **7** and **9**

Treatment of the salt **5** with the reagent (Et$_2$N)$_2$ZrCl$_2$(THF)$_2$[14] resulted in selective replacement of the two chloride ligands to form the half-sandwich complex **3b**. The spectral data of **3b** indicate analogous bonding of the ligand system to zirconium as that seen in **3a**, i.e. through both the C$_5$H$_4$ moiety and the pendant imidato substituent, the latter being κ-*O*-bonded. The Cp–C(=CH$_2$)–N=C(Ph)–O ligand gives rise to characteristic NMR signals at δ = 160.7 (^{13}C of the imidato carbonyl carbon) and at δ = 5.38, 5.10 (^{1}H of the =CH$_2$ group, ^2J = 1.5 Hz). In complex **3b**, only two CH resonances of the monosubstituted Cp ligand are seen (^{1}H: δ = 5.97, 5.95; ^{13}C: δ = 110.64, 110.56). The complex is prochiral at the pseudotetrahedral zirconium center. Therefore, a single set of NCH$_2$CH$_3$ NMR resonances is observed, although the NCH$_2$ protons are diastereotopic.

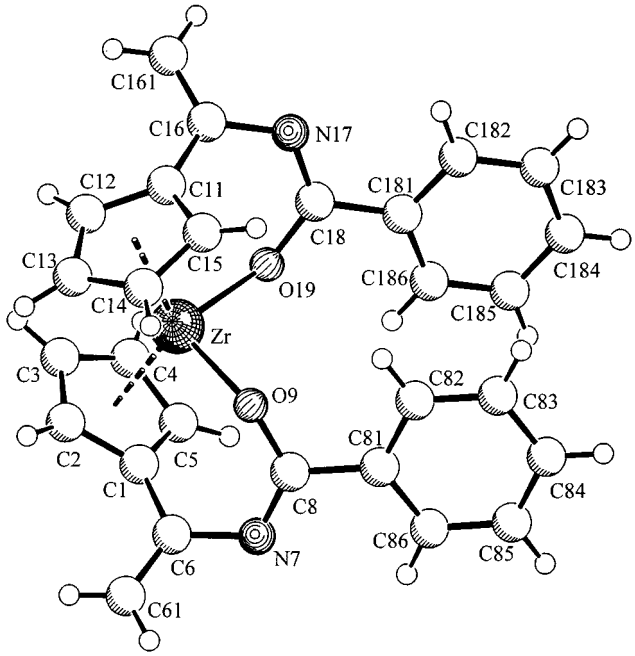


Figure 1. Molecular structure of **3a** showing the non-systematic atom numbering scheme; selected bond lengths [Å] and angles [°]: Zr–O9 2.032(2), Zr–O19 2.047(2), Zr–C$_{Cp(1-5)}$ 2.504(4), Zr–C$_{Cp(11-15)}$ 2.491(4), C8–O9 1.327(4), C18–O19 1.335(4), C8–N7 1.277(5), C18–N17 1.281(5), C8–C81 1.490(5), C18–C181 1.481(5), N7–C6 1.417(5), N17–C16 1.414(5), C6–C61 1.328(6), C16–C161 1.322(6), C1–C6 1.485(5), C11–C16 1.473(6); O9–Zr–O19 96.9(1), Zr–O9–C8 132.2(2), Zr–O19–C18 134.2(2), O9–C8–N7 125.9(3), O19–C18–N17 125.3(3), O9–C8–C81 114.0(3), O19–C18–C181 115.0(3), C81–C8–N7 120.0(3), C181–C18–N17 119.7(3), C8–N7–C6 117.1(3), C18–N17–C16 118.9(3), N7–C6–C61 120.0(4), N17–C16–C161 120.9(4), N7–C6–C1 117.2(3), N17–C16–C11 116.9(3), C1–C6–C61 122.7(4), C11–C16–C161 122.2(4)

The organometallic *spiro*-complex **3a** was treated with two molar equivalents of the electrophilic borane HB(C$_6$F$_5$)$_2$ in benzene solution. The reaction reached completion within 2 days at ambient temperature and a product fraction of low solubility (ca. 16%) precipitated from the reaction medium. Crystallization from [D$_6$]benzene gave single crystals of this material suitable for X-ray crystal structure analysis. This showed the crystals to be composed of a single isomerically pure 2:1 adduct of the borane with **3a**, resulting from addition of the borane to the exocyclic carbon–carbon double bonds of the pendant –C(=CH$_2$)–N=C(Ph)–O moiety. This hydroboration proceeded with complete *anti*-Markovnikov orientation, as is usual. Thus, the B(C$_6$F$_5$)$_2$ group was attached at the former olefinic methylene group, while the hydrogen was attached at C$_α$. The most remarkable structural feature of the hydroboration product **7a** is the strong coordination of the =N(R)

nitrogen atom to the adjacent electrophilic boron center.[15] This leads to the formation of two four-membered heterocycles in the approximately C_2-symmetric metallocene product. The corresponding bond lengths (in Å) at the substituted azaboretidine-type ring systems are 1.597(10) (B1–N13), 1.492(9) (N13–C14), 1.640(12) (B1–C20), 1.301(9) (N13–C12). The corresponding bond angles measure 83.9(5)° (C20–B1–N13), 92.0(5)° (B1–N13–C14), 126.8(6)° (C12–N13–C14), 138.7(6)° (C12–N13–B1), and 90.8(5)° (N13–C14–C20) (the approximately symmetry-equivalent second azaboretidine ring shows similar values, see Figure 2). The remaining bonding parameters of the framework of complex **7a** resemble those of its immediate precursor **3a**. In **7a**, the O11–Zr–O51 angle measures 98.3(2)°. The bond angles at the two oxygen atoms are 144.4(5)° (Zr–O11–C12) and 143.4(5)° (Zr–O51–O52) and the corresponding metal–oxygen bond lengths were determined as 2.041(5) Å (Zr–O11) and 2.043(5) Å (Zr–O51), respectively.

