Organic Functional Group Transformations in the Periphery of a Group-4 Metallocene Complex: 2*H*-Pyrrole Formation at a Pendant Boron Lewis Acid

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The allyl-substituted *ansa*-zirconocene dichloride [$Me_2Si(C_5H_4)(C_5H_3CH_2CH{=}CH_2)ZrCl_2$] (**1**) cleanly adds the borane 9-BBN to the allyl C=C double bond to yield the corresponding hydroboration product **2**. The borane $HB(C_6F_5)_2$ (**3**) is also added regioselectively to **1** to yield [$Me_2Si(C_5H_4)\{C_5H_3(CH_2)_3B(C_6F_5)_2\}ZrCl_2$] (**4**). The strongly electrophilic boron Lewis acid in **4** adds 2-methyl-4,5-dihydrooxazole to yield **6**. Treatment of **4** with pyrrole results in the formation of the respective borane adduct **7** of the pyrrole tautomer 2*H*-pyrrole. The 2*H*-pyrrole ligand in **7** is deprotonated at C-2 upon treatment with pyridine, followed by proton transfer and replacement of pyrrole with formation of the corresponding pyridine adduct **12**. The complexes **1**, **4** and **7** were characterized by X-ray diffraction.

Introduction

There are numerous examples showing that typical organic functional group chemistry can be carried out at the Cp ligands of many transition metals from the middle and the right-hand side of the Periodic Table.[1] This is much more difficult to achieve in the case of the Group-4 metallocenes (and the corresponding complexes of the oxophilic f-block elements). Functional group chemistry here is usually carried out at the stage of the free ligand. Usually the functionalized Cp ligands are then subsequently attached to the respective metal centre.[2,3] Introduction of functional groups at the Cp rings of Cp_2ZrCl_2, for example, or conversion of functional groups at the zirconocene Cp rings is much more difficult, and consequently only a limited number of examples of such chemistry has so far been described in the literature. Noteworthy examples include Mannich-type enamine coupling reactions[4] and photochemical [2+2] cycloadditions,[5] both producing novel variants of *ansa*-metallocenes. The olefin metathesis reaction has been used for intra- and intermolecular carbon coupling reactions at bent metallocenes.[6] Moreover, various types of borylation[7] and hydroboration reactions[8] have been shown to be compatible with the general chemical features of many Group-4 metallocene complexes and related systems. We have now used such a reaction to attach a highly electrophilic borane at a Cp side chain of an *ansa*-metallocene and to carry out Lewis acid promoted reactions at the boron centre in the direct vicinity of the mildly electrophilic Group-4 metal centre. A first example is described in this article. We hope that our findings may contribute to the eventual development of novel bifunctional transition metal/main group element systems well suited for selective organic reactions, that may otherwise be hard to achieve, within such specific frameworks.

Results and Discussion

We had previously shown that [(allyl-C_5H_4)Cp] zirconium dichloride complexes can be cleanly hydroborated at the pendant allyl group.[8] Piers recently showed that similar $HB(C_6F_5)_2$[9] additions at such systems were feasible.[10] Such hydroboration reactions at open, unbridged Group-4 metallocenes (and at some related "constrained geometry" Zr complexes[10]) provided the synthetic basis for this work. We have now extended these reactions to the allyl-substituted rigid *ansa*-metallocene dichloride complex **1**. In contrast to the previously employed unbridged bent metallocenes,[8,10] the system **1** is no longer conformationally flexible but has its pendant functional group oriented towards the (chemically active) front side of the bent metallocene wedge.

Complex **1** was prepared as recently described by us[11] by adaptation of established literature procedures.[12] The X-ray crystal structure analysis of **1** was carried out and described previously.[11]

Treatment of **1** with 9-BBN was carried out in toluene at room temperature. The reaction was rather slow and required overnight stirring to go to completion. The hydroborated product **2** was isolated as a solid in almost quantitative yield. Complex **2** contains a chiral *ansa*-metallocene backbone, and therefore shows a total of seven ^1H NMR

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methine signals of the two substituted Cp-type ligands [δ = 6.61, 5.91, 5.54 (C_5H_3), 7.02, 6.92, 5.98, 5.82 (C_5H_4) ppm] and a 1:1 intensity pair of Si−CH_3 signals (δ = 0.72, 0.69 ppm). It also shows three distinct ^{1}H NMR multiplets for the connecting trimethylene bridging unit (δ = 2.69, 1.75, 1.40 ppm) and the signals of the BBN residue.

Single crystals suitable for the X-ray crystal structure determination of **2** were obtained from a dichloromethane solution at −30 °C. In the solid state, complex **2** has a rigid *ansa*-metallocene framework. Because of the geometric constraints in such a system the Zr−C(Cp) bond lengths vary from 2.443(3) to 2.596(3) Å inside the C_5H_3 unit and from 2.471(3) to 2.535(3) Å inside the Zr(C_5H_4) moiety. The smaller values are found at the narrow backside of the bent metallocene wedge oriented toward the $SiMe_2$ unit. The C1−Si and C8−Si bond lengths are 1.866(3) and 1.862(3) Å, respectively. These (sp^2)C−Si bonds are slightly longer than the adjacent (sp^3)C−Si linkages [C6−Si 1.846(4) Å, C7−Si 1.849(4) Å], which is an additional indication that the *ansa*-metallocene framework is strained. The C1−Si−C8 angle is found at 93.6(1)° and the Cp(centroid)−Zr−Cp(centroid) angle in **2** is 126.0°. The Cl1−Zr−Cl2 angle is in the normal range at 99.60(4)°.

