# Borane Insertion into Group-4 Metal-to-Carbon Bonds: The Reaction of $HB(C_6F_5)_2$ with ($\eta^2$-Formaldehyde)zirconocene Dimer and with (Butadiene)zirconocene

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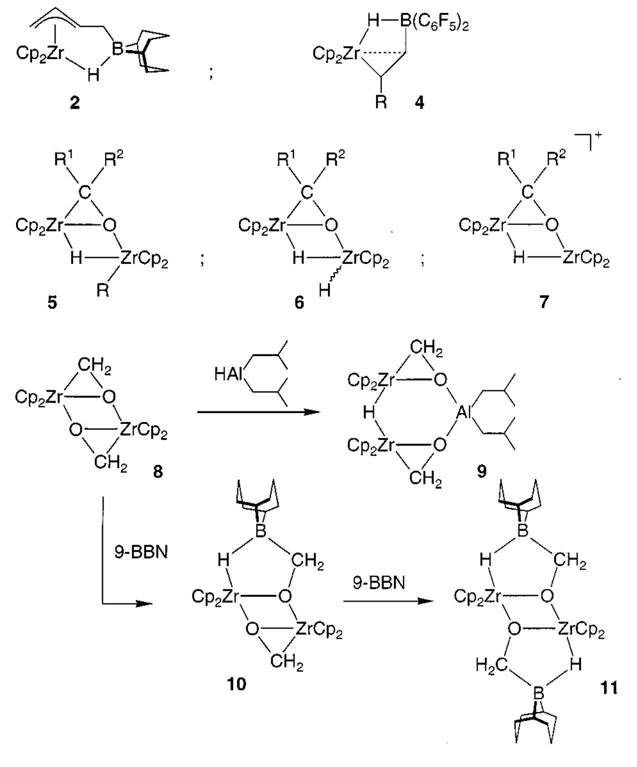
($\eta^2$-Formaldehyde)zirconocene dimer (**8**) cleanly adds one or two molar equivalents of the borane $HB(C_6F_5)_2$ by insertion of the H–[B] unit into the zirconium–carbon bond of the metallaoxirane moieties to form the mono- and bis-insertion products **16** and **17**, respectively. These systems contain five-membered heterocyclic rings that are built up by connecting five different elements, namely H, B, C, O, and Zr. The bis(borane) insertion product **17** was characterized by an X-ray crystal structure analysis. (Butadiene)zirconocene reacts with $HB(C_6F_5)_2$ in a similar way by insertion of the H–[B] unit into the (butadiene)C4–Zr linkage to form the metallacycle **18**.

## Introduction

Main-group and transition-metal hydrides react in various ways with ($\eta^2$-alkene) group-4 metallocene complexes and with their heteroatom analogues, the ($\eta^2$-aldehyde- and -ketone)metallocenes. 9-BBN adds cleanly to (butadiene)zirconocene (**1**)[1] to yield **2**;[2] similarly the electrophilic $H-B(C_6F_5)_2$ (**3**) ("Piers′ borane")[3] adds to ($\eta^2$-alkene)zirconocenes, generated in situ, to yield **4** (see Scheme 1).[4–6] ($\eta^2$-Ketone and $\eta^2$-aldehyde)zirconocenes show a more diverse reactivity. They form the 1:1 addition products with $Cp_2M^{IV}H_2$ or $Cp_2M^{IV}(R)H$ units, and even with the elusive monomeric $Cp_2Zr-H^+$ cation (to yield the dinuclear systems **5**, **6**, and **7**, respectively).[7][8] ($\eta^2$-Formaldehyde)zirconocene dimer (**8**) is known to add diisobutylaluminium hydride to form **9**, which exhibits the intact metallaoxirane subunits,[9][10] whereas 9-BBN reacts differently with **8** and inserts sequentially into the $Zr-CH_2$ bond of the metallaoxirane to give the respective HBCOZr-containing five-membered heterocyclic systems **10** and **11** (see Scheme 1).[11][12] We have now extended this series of studies and reacted ($\eta^2$-formaldehyde)zirconocene dimer (**8**) as well as (butadiene)zirconocene (**1**) with $HB(C_6F_5)_2$ (**3**). The outcome of these reactions is described in this article.



Scheme 1. Previously reported main-group and transition-metal hydride adducts to (diene-, alkene-, and $\eta^2$-ketone and -aldehyde)zirconocene complexes

## Results and Discussion

### Reaction of ($\eta^2$-Formaldehyde)zirconocene Dimer with $HB(C_6F_5)_2$

($\eta^2$-Formaldehyde)zirconocene was prepared starting from $[Cp_2Zr(H)Cl]_n$ (**12**). Carbonylation resulted in the formation of the dinuclear complex **13**, as described by C. Floriani et al.[13] Subsequent treatment with two molar equivalents of methyllithium led to the direct formation of $[Cp_2Zr(OCH_2)]_2$ (**8**) and dimethylzirconocene (**15**), as we had described previously.[9] The reaction probably proceeded via the unstable adduct $[Cp_2Zr(OCH_2) \cdot Me_2ZrCp_2]$ (**14**).