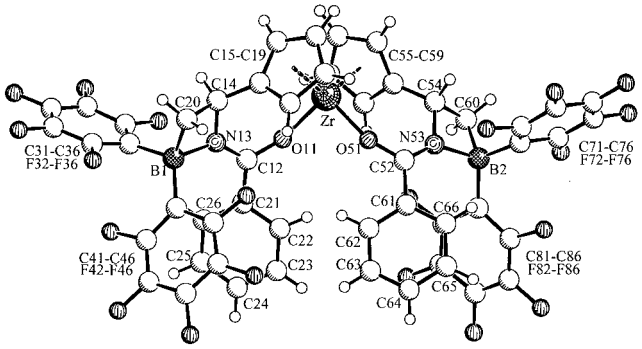


Figure 2. Molecular structure of **7a** showing the non-systematic atom numbering scheme; selected bond lengths [Å] and angles [°]; additional values are given in the text: Zr–O11 2.041(5), Zr–O51 2.043(5), Zr–$C_{Cp(15–19)}$ 2.485(8), Zr–$C_{Cp(55–59)}$ 2.479(8), C12–O11 1.300(8), C52–O51 1.305(7), C12–N13 1.301(9), C52–N53 1.278(8), C12–C21 1.473(10), C52–C61 1.493(9), N13–C14 1.492(9), N53–C54 1.493(8), C14–C20 1.548(10), C54–C60 1.539(10), C14–C15 1.483(10), C54–C55 1.498(9), N13–B1 1.597(10), N53–B2 1.602(9), C20–B1 1.640(12), C60–B2 1.647(11), B1–C31 1.634(12), B2–C71 1.617(11), B1–C41 1.621(11), B2–C81 1.619(11); O11–Zr–O51 98.3(2), Zr–O11–C12 144.4(5), Zr–O51–C52 143.4(5), O11–C12–N13 122.0(6), O51–C52–N53 123.4(6), O11–C12–C21 116.8(6), O51–C52–C61 114.7(6), C21–C12–N13 121.2(6), C61–C52–N53 121.8(6), C12–N13–C14 126.8(6), C52–N53–C54 126.9(5), N13–C14–C20 90.8(5), N53–C54–C60 91.8(5), N13–C14–C15 118.7(5), N53–C54–C55 118.2(5), C15–C14–C20 117.6(7), C55–C54–C60 117.7(7), C12–N13–B1 138.7(6) C52–N53–B2 141.2(5), C14–N13–B1 92.0(5), C54–N53–B2 90.7(5), C14–C20–B1 88.3(6), C54–C60–B2 87.4(6), N13–B1–C20 83.9(5), N53–B2–C60 84.2(5), N13–B1–C31 112.5(7), N53–B2–C71 110.8(6), N13–B1–C41 113.3(6), N53–B2–C81 113.4(6), C20–B1–C31 107.5(6), C60–B2–C71 107.4(6), C20–B1–C41 118.5(7), C60–B2–C81 118.2(7), C31–B1–C41 116.7(7), C71–B2–C81 117.9(6)

The stereochemistry of the complexes **7** is interesting. The *spiro*-metallocene framework of **7** (and also that of **3a**) is axially chiral. The hydroboration reaction introduced two new chiral centers at the carbon atoms α to the Cp rings (C14 and C54 in Figure 2). Therefore, a mixture of four chiral diastereomers could, in principle, have been formed (2^3 stereoisomers), each of course as a racemate. However, in the specific system **7** under consideration here, the two newly formed chiral carbon centers are topologically equivalent. Therefore, two of the four possible diastereomers are in fact identical. It thus remains that three diastereoisomers could possibly be formed upon hydroboration of the *spiro*-metallocene **3a**, their relative configurations being (a*R*,*S*,*S*)* (**7a**), (a*R*,*R*,*S*)* [**7b**, identical to (a*R*,*S*,*R*)*], and (a*R*,*R*,*R*)* (**7c**).[16] The single isomer found in the crystal conformed to the first case, i.e. the (a*R*,*S*,*S*)* diastereoisomer **7a** was characterized by X-ray diffraction analysis.

The hydroboration reaction of **3a** with $HB(C_6F_5)_2$ was, however, far from diastereoselective. Workup of the mother liquor after removal of the first batch of precipitated product gave a major fraction (ca. 40% yield) that was found to contain all three products **7a**, **7b**, and **7c** in a 2:10:3 ratio. This ratio may not accurately reflect the actual diastereoselectivity of the hydroboration reaction under the employed reaction conditions due to the separation of isomers during the workup, but it is rather close to the expected statistical ratio. This probably indicates that the two new stereogenic centers are formed independently of one another. The C_1-symmetric (a*R*,*R*,*S*)* isomer **7b** could readily be distinguished from its C_2-symmetric counterparts **7a** and **7c** by the characteristic splitting of the respective pairs of $^1H/^{13}C$-NMR resonances. For instance, complex **7b** shows a total of eight equally intense cyclopentadienyl methine proton ^1H-NMR signals (at δ = 7.16, 6.89, 6.60, 6.56, 6.51, 6.41, 6.29, 6.24 in [D_2]dichloromethane), whereas for **7a** and **7c** only four such resonances are seen in each case (**7a**: δ = 6.81, 6.55, 6.46, 6.37; **7c**: δ = 7.32, 7.27, 6.54, 6.19).

Hydroboration of the cyclic half-sandwich complex **3b** with $HB(C_6F_5)_2$ proceeds in a similar manner, but is of course stereochemically much simpler because, as expected, only a single isomerically pure product is obtained. H–[B] addition occurs cleanly (and regioselectively) at the *exo*-methylene functionality of the organometallic ring system, and the product **9** again contains a strong N–B interaction. This is evident from the characteristic ^{11}B-NMR shift at δ = –2.2 (**7a**: δ = –1.1). Moreover, ^{15}N-NMR data have proved very useful in characterizing the obtained structural type.[17] Complex **9** shows the ^{15}N-NMR resonance of the planar tricoordinate $=N^+$ nitrogen atom of the azaboretidine ring at δ = –205, very similar to the corresponding signal of complex **7a** (δ = –209). In contrast, the ^{15}N-NMR signals of the sp^2-hybridized dicoordinate nitrogen atoms in the starting materials **3a** and **3b** are seen at δ = –148 and δ = –145, respectively.

Complex **9** contains a single chiral center, i.e. at the tertiary carbon atom of the azaboretidine ring. Therefore, a set of four separated methine CH resonances due to the monosubstituted Cp ring are observed in the ^1H-NMR spectrum (at δ = 6.32, 6.15, 5.89, 5.82). The two metal-bonded $–N(CH_2CH_3)_2$ groups are diastereotopic, and thus give rise to two ^{15}N-NMR signals at δ = –171 and –187 and two ^1H-NMR methyl signals at δ = 0.85 and 0.73. The ethyl groups at each of the apparently trigonal-planar nitrogens behave homotopically, but the protons of each $–N(CH_2–)$ group are diastereotopic, giving rise to a total of four separated *AB*X_3 multiplets (at δ = 3.24, 3.04, 2.97, and 2.95 in [D_6]benzene at 298 K).