The attached −$(CH_2)_3$−BBN side chain is pointing toward the open front side of the bent metallocene wedge [C11−C13 1.499(5) Å] and is arranged at a maximum extension such as to bring the bulky −BBN group away from the $ZrCl_2$ unit (see Figure 1). This extended conformational arrangement is characterized by the corresponding dihedral angles C12−C11−C13−C14 −85.0(4)°, C11−C13−C14−C15 −179.2(3)°, and C13−C14−C15−B −172.3(4)°.

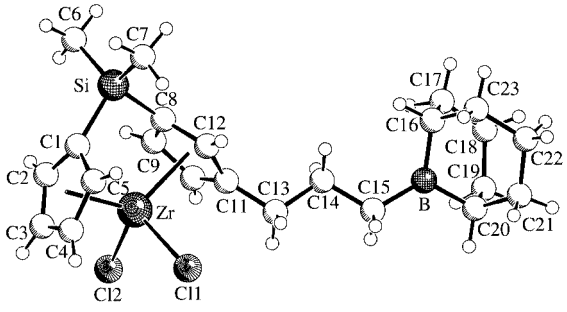


Figure 1. A view of the molecular geometry of complex **2**; selected bond lengths [Å] and angles (°): Zr−Cl1 2.431(1), Zr−Cl2 2.431(1), Si−C1 1.866(3), Si−C8 1.862(3), Si−C6 1.846(4), Si−C7 1.849(4), C11−C13 1.499(5), C13−C14 1.526(5), C14−C15 1.517(5), C15−B 1.555(6), B−C16 1.569(6), B−C20 1.566(6); Cl1−Zr−Cl2 99.60(4), C1−Si−C8 93.6(1), C1−Si−C6 112.6(2), C1−Si−C7 110.8(2), C8−Si−C6 112.7(2), C8−Si−C7 110.4(2), C6−Si−C7 114.8(2), C11−C13−C14 111.5(3), C13−C14−C15 113.6(3), C14−C15−B 118.3(3), C15−B−C16 126.3(4), C15−B−C20 122.5(4), C16−B−C20 111.1(4)

From its monomer/dimer equilibrium[9] the borane $HB(C_6F_5)_2$ (**3**) reacts much more rapidly with **1**. The hydroboration reaction was complete after ca. 30 min at room temperature in toluene solution, and the product **4** was isolated in a close to quantitative yield. It shows NMR spectroscopic features very similar to those of **2**, which let us assume that both complexes have similar structures. The chiral metallocene core shows a total of seven ^{1}H NMR methane signals, at δ = 6.56, 5.87, 5.47 (C_5H_3) and 7.00, 6.92, 5.96, 5.80 (C_5H_4) ppm. The ^{1}H NMR resonances of the trimethylene side chain of **4** occur at δ = 2.72, 1.96 and 1.80 ppm, with corresponding ^{13}C NMR features at δ = 32.3, 30.9 and 25.5 ppm. As would be expected, the pair of C_6F_5 groups at the boron atom behaves in symmetry-equivalent fashion in solution, producing a single set of *o*-, *p*- and *m*-^{19}F resonances at δ = −130.2, −148.6 and −160.8 ppm, respectively. The strongly electrophilic boron centre does not interact with the $ZrCl_2$ moiety in **4**. The ^{11}B NMR chemical shift of δ = 75.6 ppm ($\nu_{1/2} \approx 190$ Hz) indicates the presence of a coordinatively unsaturated tricoordinate boron centre [similarly to $B(C_6F_5)_3$:[13] δ(^{11}B) = 60.0 ($\nu_{1/2} \approx 400$ Hz); in contrast the dimeric $[HB(C_6F_5)_2]_2$ reagent features δ(^{11}B{^{1}H}) = 19.5 ($\nu_{1/2} \approx$ 320 Hz), as would be expected for a dimeric doubly H-bridged structure with two tetracoordinate boron atoms present].

Complex **4** reacts rapidly with a variety of two-electron donor ligands.[14] A typical product is the 2-methyl-4,5-dihydrooxazole adduct **6**, the molecular structure of which is depicted in Figure 2. Complex **6** was formed readily by treatment of **4** with the heterocyclic donor ligand in toluene solution at room temperature (see the Exp. Sect. for details). The attached trimethylene chain again adopts a fully extended "zigzag" conformation featuring a series of antiperiplanar conformational arrays [dihedral angles C11−C13−C14−C15 −175.4(2)°, C13−C14−C15−B −176.6(2)°]. This arrangement resembles the conformation of the side chain in **4** (see above and Figure 1), except that its torsional orientation relative to the adjacent Cp ring is quite different. In **4** (see above), the substituent chain is rotated *away* from the Cp plane, whereas in **6** it is rotated almost by 90° so that the w-shaped carbon skeleton of the side chain is now lying almost coplanar with its adjacent C8−C11 η^5-C_5H_4 ring [dihedral angle C10−C11−C13−C14 −25.8(3)°]. This brings the boron centre in the adduct **6** much closer to the zirconium atom (B···Zr separation in **6**: 6.395Å, in **2**: 7.621Å) and it brings the attached heterocycle almost in a direct opposition to the $ZrCl_2$ unit at the front side of the bent metallocene unit. The corresponding dihedral angles are −77.5(3)° (C14−C15−B−N1) and −2.8(4)° (C15−B−N1−C18). The bonding features of the dihydrooxazole heterocycle have not changed much upon complexation to the boron atom [N1−C16 1.277(3) Å, C16−O1 1.323(3) Å, N1−C18 1.507(4) Å].[15] The N1−B bond length is 1.626(4) Å, which is similar to the adjacent B−C bond lengths [B−C(aryl) 1.651(4) and 1.664(4) Å; B−C15 1.636(4) Å]. The N−B−C15 bond angle was found to be 110.1(2)°. The remaining bond angles at the boron atom were found to lie in a range between 105.0(2)° (N1−B−C31) and 114.0(2)° (C21−B−C31). With regard to their conformational orientation, the B−N vector is oriented almost coplanar with the C21−C26 aryl plane [dihedral angle C22−C21−B−N1 14.3(3)°] whereas it adopts a gauche orientation with the C31−C36 aryl ring [C32−C31−B−N1 −69.5(3)°].