The borane $HB(C_6F_5)_2$ (**3**) was added to the ($\eta^2$-formaldehyde)zirconocene dimer at ambient temperature. The reaction was first carried out in deuterated solvent ([D$_6$]benzene or [D$_2$]dichloromethane) and monitored directly by

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[+] X-ray crystal structure analysis

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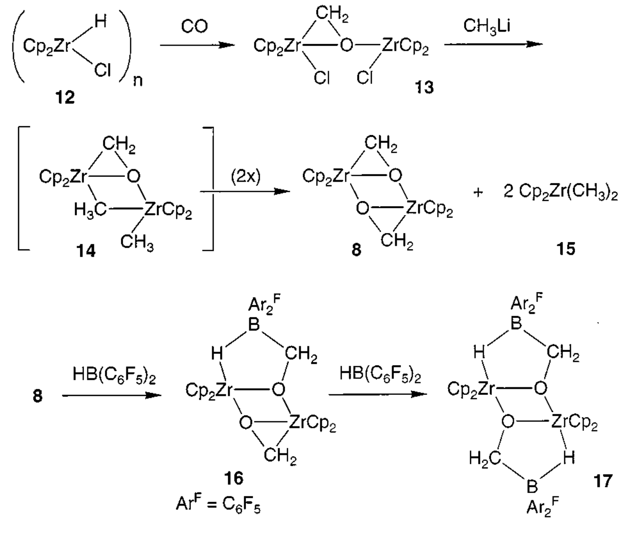
NMR spectroscopy. Combination of the two components in a ca. 1:1 ratio at room temperature resulted in the instantaneous formation of a single new compound, showing two Cp singlets at δ = 6.23 and 5.99 ($^1$H)/113.8 and 108.9 ($^{13}$C NMR) in a 10:10 ratio in addition to signals of two $CH_2$ groups [$^1$H/$^{13}$C NMR: δ = 4.26 (br., 2 H)/78.2 (br., $B-CH_2$) and δ = 3.22 (s, 2 H)/72.0 ($Zr-CH_2$)]. Although the $B-H$ signal was not located, we assumed that insertion of the HB moiety of the $HBAr^F_2$ reagent into the $Zr-CH_2$ linkage of one of the metallaoxirane subunits of **8** had taken place with formation of the unsymmetrical dimetallatricyclic product **16**. In agreement with this interpretation was the observation of a $^{11}$B-NMR resonance of **16** at δ = −13.5 − at a typical tetracoordinate borate chemical shift value − as a doublet with a $^1J_{BH}$ coupling constant of 65 Hz. This value was markedly reduced from a typical $HB(R)_3^-$ coupling constant (ca. 80−85 Hz), which probably indicated a reduced B···H bond order of the bridging Zr−(μ-H)−B situation in the heterocyclic addition complex **16**.



Scheme 2. Preparation of ($\eta^2$-formaldehyde)zirconocene dimer and its reaction with $HB(C_6F_5)_2$

Further addition of $HB(C_6F_5)_2$ to the solution rapidly resulted in HB insertion into the remaining ($ZrOCH_2$) moiety with formation of the double insertion product (**17**). The reaction was carried out in toluene solution (5 min at ambient temperature) to give **17** in ca. 50% yield. The rather poorly soluble product **17** exhibited a Cp singlet at δ = 6.43 (20 H) in [D$_2$]dichloromethane in addition to a $CH_2$ singlet (4 H) at δ = 4.45. The $H-B$ signal was not located. The $^{11}$B-NMR resonance is at δ = −13.2 (very broad signal, $\nu_{1/2} \approx 170$ Hz).

Single crystals suitable for X-ray structure determination of **17** were obtained from [D$_2$]dichloromethane. The Zr−(μ-H)−B hydrogen atoms could be located in the difference Fourier map. Figure 1 shows a view of the structure of **17** that contains a (disordered) molecule of the [D$_2$]dichloromethane solvent in the crystal.

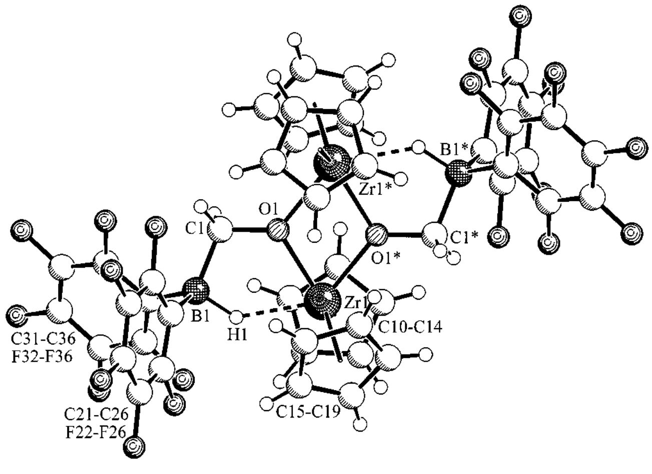


Figure 1. A view of the molecular structure of **17**

Table 1. A comparison of related structural parameters of **17** {i.e. **8** + 2[$HB(C_6F_5)_2$]} and **11** {i.e. **8** + 2[9-BBN]}[a]