Under carefully controlled conditions, we were able to observe experimentally the formation of a 1:1 adduct (**8**) between the strongly electrophilic borane $HB(C_6F_5)_2$ and the metal complex **3b**. The addition product **8** was obtained in [D_8]toluene solution after mixing the two components at low temperature (–78 °C), allowing them to react briefly at ambient temperature (1 min), and then cooling the mixture to ca. 5 °C to record the NMR spectra. Under these conditions, complex **8** is relatively stable and is only slowly converted into the final product **9**. In **8**, the C=CH_2 double bond conjugated to the Cp ring remains intact [^{1}H NMR: δ = 5.41, 5.04; ^{13}C NMR: δ = 141.3, 109.6 (C=CH_2)]. The ^{13}C-NMR resonance of the C=N moiety is seen at δ = 177.5, i.e. downfield shifted relative to the starting material **3b** (δ = 160.7)[15] and no proton is attached to this carbon. The ^{15}N-NMR signal of **8** is found to be considerably shifted (**8**: δ = –204; **3b**: δ = –145). The broad ^{11}B-NMR signal at δ = –10.9 is indicative of the presence of a tetravalent borane adduct. The combined spectroscopic evidence indicates simple adduct formation between $HB(C_6F_5)_2$ and the imidato nitrogen atom of **3b** to give **8**. Complex **8** slowly undergoes conversion into the final hydroboration product **9**. Geometrically, this could take place by an intramolecular rearrangement process, since the large bending of the Cp–C(=CH_2)–N=C 2-azadiene unit from planarity [θ C61–C6–N7–C8 in the related system **3a** is –48.1(4)°] would probably allow H-transfer from boron to the trisubstituted sp^2 carbon. However, on electronic grounds, we regard it as more likely that the final hydroboration to give **9** may simply be preceeded by a reversible formation of the $HB(C_6F_5)_2$ adduct **8**.

The organometallic hydroboration products **7** and **9** are quite stable and can be used as homogeneous Ziegler-type catalyst precursors. Exploratory propene polymerization experiments were carried out by activating the respective catalyst precursors by treatment with a large excess of methylalumoxane (see Table 1).[18] Under the typical reaction conditions (for details, see the Experimental Section), the mixture of diastereomers **7a**–**c** gave a medium activity propene polymerization catalyst upon such MAO activation. A similar activity was obtained by employing the pure diastereoisomer **7a** as a precursor. It is clear that the Zr–O linkage in **7** must be cleaved during its conversion into an active catalyst. Consequently, pre-activation with excess MAO solution in toluene resulted in a slightly increased catalyst activity in these cases. Atactic polypropylene was generated in the experiments employing **7**.

Table 1. Propene polymerization experiments with the **3**, **7**, **9**/MAO systems

Precursor (mg/μmol)	Al/Zr ratio	PP[a]	activity[b]	σ[c]
3a (20/39)	0.82×10^3	[d]	–	–
3a (21/41)[e]	0.78×10^3	[d]	–	–
3b (23/52)	0.62×10^3	[d]	–	–
7 (20/17)	1.9×10^3	0.71	11	0.55
7 (15/12)[e]	2.6×10^3	0.71	14	0.57
7a (16/13)	2.4×10^3	0.66	12	0.50
7a (17/14)[e]	2.3×10^3	1.3	23	0.55
9 (20/25)	1.3×10^3	2.4	24	0.20

[a] g of polypropylene isolated. – [b] a in g polymer/mmol [Zr]·bar·h. – [c] Probability of obtaining an m diad under chain-end control. – [d] Traces. – [e] Pre-activation of the precursor with 2.5 mL of a 10% (1.6 M) methylalumoxane solution in toluene for 15 min.

The diethylamido ligands of **9** are seemingly more readily displaced during the activation process with MAO. Without pre-treatment, polypropylene was obtained with a medium activity (a = 24). In this case, the obtained polypropylene turned out to be slightly syndiotactic [with σ = 0.2 (where σ expresses the probability of having an m diad formed at the catalyst center by stereochemical chain-end control)], which probably just represents another example of an ordinary behavior of such a catalyst system in the high temperature regime.[19]

In contrast to **7** and **9**, similar treatment of their unsaturated precursors **3a** and **3b** did not produce active Ziegler-type catalysts for propene polymerization under the applied conditions. This may be due to the dominant role played by the nucleophilic imidato nitrogen center in these complexes, which renders them liable to form reasonably strong adducts with Lewis acidic reagents [for example, the $HB(C_6F_5)_2$ adduct described above]. One might speculate that such complex formation takes place preferentially upon treatment of **3a** or **3b** with the bulky MAO Lewis acid, leading to strong steric shielding of the potential catalytic centers in these adducts. On the basis of our observations, we conclude that hydroboration of these systems leading to azaboretidine formation very effectively inhibits the catalyst deactivation. We have thus, in effect, employed the $HB(C_6F_5)_2$ reagent as an organometallic protecting group that has facilitated conversion of the functionalized (CpX)Zr systems to active homogeneous Ziegler-type catalyst systems without complete loss of the pendant functional groups at the central organometallic framework. We are hopeful that the use of such protective groups might open ways of using a variety of functionalized Group 4 metal complexes in homogeneous Ziegler catalysis and related catalytic processes. Such studies are being actively pursued in our laboratory.

Experimental Section

All the described compounds (other than **4**) are air- and moisture-sensitive. They were thus prepared and handled under argon atmosphere using Schlenk-type glassware or in an argon-filled glovebox. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. – NMR spectra were recorded on Varian Unity Plus, Bruker AMX 400, Bruker ARX 300, and Bruker AC 200 P-FT-NMR spectrometers. Spectroscopic characterization usually included ^{1}H,^{1}H GCOSY, ^{1}H,^{13}C (G)HMBC, and (G)HMQC experiments, even where not explicitly stated. – IR spectra were recorded on a Nicolet 5 DXC FT-IR spectrometer in KBr pellets or from films between NaCl plates. – Elemental analyses were carried out using a Foss Heraeus CHN-O-Rapid analyser, while DSC measurements were made on a Texas Instruments DSC 2010. – X-

ray crystal structure analyses: Data sets were collected with Enraf–Nonius CAD4 and Nonius KappaCCD diffractometers. Programs used: data collection: Express and Collect; data reduction: MolEN or Denzo-SMN; structure solution: SHELXS-86; structure refinement: SHELXL-93 and SHELXL-97; graphics: SCHAKAL.[20] – 7-Aza-hydroxybenzotriazole (HOAt),[9b] 6-amino-6-methylfulvene,[8] $ZrCl_4(thf)_2$,[21] $ZrCl_2(NEt_2)_2(thf)_2$,[14] and $HB(C_6F_5)_2$[7] were prepared according to literature procedures.