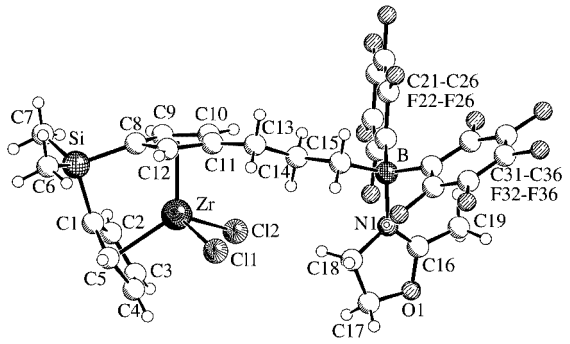
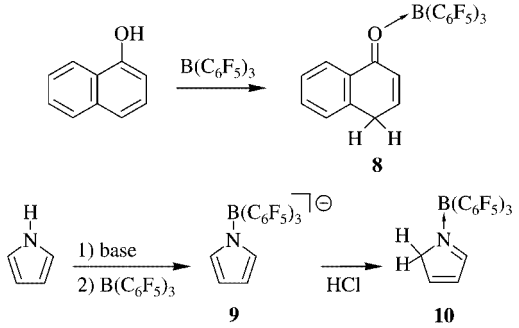


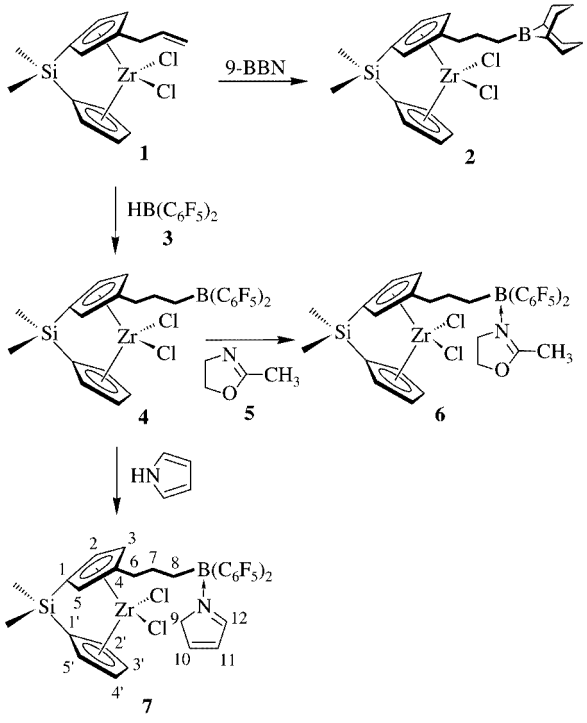
Figure 2. Molecular structure of the adduct **6**; selected bond lengths [Å] and angles [°]: Zr−Cl1 2.440(1), Zr−Cl2 2.445(1), Si−C1 1.868(2), Si−C8 1.877(2), Si−C6 1.847(3), Si−C7 1.846(3), C11−C13 1.501(3), C13−C14 1.527(3), C14−C15 1.528(3), C15−B 1.636(4), B−N1 1.626(4), B−C21 1.651(4), B−C31 1.664(4), N1−C16 1.277(3), N1−C18 1.507(4), C16−O1 1.323(3), C16−C19 1.467(4), O1−C17 1.451(4), C17−C18 1.491(4); Cl1−Zr−Cl2 95.56(3), C1−Si−C8 93.8(1), C1−Si−C6 110.9(1), C1−Si−C7 112.6(1), C8−Si−C6 112.7(1), C8−Si−C7 111.7(1), C6−Si−C7 113.5(1), C11−C13−C14 113.3(2), C13−C14−C15 114.1(2), C14−C15−B 115.8(2), C15−B−N1 110.1(2), C15−B−C21 106.4(2), C15−B−C31 110.1(2), N1−B−C21 111.2(2), N1−B−C31 105.0(2), C21−B−C31 114.0(2), B−N1−C16 128.9(2), B−N1−C18 123.4(2), C16−N1−C18 107.7(2), N1−C16−O1 116.5(3), N1−C16−C19 127.6(3), C19−C16−O1 115.9(2), C16−O1−C17 107.6(2), O1−C17−C18 105.3(2), C17−C18−N1 102.9(2)

We had previously shown that unstable tautomers of a variety of aromatic and heteroaromatic compounds can be formed and stabilized by coordination to the strong organometallic Lewis acid $B(C_6F_5)_3$. The first examples included the α-naphthol/benzocyclohexadienone tautomerism (see Scheme 1).[16] We have also formed the 2*H*-pyrrole tautomer from its parent hetarene in the $B(C_6F_5)_3$ coordination sphere by a three-step procedure involving deprotonation at the nitrogen atom, attachment at the boron atom, and then protonation at the carbon atom to yield the 2*H*-pyrrole/$B(C_6F_5)_3$ adduct **10**.[17] Resconi has recently found a direct route yielding examples of the compound type **10** by treatment of pyrrole derivatives with $B(C_6F_5)_3$.[18]