Preparation of 6-Amido-*N*-benzoyl-6-methylfulvene (4): To a yellow suspension of benzoic acid (2.44 g, 20.0 mmol) and 7-aza-hydroxybenzotriazole (2.72 g, 20.0 mmol) in dichloromethane (50 mL) at 0 °C was added dicyclohexylcarbodiimide (4.13 g, 20.0 mmol). The resulting suspension was stirred for 30 min at 0 °C until the active ester and dicyclohexylurea had been formed and the yellow colour of the suspension had turned to white. The suspension was then filtered into a cold (0 °C) solution of 6-amino-6-methylfulvene (2.14 g, 20.0 mmol) and triethylamine (7.0 mL, 50 mmol) in dichloromethane (30 mL). The filter cake was washed with 30 mL of dichloromethane and the filtrate was combined with the fulvenic solution. The resulting brown reaction mixture was allowed to warm to room temperature and then stirred for 3 days. It was subsequently washed with 5% aq. sodium bicarbonate solution (3 × 50 mL) and with water (3 × 30 mL). The organic phase was dried with magnesium sulfate and the solvent was removed in vacuo. The residual brown oil was purified by chromatography on silica gel 60, eluting with a mixture of diethyl ether/pentane (1:3), to which 1% (*v*/*v*) of *N*,*N*-dimethylethylamine had been added. Removal of the solvent in vacuo afforded 2.78 g (66%) of the product in the form of orange needles. DSC: 78 °C (m.p.), 131 °C (dec.). – $C_{14}H_{13}NO$ (211.26): calcd. C 79.59, H 6.20, N 6.63; found C 79.32, H 6.38, N 6.35. – IR (KBr): $\tilde{\nu}$ = 3304, 1659, 1633 cm^{-1}. – ^1H NMR (400.1 MHz, [D$_2$]dichloromethane, 300 K): δ = 8.62 (br. s, 1 H, NH), 7.87 (m, 2 H, *o*-Ph), 7.62 (m, 1 H, *p*-Ph), 7.53 (m, 2 H, *m*-Ph), 6.65, 6.53 (each m, each 1 H, α-Fulv), 6.49, 6.43 (each m, each 1 H, β-Fulv), 2.81 (s, 3 H, CH_3). – ^{13}C NMR (100.6 MHz, [D$_2$]dichloromethane, 300 K): δ = 166.0 (C=O), 146.4 (C-6), 135.1 (*i*-Ph), 133.3 (*p*-Ph), 130.8, 129.5 (β-Fulv), 130.3 (C-1), 129.7 (*m*-Ph), 128.0 (*o*-Ph), 122.6, 115.2 (α-Fulv), 15.9 (CH_3).

Preparation of Bis{η^5:κ*O*-1-(*N*-benzoylamido)ethenylcyclopentadienyl}zirconium (3a): Compound **4** (1.30 g, 6.15 mmol) and lithium diisopropylamide (1.32 g, 12.3 mmol) were weighed into a Schlenk vessel, which was subsequently cooled to –78 °C, whereupon diethyl ether (100 mL) was added. The cooling bath was removed and the suspension was stirred for 2 h while slowly warming to room temperature. The reaction was seen to be complete by the appearance of a light-yellow precipitate of the dilithium salt. The suspension was then cooled to –50 °C and a suspension of tetrachlorozirconium–bis(tetrahydrofuran) (1.16 g, 3.07 mmol) in diethyl ether (50 mL) was added. The cooling bath was removed once more, allowing the suspension to warm to room temperature, and stirring was continued for 12 h. The resulting yellow suspension was then concentrated to dryness and the remaining yellow powder was extracted with diethyl ether (5 × 100 mL). The ethereal solution was filtered and the filtrate was concentrated in vacuo. The product was isolated as a deep-yellow solid; yield 641 mg (41%). – DSC: 189 °C (m.p., followed by decomp.). – IR (KBr): $\tilde{\nu}$ = 1616, 1590, 1560 cm^{-1}. – ^1H NMR (599.9 MHz, [D$_6$]benzene, 298 K): δ = 8.31 (m, 4 H, *o*-Ph), 7.15 (m, 6 H, *m,p*-Ph), 5.74 (m, 2 H, 2-H), 5.65 (m, 2 H, 5-H), 5.61 (m, 2 H, 3-H), 5.47 (m, 2 H, 4-H), 5.38 (d, $^2J_{HH}$ = 1.1 Hz, 2 H, C=CH_2^{cis}), 5.00 (d, $^2J_{HH}$ = 1.1 Hz, 2 H, C=CH_2^{trans}). – ^{13}C NMR (gated decoupled) (150.8 MHz, [D$_6$]benzene, 298 K): δ = 162.9 (s, OC=N), 146.1 (s, *C*=CH_2), 135.6 (m, *i*-Ph), 130.8 (dm, $^1J_{CH}$ = 160 Hz, *p*-Ph), 128.9 (dm, $^1J_{CH}$ = 159 Hz, *o*-Ph), 128.3 (dm, $^1J_{CH}$ = 160 Hz, *m*-Ph), 120.9 (dm, $^1J_{CH}$ = 175 Hz, C-3), 112.7 (dm, $^1J_{CH}$ = 174 Hz, C-2), 108.3 (dm, $^1J_{CH}$ = 173 Hz, C-4), 105.4 (dm, $^1J_{CH}$ = 173 Hz, C-5), 104.8 (ps. t, $^1J_{CH}$ = 159 Hz, C=*C*H$_2$), the resonance of C-1 is obscured by the solvent signal. – ^{15}N,^1H GHMBC (60.8/599.9 MHz, [D$_6$]benzene): $\delta^{15}N/\delta^1H$ = –148/5.38 (C=N/C=CH_2^{cis}), –148/5.00 (C=N/C=CH_2^{trans}).

X-ray Crystal Structure Analysis of 3a: Formula $C_{28}H_{22}N_2O_2Zr$, M_r = 509.70, yellow crystal, 0.35 × 0.25 × 0.10 mm, *a* = 23.282(2) Å, *b* = 11.318(1) Å, *c* = 17.345(3) Å, β = 96.11(1)°, *V* = 4544.5(10) Å^3, ρ_{calcd} = 1.490 g cm^{-3}, *F*(000) = 2080 e, μ = 5.12 cm^{-1}, empirical absorption correction based on ψ scan data (0.951 ≤ *C* ≤ 0.999), *Z* = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 0.71073 Å, *T* = 223 K, 4771 reflections collected (±*h*, –*k*, +*l*), $[(\sin\theta)/\lambda]_{max}$ = 0.62 Å^{-1}, 4610 independent and 3377 observed reflections [$I \geq 2\sigma(I)$], 298 refined parameters, *R* = 0.037, wR^2 = 0.106, max. residual electron density 0.68 (–0.63) eÅ^{-3}.

Preparation of Bis{dimethylamido}{η^5:κ*O*-1-(*N*-benzoylamido)-ethenylcyclopentadienyl}zirconium (3b): Compound **4** (1.10 g, 5.21 mmol) and lithium diisopropylamide (1.12 g, 10.4 mmol) were weighed into a Schlenk vessel, which was then cooled to –78 °C, whereupon diethyl ether (100 mL) was added. The cooling bath was removed and the suspension was stirred for 2 h while slowly warming to room temperature. The suspension was then cooled to –50 °C, whereupon $(Et_2N)_2ZrCl_2(THF)_2$ (2.35 g, 5.21 mmol) in 50 mL of diethyl ether was added. The cooling bath was then removed once more, allowing the mixture to warm to room temperature, and stirring was continued for 12 h. The solvent was evaporated in vacuo from the resulting brown suspension and the residual brown oil was extracted with 150 mL of pentane. The light-brown suspension thus obtained was filtered and the filtrate was concentrated in vacuo to leave 1.88 g (81%) of a very viscous red-brown oil. – $C_{22}H_{31}N_3OZr$ (444.73): calcd. C 59.42, H 7.03, N 9.45; found C 58.92, H 6.93, N 9.39. – IR (NaCl): $\tilde{\nu}$ = 1609, 1591, 1558 cm^{-1}. – ^1H NMR (599.9 MHz, [D$_6$]benzene, 298 K): δ = 8.50 (m, 2 H, *o*-Ph), 7.23 (m, 2 H, *m*-Ph), 7.18 (m, 1 H, *p*-Ph), 5.97, 5.95 (each m, each 2 H, Cp), 5.38 (m, 1 H, C=CH_2), 5.10 (ps. d, $^2J_{HH}$ = 1.5 Hz, 1 H, C=CH'$_2$), 3.16 (ABX_3, $^{2/3}J_{HH}$ = 7.2 Hz, 4 H, C*H*$_2$CH$_3$), 3.12 (ABX_3, $^{2/3}J_{HH}$ = 6.6 Hz, 4 H, C*H'*$_2$CH$_3$), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 12 H, CH$_2$C*H*$_3$). – ^{13}C NMR (gated decoupled) (150.8 MHz, [D$_6$]benzene, 298 K): δ = 160.7 (t, $^3J_{CH}$ = 4 Hz, OC=N), 147.1 (s, *C*=CH_2), 136.6 (t, $^3J_{CH}$ = 7 Hz, *i*-Ph), 130.4 (dm $^1J_{CH}$ = 159 Hz, *p*-Ph), 129.0 (dm, $^1J_{CH}$ = 161 Hz, *o*-Ph), 128.1 (dm, $^1J_{CH}$ = 159 Hz, *m*-Ph), 126.0 (m, *i*-Cp), 110.64, 110.56 (each dm, each $^1J_{CH}$ = 171 Hz, Cp), 104.4 (ps. t, $^1J_{CH}$ = 159 Hz, C=*C*H$_2$), 44.1 (t, $^1J_{CH}$ = 131.7 Hz, N*C*H$_2$CH$_3$), 15.7 (qt, $^1J_{CH}$ = 125 Hz, $^2J_{CH}$ = 3 Hz, NCH$_2$*C*H$_3$). – ^{15}N,^1H GHMBC (60.8/599.9 MHz, [D$_6$]benzene, 298 K): $\delta^{15}N/\delta^1H$ = –145/5.10 (C=*N*/C=C*H'*$_2$), –192/0.89 (*N*CH$_2$CH$_3$/C*H*$_2$CH$_3$).

Reaction of 3a with $HB(C_6F_5)_2$ – Formation of 7: Compound **3a** (255 mg, 500 μmol) and bis(pentafluorophenyl)borane (346 mg, 1.0 mmol) were weighed into a Schlenk vessel, which was then cooled to 0 °C, whereupon benzene (10 mL) was added. The resulting orange solution was allowed to warm to room temperature and stirred for 2 days. The yellow suspension obtained was filtered and the collected light-yellow precipitate was dried in vacuo yielding 102 mg (16%) of isomer **7a**. Concentration of the filtrate to dryness afforded a yellow powder (235 mg, 40% overall yield), which was found to contain the three diastereomers **7a**, **7b**, and **7c** in a ratio of 2:10:3.

Isomer 7a: $C_{52}H_{24}B_2F_{20}N_2O_2Zr \cdot C_6H_6$ (1279.70): calcd. C 54.44, H 2.36, N 2.19; found C 54.07, H 2.44, N 1.98. – DSC: 257 °C (m.p.), 267 °C (dec.). – ^1H NMR (599.9 MHz, [D$_2$]dichloromethane, 298 K): δ = 7.44 (ps. d, $^3J_{HH}$ = 7.78 Hz, 4 H, *o*-Ph), 7.34