Scheme 1

We were able to carry out such a pyrrole/2*H*-pyrrole tautomerism reaction at the *ansa*-zirconocene−trimethylene−$B(C_6F_5)_2$ complex **7**. A mixture of **4** and pyrrole was stirred in toluene/diethyl ether solution at room temperature for 18 h. During this time a close to quantitative conversion of the hetarene took place, with formation of the 2*H*-pyrrole adduct **7**. The coordination of the "isopyrrole tautomer" to the boron atom was apparent from the characteristic NMR spectra. The 2*H*-pyrrole moiety gave rise to a set of three methine ^{1}H NMR signals, one at rather low field (δ = 7.65 ppm, −N=C*H*−), the other two at δ = 6.42 ppm (10-H, see Scheme 2) and 5.61 (11-H) [corresponding ^{13}C NMR signals at δ = 169.3 (−N=*C*H−), 127.1 (C-11), 154.2 ppm (C-10)]. The remaining $N-CH_2$ group gives rise to a characteristic AB pattern at δ = 3.72 and 3.68 ppm ($^2J_{H,H}$ = 27 Hz, ^{13}C signal at δ = 65.0 ppm). The diastereotopic splitting of the 9-H/H′ ^{1}H NMR resonance of the 2*H*-pyrrole moiety is due to the chirality of the metal complex backbone. This also becomes evident in **7** in the partial splitting of the 7-H/H′ (δ = 1.52/1.36) and 8-H/H′ (δ = 1.36/1.21) signals of the bridging trimethylene unit (6-H/H′ ^{1}H NMR resonance at δ = 2.83 ppm). As would be expected, a 1:1 intensity pair of $SiMe_2$ ^{1}H NMR methyl resonances is observed for **7** (δ = 0.14 and 0.08 ppm). The diastereotopic splitting is even extended into the $B(C_6F_5)_2$ unit. The two pentafluorophenyl groups at the tetravalent boron centre [δ(^{11}B) = 4.7, $\nu_{1/2} \approx 414$ Hz)] have become diastereotopic. Consequently, we observed equal intensity pairs of ^{19}F NMR signals of the *ortho*- (δ = −158.1 and −158.2 ppm) and *para*-C_6F_5 signals (δ = −132.6 and −132.9 ppm). The *meta*-C_6F_5 resonances of the two diastereotopic C_6F_5 ligands are isochronous (δ = −163.3 ppm).



Scheme 2

Single crystals of **7** were obtained from a concentrated toluene solution at room temperature. The X-ray crystal

structure analysis confirms the formation of the 2*H*-pyrrole unit. The C_4H_5N moiety shows a short N=C bond inside the heterocyclic ring system [see Figure 3, N1−C16 1.294(4) Å], whereas the adjacent N1−C19 linkage [1.462(4) Å] denotes the presence of a single bond. The remaining framework of the five-membered nitrogen heterocycle exhibits a typical bond alternation [C16−C17 1.443(5) Å, C17−C18 1.326(5) Å, C18−C19 1.474(4) Å]. The N1−B bond length amounts to 1.612(4) Å, and the N1−B−C15 bond angle is found at 107.9(2)°. The remaining bond angles at the boron atom are within a range of 103.3(2) to 116.1(2)°.

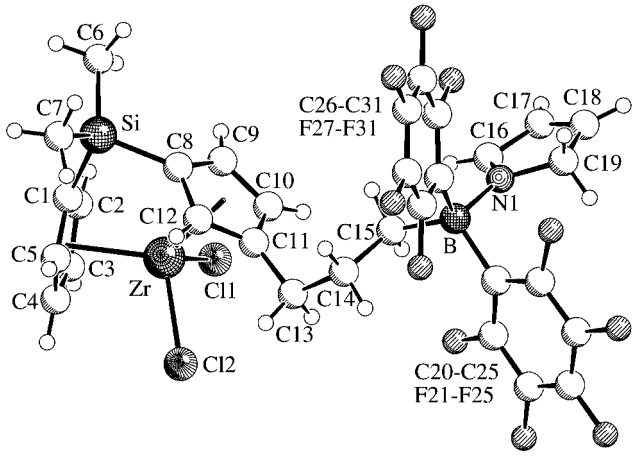
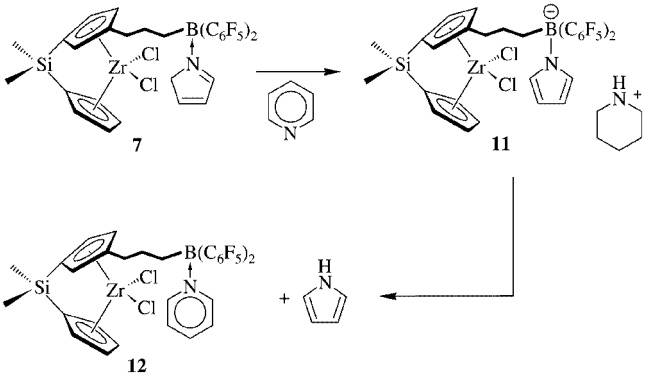