(ps. t, $^3J_{HH}$ = 7.5 Hz, 2 H, *p*-Ph), 7.07 (m, 4 H, *m*-Ph), 6.81 (m, 2 H, Cp_β), 6.55 (m, 2 H, Cp_α), 6.46 (m, 2 H, Cp_α), 6.37 (m, 2 H, Cp_β), 5.20 (ps. t, $^3J_{HH}$ = 9.0 Hz, 2 H, NCH), 1.80 (ps. t, $^{2/3}J_{HH}$ = 10.5 Hz, 2 H, CH_2B), 1.67 (ps. t, $^{2/3}J_{HH}$ = 10.5 Hz, 2 H, CH'_2B). – ^{13}C NMR (gated decoupled) (150.8 MHz, [D$_2$]dichloromethane, 298 K): δ = 166.2 (s, OC=N), 136.6 [br. m, obscured by the carbon resonance of $B(C_6F_5)$, *i*-Cp], 133.1 (dt, $^1J_{CH}$ = 161 Hz, $^3J_{CH}$ = 8 Hz, *p*-Ph), 129.5 (d ps. t, $^1J_{CH}$ = 161 Hz, $^3J_{CH}$ = 7 Hz, *o*-Ph), 128.9 (t, $^3J_{CH}$ = 7 Hz, *i*-Ph), 128.1 (dd, $^1J_{CH}$ = 162 Hz, $^3J_{CH}$ = 7 Hz, *m*-Ph), 121.6 (dm, $^1J_{CH}$ = 175 Hz, Cp_β), 113.4 (dm, $^1J_{CH}$ = 175 Hz, Cp_α), 111.5 (dm, $^1J_{CH}$ = 175 Hz, Cp_β), 107.6 (dm, $^1J_{CH}$ = 174 Hz, Cp_α), 59.1 (d, $^1J_{CH}$ = 145 Hz, NCH), 27.2 (tm, $^1J_{CH}$ = 126 Hz, CH_2B). – ^{11}B NMR (64.2 Hz, [D$_2$]dichloromethane, 300 K): δ = –1.1 ($\nu_{1/2}$ = 670 Hz). – ^{15}N,^{1}H GHMBC (60.8 MHz/599.9 MHz, [D$_2$]dichloromethane, 298 K): $\delta^{15}N/\delta^1H$ = –209.3/5.20 (*N*C*H*), –209.3/1.67 (*N*CH/C*H'*$_2$B). – ^{19}F NMR (564.3 MHz, [D$_2$]dichloromethane, 298 K): δ = –133.3 [m, 2 F, *o*-$B(C_6F_5)$], –135.9 [m, 2 F, *o*-$B(C_6F_5)$'], –158.2 [t, $^3J_{FF}$ = 20.1 Hz, 1 F, *p*-$B(C_6F_5)$], 159.4 [t, $^3J_{FF}$ = 20.1 Hz, 1 F, *p*-$B(C_6F_5)$'], –164.5 [m, 2 F, *m*-$B(C_6F_5)$], –164.6 [m, 2 F, *m*-$B(C_6F_5)$'].

Isomer 7c: ^{1}H NMR (599.9 MHz, [D$_2$]dichloromethane, 298 K): δ = 7.51 (m, 4 H, *o*-Ph), 7.39 (m, 2 H, *p*-Ph), 7.32 (m, 2 H, Cp_β), 7.27 (m, 4 H, *m*-Ph), 6.54 (m, 2 H, Cp_α), 6.35 (m, 2 H, Cp_β), 6.19 (m, 2 H, Cp_α), 5.43 (ps. t, $^3J_{HH}$ = 9.1 Hz, 2 H, NCH), 1.88 (m, 2 H, CH_2B), 1.54 (m, 2 H, CH'_2B). – ^{1}H TOCSY (599.9 MHz, [D$_2$]dichloromethane, 298 K, irradiated at/response at): δ = 5.43 (NC*H*)/1.88 (C*H*$_2$B), 1.54 (C*H'*$_2$B). – ^{13}C NMR (gated decoupled) (150.8 MHz, [D$_2$]dichloromethane, 298 K): δ = 164.9 (s, OC=N), 132.7 (dm, $^1J_{CH}$ = 164 Hz, *p*-Ph), 131.1 (m, *i*-Cp), 124.3 (dm, $^1J_{CH}$ = 174 Hz, Cp_α), 116.9 (dm, $^1J_{CH}$ = 174 Hz, Cp_β), 109.6 (dm, $^1J_{CH}$ = 177 Hz, Cp_β), 109.1 (dm, $^1J_{CH}$ = 174 Hz, Cp_α), 59.2 (dm, $^1J_{CH}$ = 145 Hz, NCH), 27.3 (dm, $^1J_{CH}$ = 133 Hz, CH_2B) (signal obscured by those of the other isomers). The signals of the carbon atoms of the $B(C_6F_5)_2$ moiety are also obscured by those of the other isomers. The signals due to the phenyl carbon atoms cannot be distinguished from those due to the isomer **7b** and hence they are listed together. – ^{19}F NMR (564.3 MHz, [D$_2$]dichloromethane, 298 K): δ = –132.6 [m, 4 F, *o*-$B(C_6F_5)$], –136.2 [m, 4 F, *o*-$B(C_6F_5)$'], –158.2 [t, $^3J_{FF}$ = 20 Hz, 2 F, *p*-$B(C_6F_5)$], –159.9 [t, $^3J_{FF}$ = 20 Hz, 2 F, *p*-$B(C_6F_5)$'], –164.6 [m, 4 F, *m*-$B(C_6F_5)$'], –164.8 [m, 4 F, *m*-$B(C_6F_5)$].

Isomer 7b: ^{1}H NMR (599.9 MHz, [D$_2$]dichloromethane, 298 K): δ = 7.58 (m, 2 H, *o*-Ph), 7.42 (m, 2 H, *o*-Ph*), 7.41 (m, 1 H, *p*-Ph*), 7.40 (m, 1 H, *p*-Ph), 7.28 (m, 2 H, *m*-Ph), 7.27 (m, 2 H, *m*-Ph*), 7.16 (m, 1 H, Cp_β), 6.89 (m, 1 H, Cp_β*), 6.60 (m, 1 H, Cp_β*), 6.56 (m, 1 H, Cp_α*), 6.51 (m, 1 H, Cp_α*), 6.41 (m, 1 H, Cp_α), 6.29 (Cp_β), 6.24 (Cp_α), 5.51 (ps. t, $^3J_{HH}$ = 9.1 Hz, 1 H, NCH), 5.11 (ps. t, $^3J_{HH}$ = 9.0 Hz, 1 H, NCH*), 1.94 (m, 1 H, CH_2B), 1.91 (m, 1 H, CH_2B*), 1.52 (m, 1 H, CH'_2B*), 1.50 (m, 1 H, CH'_2B). – ^{1}H TOCSY (599.9 MHz, [D$_2$]dichloromethane, 298 K, irradiated at/response at): δ = 5.51 (NC*H*)/1.94 (C*H*$_2$B), 1.50 (C*H'*$_2$B); 5.11 (NC*H*)/1.91 (C*H*$_2$B*), 1.52 (C*H'*$_2$B*). – ^{13}C NMR (gated decoupled) (150.8 MHz, [D$_2$]dichloromethane, 298 K): δ = 166.7 (s, OC=N), 164.7 (s, OCN), 134.0 (m, *i*-Cp*), 133.0 (dm, $^1J_{CH}$ = 164 Hz, *p*-Ph*), 132.8 (dm, $^1J_{CH}$ = 164 Hz, *p*-Ph), 126.4 (m, *i*-Cp), 125.8 (dm, $^1J_{CH}$ = 175 Hz, Cp_α), 124.5 (dm, $^1J_{CH}$ = 175 Hz, Cp_β*), 116.2 (dm, $^1J_{CH}$ = 175 Hz, Cp_β), 112.4 (dm, $^1J_{CH}$ = 179 Hz, Cp_α*), 110.9 (dm, $^1J_{CH}$ = 174 Hz, Cp_α), 110.0 (dm, $^1J_{CH}$ = 175 Hz, Cp_β*), 109.1 (dm, $^1J_{CH}$ = 177 Hz, Cp_α*), 108.2 (dm, $^1J_{CH}$ = 177 Hz, Cp_β), 59. 6 (dm, $^1J_{CH}$ = 144 Hz, NCH), 59.0 (dm, $^1J_{CH}$ = 145 Hz, NCH*), 27.3 (tm, $^1J_{CH}$ = 133 Hz, CH_2B*), 27.0 (tm, $^1J_{CH}$ = 130 Hz, CH_2B). – ^{11}B NMR (64.2 MHz, [D$_2$]dichloromethane, 300 K): δ = –1.5 ($\nu_{1/2}$ = 920 Hz). – ^{15}N,^{1}H GHMBC (60.8 MHz/599.9 MHz, [D$_2$]dichloromethane, 298 K): $\delta^{15}N/\delta^1H$ = –208.6/5.51 (*N*C*H*), –208.6/1.50 (*N*CH/CH'$_2$B), –209.1/5.11 (*N*C*H**), –209.1/1.52 (*N*CH/C*H'*$_2$B*). – ^{19}F NMR (564.3 MHz, [D$_2$]dichloromethane, 298 K): δ = –132.1 [m, 2 F, *o*-$B(C_6F_5)$], –132.4 [m, 2 F, *o*-$B^*(C_6F_5)$], –136.7 [m, 2 F, *o*-$B(C_6F_5)$'], –137.3 [br. m, 2 F, *o*-$B^*(C_6F_5)$'], –158.0 [m, 1 F, *p*-$B(C_6F_5)$], –158.1 [m, 1 F, *p*-$B^*(C_6F_5)$], –159.8 [m, 1 F, *p*-$B^*(C_6F_5)$'], –159.9 [m, 1 F, *p*-$B(C_6F_5)$'], –164.2 [m, 2 F, *m*-$B^*(C_6F_5)$'], –164.6 [m, 2 F, *m*-$B(C_6F_5)$'], –164.7 [m, 2 F, *m*-$B(C_6F_5)$], –164.9 [m, 2 F, *m*-$B^*(C_6F_5)$].