Figure 3. A projection of the molecular geometry of the 2*H*-pyrrole addition product **7**; selected bond lengths [Å] and angles [°]: Zr−Cl1 2.448(1), Zr−Cl2 2.414(1), Si−C1 1.877(3), Si−C8 1.875(3), Si−C6 1.845(4), Si−C7 1.857(4), C11−C13 1.506(4), C13−C14 1.541(4), C14−C15 1.531(4), C15−B 1.631(4), B−N1 1.612(4), B−C20 1.653(5), B−C26 1.651(4), N1−C16 1.294(4), N1−C19 1.462(4), C16−C17 1.443(5), C17−C18 1.326(5), C18−C19 1.474(4); Cl1−Zr−Cl2 98.76(4), C1−Si−C8 94.8(1), C1−Si−C6 112.5(2), C1−Si−C7 110.7(2), C8−Si−C6 110.6(2), C8−Si−C7 112.1(2), C6−Si−C7 114.5(2), C11−C13−C14 113.8(3), C13−C14−C15 113.1(3), C14−C15−B 115.9(2), C15−B−N1 107.9(2), C15−B−C20 116.1(2), C15−B−C26 108.4(2), N1−B−C20 103.3(2), N1−B−C26 108.8(2), C20−B−C26 112.0(2), B−N1−C16 126.9(3), B−N1−C19 125.3(2), C16−N1−C19 107.8(3), N1−C16−C17 111.8(3), C16−C17−C18 107.3(3), C17−C18−C19 108.7(3), C18−C19−N1 104.3(3)

The 2*H*-pyrrole unit is oriented in plane with the B1−C15 vector [dihedral angle C16−N1−B−C15 2.5(4)°]. The connecting trimethylene chain between the *ansa*-metallocene framework and the borate section of **7** adopts a conformation different from those of the two complexes **2** and **6** (see above). As can be seen from the projection of **7**, depicted in Figure 3, the $-(CH_2)_3-$ chain in **7** contains an additional gauche conformation [C11−C13−C14−C15 −63.0(4)°]. The C13−C14−C15−B1 arrangement is antiperiplanar [θ = −165.9(3)°] and the C10−C11−C13−C14 dihedral angle [84.1(4)°] removes the borate end away from the centre of the metallocene unit. Consequently, the Zr···B separation in **7** (6.837Å) is smaller than in **2** (7.621Å) but larger than in **6** (6.395Å).

The methylene hydrogen atoms of the previously prepared and studied 2*H*-pyrrole/$B(C_6F_5)_3$ adduct **10** are rather acidic. The system **10** has been used as a Brønsted acid activator component for generating homogeneous Ziegler−Natta catalyst systems.[17] The 2*H*-pyrrole methylene hydrogen atoms are also acidic. Treatment with pyridine as a base removed one of these hydrogen atoms. We assume that salt **11** may be formed as an intermediate, and may then have reacted further in an acid/base reaction to yield the stable adduct **12** and free pyrrole (see Scheme 3).



Scheme 3

We next intend to try to make use of the specific coordinative features of such main group element/transition metal combinations and to investigate whether the zirconocene units in adducts such as **6** or **7** can be activated to undergo, for example, C−H or C−C activation reactions with substrates attached at their neighbouring electrophilic borane centre.

Experimental Section

General: All reactions were carried out under dry argon in Schlenk-type glassware or in a glove-box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. For additional general conditions, including a list of instruments used for a physical characterization of the compounds see ref.[6] Most NMR assignments were secured by carrying out a variety of 2D NMR experiments.[19]

X-ray Crystal Structure Analyses: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., **1998**), data reduction Denzo-SMN,[20] absorption correction SORTAV,[21] structure solution SHELXS-97,[22] structure refinement SHELXL-97,[23] graphics SCHAKAL.[24] CCDC-202081 to -202083 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of the *ansa*-Zirconocene Dichloride Complex 1: Chilled toluene (250 mL, −78 °C) was added to a solid mixture of the reagent $[Me_2Si(3\text{-}C_5H_3CH_2CH{=}CH_2)(C_5H_4)Li_2]$ (3.47 g, 14.5 mmol) and $ZrCl_4$ (3.37 g, 14.5 mmol). The suspension immediately became yellow. It was allowed to warm to room temperature with stirring. After stirring overnight, the yellow suspension was filtered through Celite. Removal of the volatiles in vacuo pro-

vided the product (3.23 g, 57%) as a yellow solid. M.p. 104 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.03 (m, 1 H, 4′-H), 6.93 (m, 1 H, 3′-H), 6.60 (m, 1 H, 3-H), 5.98 (m, 1 H, 2′-H), 5.92 (m, 3 H, 2-H, 7-H), 5.82 (m, 1 H, 5′-H), 5.54 (m, 1 H, 5-H), 5.06, 5.04 (each m, each 1 H, 8-H, 8-H′), 3.47, 3.38 (each m, each 1 H, 6-H, 6-H′), 0.72, 0.69 [each s, each 3 H, $Si(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 141.0 (C-4), 135.9 (C-7), 128.0 (C-3), 127.8 (C-3′), 127.7 (C-4′), 116.7 (C-8), 115.3 (C-2), 114.1 (C-2′), 113.6 (C-5′), 113.5 (C-5), 107.9 (C-1), 107.8 (C-1′), 34.3 (C-6), −5.1, −5.3 [$Si(CH_3)_2$] ppm. $C_{15}H_{18}Cl_2SiZr$ (388.5): calcd. C 46.37, H 4.67; found C 46.26, H 4.70.