X-ray Crystal Structure Analysis of 7a: Crystals from C_6D_6, formula $C_{62.5}H_{34.5}B_2F_{20}N_2O_2Zr$, M_r = 1338.26, light-yellow crystal, 0.25 × 0.20 × 0.20 mm, *a* = 12.621(2) Å, *b* = 14.907(2) Å, *c* = 15.900 (2) Å, α = 73.28(1)°, β = 80.74(1)°, γ = 83.67(1)°, *V* = 2821.2(7) Å^3, ρ_{calcd} = 1.575 g cm^{-3}, *F*(000) = 1339 e, μ = 3.09 cm^{-1}, empirical absorption correction based on SORTAV (0.927 ≤ *T* ≤ 0.941), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 198 K, 14406 reflections collected (±*h*, ±*k*, ±*l*), $[(\sin\theta)/\lambda]_{max}$ = 0.59 Å^{-1}, 8208 independent and 6373 observed reflections [$I \geq 2\sigma(I)$], 820 refined parameters, *R* = 0.088, wR^2 = 0.194, max. residual electron density 1.33 (–0.58) e Å^{-3}; the asymmetric unit contains two half-molecules of benzene and one three-quarter-molecule of benzene.

Reaction of 3b with $HB(C_6F_5)_2$. – Formation of 9: To a solution of compound **3b** (190 mg, 427 μmol) in toluene (20 mL) was added bis(pentafluorophenyl)borane (148 mg, 427 μmol). After stirring of the orange solution for 1 day, the solvent was removed in vacuo to provide 293 mg (87%) of the product as an orange solid. – DSC: 99 °C (dec.). – $C_{34}H_{32}BF_{10}N_3OZr$ (790.67): calcd. C 51.65, H 4.08, N 5.31; found C 51.64, H 4.34, N 4.46. – IR (KBr): $\tilde{\nu}$ = 1645, 1599, 1516 cm^{-1}. – ^{1}H NMR (599.9 MHz, [D$_6$]benzene, 298 K): δ = 7.69 (m, 2 H, *o*-Ph), 6.82 (m, 2 H, *m*-Ph), 6.77 (m, 1 H, *p*-Ph), 6.32 (m, 1 H, Cp_α), 6.15 (m, 1 H, Cp_β), 5.89 (m, 1 H, Cp_α), 5.82 (m, 1 H, Cp_β), 5.15 (ps. t, $^3J_{HH}$ = 9.1 Hz, 1 H, NCH), 3.24 (ABX_3, $^{2/3}J_{HH}$ = 7.0 Hz, 2 H, NCH_2CH_3), 3.04 (ABX_3, $^{2/3}J_{HH}$ = 7.0 Hz, 2 H, $N'CH_2CH_3$), 2.97 (ABX_3, $^{2/3}J_{HH}$ = 6.9 Hz, 2 H, NCH'_2CH_3), 2.95 (ABX_3, $^{2/3}J_{HH}$ = 7.0 Hz, 2 H, $N'CH'_2CH_3$), 2.22 (ps. t, $^{2/3}J_{HH}$ = 10.6 Hz, 1 H, CH_2B), 1.73 (ps. t, $^{2/3}J_{HH}$ = 10.3 Hz, 1 H, CH'_2B), 0.85 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, $N'CH_2CH_3$), 0.73 (t, $^3J_{HH}$ = 6.9 Hz, 6 H, NCH_2CH_3). – ^{1}H TOCSY (599.9 MHz, [D$_6$]benzene, 298 K, irradiation at/response at): δ = 7.69 (o-Ph)/6.82 (*m*-Ph), 6.77 (*p*-Ph); 6.32 (Cp_α)/6.15 (Cp_β), 5.89 (Cp_α), 5.82 (Cp_β); 5.15 (NC*H*)/2.22 (C*H*$_2$B), 1.73 (C*H'*$_2$B); 3.24 (NCH_2CH_3)/2.97 (NCH'_2CH_3), 0.73 (NCH_2CH_3); 1.73 (C*H'*$_2$B)/5.15 (NC*H*), 2.22 (C*H*$_2$B); 0.85 ($N'CH_2CH_3$)/3.04 ($N'CH_2CH_3$), 2.95 ($N'CH'_2CH_3$); 0.73 (NCH_2CH_3)/3.24 (NCH_2CH_3), 2.97 (NCH'_2CH_3). – ^{13}C NMR (gated decoupled) (150.8 MHz, [D$_8$]toluene, 298 K): δ = 166.0 (s, OC=N), 149.0 (dm, $^1J_{CF}$ = 243 Hz) and 148.1 (dm, $^1J_{CF}$ = 238 Hz) [*o*-$B(C_6F_5)$, *o*-$B(C_6F_5)$'], 139.8 [ps. d, $^1J_{CF}$ = 247 Hz, *p*-$B(C_6F_5)$, *p*-$B(C_6F_5)$'], 137.7 (dm, $^1J_{CF}$ = 251 Hz) and 137.4 (dm, $^1J_{CF}$ = 251 Hz) [*m*-$B(C_6F_5)$, *m*-$B(C_6F_5)$'], 132.0 (dm, $^1J_{CH}$ = 161 Hz, *p*-Ph), 131.4 (s, *i*-Ph), 123.6, 118.8 [each m, *i*-$B(C_6F_5)_2$], 113.7 (dm, $^1J_{CH}$ = 171 Hz, Cp_α), 113.1 (dm, $^1J_{CH}$ = 174 Hz, Cp_β), 110.2 (dm, $^1J_{CH}$ = 171 Hz, Cp_α), 109.2 (dm, $^1J_{CH}$ = 172 Hz, Cp_β), 60.2 (d, $^1J_{CH}$ = 144 Hz, NCH), 44.0 (t, $^1J_{CH}$ = 132 Hz, $N'CH_2CH_3$), 43.3 (t, $^1J_{CH}$ = 132 Hz, NCH_2CH_3), 27.8 (tm, $^1J_{CH}$ = 134 Hz, CH_2B), 15.8 (q, $^1J_{CH}$ = 126 Hz, $N'CH_2CH_3$), 15.2 (t, $^1J_{CH}$ = 126 Hz, NCH_2CH_3). – ^{11}B NMR (64.2 MHz, [D$_6$]benzene, 300 K): δ = –2.4 ($\nu_{1/2}$ = 420 Hz). – ^{15}N,^{1}H GHMBC (60.8/599.9 MHz, [D$_6$]benzene, 298 K): $\delta^{15}N/\delta^1H$ = –171/0.85 (NCH_2CH_3), –187/0.73 ($N'CH_2CH_3$), –205/5.15 (*N*C*H*). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene, 298 K): δ = –132.5 [m, 2 F, *o*-$B(C_6F_5)$], –136.4 [m, 2 F, *o*-$B(C_6F_5)$'], –158.2 [ps. t, $^3J_{FF}$ = 21 Hz,