Treatment of Complex 1 with 9-BBN; Preparation of Complex 2: 9-BBN (95 mg, 78.0 mmol) and **1** (302 mg, 78.0 mmol) were combined in a flask, and toluene (20 mL) was added at room temperature. The reaction mixture was stirred for 12 h. The solvent was removed in vacuo, which provided the product (381 mg, 97%) as a light yellow solid. Crystals suitable for an X-ray crystal structure analysis were obtained from a concentrated solution in dichloromethane at −30 °C. M.p. 155 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.02 (m, 1 H, 4′-H), 6.92 (m, 1 H, 3′-H), 6.61 (m, 1 H, 3-H), 5.98 (m, 1 H, 2′-H), 5.91 (m, 1 H, 2-H), 5.82 (m, 1 H, 5′-H), 5.54 (m, 1 H, 5-H), 2.69 (m, 2 H, 6-H), 1.81, 1.64 (each m, each 4 H, 10-H), 1.81, 1.18 (each m, each 2 H, 11-H), 1.75 (m, 2 H, 7-H), 1.64 (m, 2 H, 9-H), 1.40 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, 8-H), 0.72, 0.69 [each s, each 3 H, $Si(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 143.9 (C-4), 127.9 (C-3), 127.7 (C-3′), 127.5 (C-4′), 115.2 (C-2), 113.9 (C-2′), 113.7 (C-5), 113.6 (C-5′), 107.6 (C-1), 107.5 (C-1′), 33.1 (C-6), 33.1 (C-10), 31.0 (br., C-9), 27.9 (br., C-8), 25.4 (C-7), 23.2 (C-11), −5.1, −5.2 [$Si(CH_3)_2$] ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 64 MHz): δ = 86.8 ($\nu_{1/2}$ = 320 Hz) ppm. $C_{23}H_{33}BCl_2SiZr$ (510.5): calcd. C 54.11, H 6.52; found C 53.09, H 6.54.

X-ray Crystal Structure Analysis of 2: Empirical formula $C_{23}H_{33}BCl_2SiZr$, M = 510.51, colourless crystal 0.40 × 0.25 × 0.05 mm, a = 8.175(1), b = 26.251(1), c = 11.251(1) Å, β = 98.13(1)°, V = 2390.2(4) Å^3, $\rho_{calcd.}$ = 1.419 g cm^{-3}, μ = 7.41 cm^{-1}, empirical absorption correction (0.756 ≤ T ≤ 0.964), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 9625 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.65 Å^{-1}, 5428 independent (R_{int} = 0.028) and 4617 observed reflections [$I \geq 2\ \sigma(I)$], 255 refined parameters, R = 0.045, wR^2 = 0.105, max. residual electron density 1.27 (−0.68) e·Å^{-3} close to the $ZrCl_2$ core, hydrogen atoms calculated and refined as riding atoms.

Treatment of Complex 1 with $HB(C_6F_5)_2$ (3); Preparation of Complex 4: Bis(pentafluorophenyl)borane (254 mg, 73.0 mmol) and **1** (285 mg, 73.0 mmol) were combined in a flask, and toluene (50 mL) was transferred into the flask at 0 °C. The reaction mixture was stirred while being allowed to warm to room temperature, and the volatiles were removed in vacuo, resulting in the product (524 mg, 97%) as a light yellow solid. M.p. 142 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.00 (m, 1 H, 4′-H), 6.92 (m, 1 H, 3′-H), 6.56 (m, 1 H, 3-H), 5.96 (m, 1 H, 2′-H), 5.87 (m, 1 H, 2-H), 5.80 (m, 1 H, 5′-H), 5.47 (m, 1 H, 5-H), 2.72 (m, 2 H, 6-H), 1.96 (m, 2 H, 7-H), 1.80 (m, 2 H, 8-H), 0.72, 0.66 [each s, each 3 H, $Si(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 146.8 (dm, $^1J_{C,F}$ = 246.1 Hz), 143.4 (dm, $^1J_{C,F}$ = 249.7 Hz), 137.4 (dm, $^1J_{C,F}$ = 258.0 Hz) (*o*-, *p*-, *m*-C_6F_5), 142.1 (C-4), 128.2 (C-3′), 127.8 (C-3), 126.9 (C-4′), 114.9 (C-2), 114.3 (C-5′), 113.8 (C-2′), 113.6 (C-5), 107.7 (C-1), 107.6 (C-1′), 32.3 (C-6), 30.9 (C-7), 25.5 (C-8), −5.6, −5.7 [$Si(CH_3)_2$] ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 64 MHz): δ = 75.6 ($\nu_{1/2}$ = 190 Hz). ^{19}F NMR ($CDCl_3$, 564 MHz): δ = −130.2 (m, *o*-C_6F_5), −148.6 (m, *p*-C_6F_5), −160.8 (m, *m*-C_6F_5) ppm. $C_{27}H_{19}BCl_2F_{10}SiZr$ (734.5): calcd. C 44.15, H 2.61; found C 43.23, H 2.56.