1 F, *p*-B(C_6F_5)], –159.0 [ps. t, $^3J_{FF}$ = 21 Hz, 1 F, *p*-B(C_6F_5)'], –163.7 [m, 2 F, *m*-B(C_6F_5)'], –164.4 [m, 2 F, *m*-B(C_6F_5)].

Reaction of 3b with $HB(C_6F_5)_2$ at Low Temperature. – Generation of the Adduct 8: 30 mg (67 μmol) of **3b** was dissolved in [D_8]toluene (0.4 mL) and this solution was cooled to –78 °C and then added to an NMR tube containing a suspension of bis(pentafluorophenyl)borane (23 mg, 67μmol) in [D_8]toluene (0.1 mL) at –78 °C. While warming to room temperature, the NMR tube was shaken until all of the solid had dissolved. After 1 min under ambient conditions, the solution was cooled to 0 °C. Simultaneous formation of compound **9** could not be avoided. At 5 °C, however, the subsequent reaction to **9** is very slow and the adduct **8** could still be detected after 3 weeks. – ^{1}H NMR (599.8 MHz, [D_8]toluene, 273 K): δ = 7.55 (m, 2 H, *o*-Ph), 6.89 (m, 2 H, *m*-Ph), 6.83 (m, 1 H, *p*-Ph), 6.06, 5.77 (each m, each 2 H, Cp), 5.41 (ps. s, 1 H), 5.04 (d, $^2J_{HH}$ = 0.90 Hz, 1 H, C=CH_2), 2.95–2.86 (each m, each 4 H, N$CH_2$$CH_3$, N$CH'_2$$CH_3$), 0.63 (ps. t, $^3J_{HH}$ = 6.9 Hz, 12 H, NCH_2CH_3). – ^{13}C NMR (gated decoupled) (150.8 MHz, [D_8]toluene, 273 K): δ = 135.3 (t, $^2J_{CH}$ = 8 Hz, *i*-Cp), 130.6 (dm, $^1J_{HH}$ = 162 Hz, *p*-Ph), 127.1 (dm, $^1J_{HH}$ = 163 Hz, *o*-Ph), 111.5 (d, $^1J_{CH}$ = 175 Hz, Cp), 110.6 (d, $^1J_{CH}$ = 171 Hz, Cp), 43.6 (t, $^1J_{CH}$ = 130 Hz, NCH_2CH_3), 15.3 (q, $^1J_{HH}$ = 127 Hz, NCH_2CH_3); the *m*-Ph and *i*-Cp signals are obscured by those of the solvent. – ^{11}B NMR (64.2 MHz, [D_6]benzene, 300 K): δ = –11.6 (d, $^1J_{BH}$ = 60 Hz, $\nu_{1/2}$ = 390 Hz). – ^{15}N,^{1}H GHMBC (60.8/599.8 MHz, [D_8]toluene, 273 K): δ^{15}N/δ^1H = –204/5.04 (OC=*N*/C=CH_2), –173/0.63 (*N*CH_2CH_3). – ^{19}F NMR (564.3 MHz, [D_6]benzene, 298 K): δ = –133.3 [br. ps. s, 4 F, *o*-B(C_6F_5)$_2$], –159.7 [ps. t, $^3J_{FF}$ = 20.6 Hz, 2 F, *p*-B(C_6F_5)$_2$], –164.8 [br. ps. s, 4 F, *m*-B(C_6F_5)$_2$].

Propene Polymerization Reactions. – General Procedure: A thermostated Büchi glass autoclave (25 °C) was charged with toluene (300 mL) and 20 mL of a 10% (1.6 M) methylalumoxane solution in toluene. Propene was introduced at a pressure of 2.0 bar. After 0.5 h, a solution of the organometallic catalyst precursor in 5 mL of toluene was added and the polymerization reaction allowed to proceed for 2.0 h. The system was then vented and its contents were quenched by treatment with aqueous HCl/CH_3OH (1:1). The layers were separated and the aqueous phase was extracted with toluene (3 × 100 mL). The combined organic layers were then washed with aqueous HCl (3 × 100 mL) and with water (3 × 100 mL) to remove inorganic salts. Evaporation of the solvent afforded the polymers as very viscous oils (see Table 1).

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