Treatment of 4 with 2-Methyl-4,5-dihydrooxazole; Formation of the Dihydrooxazole Adduct 6: A solution of 2-methyl-4,5-dihydrooxazole (9 mg, 104.8 mmol) in toluene (20 mL) was added at room temperature to a light yellow solution of **4** (77 mg, 104.8 mmol) in toluene (20 mL) and the mixture was stirred for 0.5 h. Removal of the volatiles in vacuo provided the product (85 mg, 99%) as a light yellow solid. Crystals suitable for an X-ray crystal structure analysis were obtained from a concentrated solution in benzene at room temperature. ^{1}H NMR (C_7D_8, 600 MHz): δ = 6.68 (m, 1 H, 4′-H), 6.67 (m, 1 H, 3′-H), 6.50 (m, 1 H, 3-H), 5.38 (m, 1 H, 2′-H), 5.37 (m, 1 H, 2-H), 5.33 (m, 1 H, 5′-H), 5.15 (m, 1 H, 5-H), 3.45/3.39 (each m, each 1 H, dihydrooxazole-CH_2), 3.38/3.26 (each m, each 1 H, dihydrooxazole-CH_2), 2.80/2.75 (each m, each 1 H, 6-H, 6-H′), 1.43/1.29 (each m, each 1 H, 7-H, 7-H′), 1.37/1.12 (each m, each 1 H, 8-H, 8-H′), 1.36 (s, 3 H, dihydrooxazole-CH_3), 0.13/0.06 [each s, each 3 H, $Si(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (C_7D_8, 150 MHz): δ = 174.4 (dihydrooxazole-C), 142.5 (C-4), 129.2 (C-3′), 128.4 (C-3), 125.8 (C-4′), 114.7 (C-5′), 114.6 (C-5), 113.6 (C-2), 112.4 (C-2′), 107.8 (C-1′), 107.2 (C-1), 67.9/51.3 (dihydrooxazole-CH_2), 33.1 (C-6), 26.9 (C-7), 22.9 (C-8), 13.1 (dihydrooxazole-CH_3), −5.7, −6.4 [$Si(CH_3)_2$]; 148.5 ($^1J_{C,F}$ = 239.7 Hz), 139.7 ($^1J_{C,F}$ = 240.6 Hz), 137.6 ($^1J_{C,F}$ = 253.9 Hz), 120.6 (*o*-, *p*-, *m*-, *ipso*-C_6F_5) ppm. $^{11}B\{^1H\}$ NMR (C_7D_8, 64 MHz): δ = −5.0 ($\nu_{1/2}$ = 290 Hz) ppm. ^{19}F NMR (C_7D_8, 564 MHz): δ = −133.2/−133.7 (each m, each 2 F, *o*-C_6F_5), −158.1/−158.4 (each t, each 1 F, $^3J_{FF}$ = 20.6/20.8 Hz, *p*-C_6F_5), −163.4/−163.5 (each m, each 2 F, *m*-C_6F_5) ppm. $C_{31}H_{26}BCl_2F_{10}NOSiZr$ (819.6): calcd. C 45.43, H 3.20, N 1.71; found C 45.15, H 3.05, N 1.65.

X-ray Crystal Structure Analysis of 6: Empirical formula $C_{31}H_{26}BCl_2F_{10}NOSiZr{\cdot}1/2C_6H_6$, M = 858.60, colourless crystal 0.30 × 0.15 × 0.10 mm, a = 8.017(1), b = 11.120(1), c = 20.434(1) Å, α = 87.13(1), β = 84.78(1), γ = 81.23(1)°, V = 1791.7(3) Å^3, $\rho_{calcd.}$ = 1.592 g cm^{-3}, μ = 5.71 cm^{-1}, empirical absorption correction (0.847 ≤ T ≤ 0.945), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 10918 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.65 Å^{-1}, 7958 independent (R_{int} = 0.017) and 6149 observed reflections [$I \geq 2\ \sigma(I)$], 463 refined parameters, R = 0.037, wR^2 = 0.083, max. residual electron density 0.38 (−0.40) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Treatment of 4 with Pyrrole; Formation of the 2*H*-Pyrrole Adduct 7: A solution of pyrrole (37 mg, 0.54 mmol) in toluene (10 mL) was added at room temperature to a light yellow solution of **4** (406 mg, 0.51 mmol) in toluene/diethyl ether (10:1, 20 mL), and the mixture was stirred for 18 h. Removal of the volatiles in vacuo provided the product (407 mg, 99%) as a light yellow solid. Crystals suitable for an X-ray crystal structure analysis were obtained from a concentrated solution in toluene at room temperature. ^{1}H NMR (C_7D_8, 600 MHz): δ = 7.65 (br. s, 1 H, 12-H), 6.72 (m, 1 H, 4′-H), 6.66 (m, 1 H, 3′-H), 6.48 (m, 1 H, 3-H), 6.42 (dq, $^3J_{10\text{-}H,11\text{-}H}$ = 5.5, $^4J_{10\text{-}H,12\text{-}H}$ = 0.9 Hz, 1 H, 10-H), 5.61 (dq, $^3J_{10\text{-}H,11\text{-}H}$ = 5.5, $^3J_{11\text{-}H,12\text{-}H}$ = 1.1, $^4J_{9\text{-}H,11\text{-}H}$ = 1.3 Hz, 1 H, 11-H), 5.43 (m, 1 H, 2′-H), 5.38 (m, 1 H, 2-H), 5.32 (m, 1 H, 5′-H), 5.17 (m, 1 H, 5-H), 3.72/3.68 (AB, $^2J_{H,H}$ = 26.7 Hz, each 1 H, 9-H, 9-H′), 2.83 (m, 2 H, 6-H, 6-H′), 1.52/1.36 (each m, each 1 H, 7-H, 7-H′), 1.36/1.21 (each m, each 1 H, 8-H, 8-H′), 0.14/0.08 [each s, each 3 H, $Si(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (C_7D_8, 150 MHz): δ = 169.3 (C-12), 154.2 (C-10), 143.1 (C-4), 128.7 (C-3′), 128.6 (C-3), 127.1 (C-11), 125.6 (C-4′), 114.2 (C-2), 114.0 (C-5), 114.0 (C-5′), 113.1 (C-

2′), 107.8 (C-1′), 107.4 (C-1), 65.0 (C-9), 33.4 (C-6), 27.0 (C-7), 24.2 (C-8), −6.8, −5.9 [Si(CH_3)$_2$]; 148.4 ($^1J_{C,F}$ = 240.0 Hz), 139.8 ($^1J_{C,F}$ = 248.6 Hz), 137.6 ($^1J_{C,F}$ = 250.3 Hz), 121.4 (*o*-, *p*-, *m*-, *ipso*-C_6F_5) ppm. $^{11}B\{^1H\}$ NMR (C_7D_8, 64 MHz): δ = 4.7 ($\nu_{1/2}$ = 415 Hz) ppm. ^{19}F NMR (C_7D_8, 564 MHz): δ = −132.6/−132.9 (each m, each 2 F, *o*-C_6F_5), −158.1/−158.2 (each t, each 1 F, $^3J_{FF}$ = 21.0/20.6 Hz, *p*-C_6F_5), −163.3 (m, 4 F, *m*-C_6F_5) ppm. $C_{31}H_{24}BCl_2F_{10}NSiZr$ (801.5): calcd. C 46.45, H 3.02, N 1.75; found C 46.84, H 3.30, N 1.40.

X-ray Crystal Structure Analysis of 7: Empirical formula $C_{31}H_{24}BCl_2F_{10}NSiZr{\cdot}C_7H_8$, M = 893.67, light yellow crystal 0.30 × 0.20 × 0.20 mm, a = 10.371(1), b = 14.683(1), c = 15.239(1) Å, α = 115.75(1), β = 96.40(1), γ = 107.10(1)°, V = 1919.0(3) Å^3, $\rho_{calcd.}$ = 1.547 g cm^{-3}, μ = 5.35 cm^{-1}, empirical absorption correction (0.856 ≤ T ≤ 0.901), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 21470 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 9013 independent (R_{int} = 0.039) and 7127 observed reflections [$I \geq 2\,\sigma(I)$], 490 refined parameters, R = 0.048, wR^2 = 0.109, max. residual electron density 1.38 (−0.70) e·Å^{-3} close to the solvate molecule, hydrogen atoms calculated and refined as riding atoms.

Treatment of 7 with Pyridine; Formation of the Pyridine Adduct 12: A solution of pyridine (7.6 mg, 96 mmol) in toluene (20 mL) was added at room temperature to a light yellow solution of **7** (77 mg, 96 mmol) in toluene (20 mL), and the mixture was stirred for 2 h. Removal of the volatiles in vacuo provided the product (77 mg, 99%) as a light yellow solid. ^1H NMR (C_7D_8, 600 MHz): δ = 8.13 (d, $^3J_{H,H}$ = 5.8 Hz, 2 H, 9-H), 6.73 (m, 1 H, 11-H), 6.72 (m, 1 H, 4′-H), 6.66 (m, 1 H, 3′-H), 6.45 (m, 2 H, 10-H), 6.44 (m, 1 H, 3-H), 5.42 (m, 1 H, 2′-H), 5.38 (m, 1 H, 2-H), 5.32 (m, 1 H, 5′-H), 5.16 (m, 1 H, 5-H), 2.84 (t, $^3J_{H,H}$ = 5.8 Hz, 2 H, 6-H, 6-H′), 1.62/1.42 (each m, each 1 H, 8-H, 8-H′), 1.50/1.26 (each m, each 1 H, 7-H, 7-H′), 0.12/0.08 [each s, each 3 H, Si(CH_3)$_2$] ppm. $^{13}C\{^1H\}$ NMR (C_7D_8, 150 MHz): δ = 145.4 (C-9), 143.0 (C-4), 140.5 (C-11), 128.2 (C-3′), 128.1 (C-3), 126.5 (C-4′), 125.3 (C-10), 114.3 (C-2), 113.8 (C-5), 113.7 (C-5′), 113.0 (C-2′), 107.7 (C-1′), 107.3 (C-1), 33.7 (C-6), 27.1 (C-7), 24.2 (C-8), −5.8, −6.3 [Si(CH_3)$_2$]; 148.6 ($^1J_{C,F}$ = 241.4 Hz), 140.0 ($^1J_{C,F}$ = 249.6 Hz), 137.7 ($^1J_{C,F}$ = 249.7 Hz), 120.9 (*o*-, *p*-, *m*-, *ipso*-C_6F_5) ppm. $^{11}B\{^1H\}$ NMR (C_7D_8, 64 MHz): δ = −0.6 ($\nu_{1/2}$ = 335 Hz) ppm. ^{19}F NMR (C_7D_8, 564 MHz): δ = −131.6 (m, 4 F, *o*-C_6F_5), −157.5/−157.7 (each t, each 1 F, $^3J_{FF}$ = 20.5/20.6 Hz, *p*-C_6F_5), −163.1/−163.3 (each m, each 2 F, *m*-C_6F_5) ppm. $C_{32}H_{24}NBCl_2F_{10}SiZr$ (813.6): calcd. C 47.24, H 2.97, N 1.72; found C 46.88, H 2.88, N 1.62.

Supporting Information: See footnote on the first page of this article. Details of the NMR spectroscopic characterization of the compounds **1**, **2**, **4**, **6**, **7** and **12**.

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