| | **17** ($\cdot CD_2Cl_2$)[b] | **11**[c] |
|---|---|---|
| Zr1−O1 | 2.127(2) | 2.148(4) |
| O1−C1 | 1.460(3) | 1.448(7) |
| C1−B1 | 1.624(4) | 1.64(1) |
| B1−H1 | 1.22(4) | 1.33(5) |
| H1−Zr1 | 2.15(4) | 1.99(5) |
| Zr1−O1A | 2.148(2) | 2.155(4) |
| Zr1−O1−C1 | 117.3(2) | 116.8(3) |
| O1−C1−B1 | 110.3(2) | 111.1(5) |
| B1−H1−Zr1 | 135(2) | 138(4) |
| H1−Zr1−O1 | 69(1) | 71(1) |
| O1−Zr1−O1A | 68.8(1) | 67.3(2) |
| Zr1−O1−Zr1A | 111.2(1) | 112.7(2) |

[a] Bond lengths in Å, angles in°, atom numbering according to Figure 1. − [b] Crystallized from [D$_2$]dichloromethane, contains one disordered $CD_2Cl_2$ molecule in the asymmetric unit. − [c] From ref.[11]

The X-ray crystal structure analysis (see Figure 1) shows that the $H-B(C_6F_5)_2$ reagent has inserted into the $Zr-CH_2$ linkage of each of the metallacyclic three-membered rings of the dinuclear starting material **8** to form the 2:1 addition product **17**. A planar dimetallatricyclic framework has resulted in which two exceptional heterocyclic ring systems − each exhibiting a five-membered ring system made up by the five different core atoms Zr, O, C, B, and H − are connected by two Zr−O linkages. Actually, the connecting metal−oxygen bonds in the central four-membered $Zr_2O_2$ ring[15] (i.e. O1−Zr1A) are shorter [2.127(2) Å] than the respective Zr1−O1 bonds [2.148(2) Å] inside the lateral five-membered heterocycles. The bond angles at O inside the central four-membered ring are 111.2(1)° (Zr1−O1−Zr1A), the adjacent angle at Zr (O1−Zr1−O1A) is much smaller at 68.8(1)°. This indicates the presence of an additional coordination at the bent metallocene unit, which is formed by the B−(μ-H)−Zr bridge inside the five-membered ring.[14] The overall arrangement of the ZrOCBH ring system in **17** is very similar, as observed in the **8** + 9-BBN addition product **11** (see Scheme 1 and Table 1),[11] only that the bridging hydrogen atom in **17** seems to be located significantly closer to the boron atom. This might reflect the increased electrophilicity of the boron atom bonded to the two strongly electron-withdrawing $C_6F_5$ substituents as compared to the 9-BBN subunit, but in view of the general uncertainty of H-atom location by X-ray diffraction, such an effect should not be overemphasized.[14]

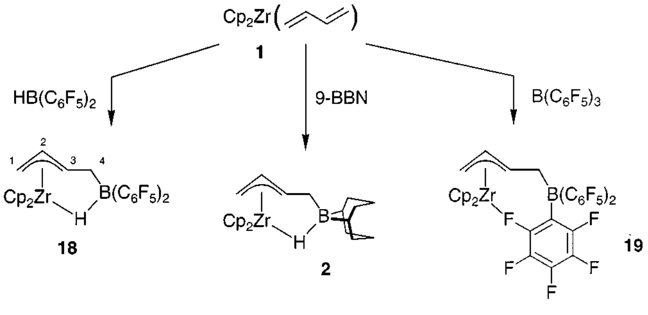
## Reaction of (Butadiene)zirconocene with $HB(C_6F_5)_2$

(Butadiene)zirconocene (**1**) reacted rapidly with $HB(C_6F_5)_2$ to form a 1:1 addition product (75% isolated). It showed the $^1H$-/$^{13}C$-NMR resonances of a pair of diastereotopic Cp ligands at zirconium ($\delta$ = 5.23, 5.08/107.8, 106.9 in [D$_6$]benzene), a pair of diastereotopic $C_6F_5$ substituents at B, a broad Zr−(μ-H)−B $^1H$-NMR signal at $\delta$ = −3.3, and a very broad $^{11}B$-NMR resonance at $\delta$ = −32 ($\nu_{1/2} \approx$ 170 Hz). The $^1H$- and $^{13}C$-NMR resonances of the $C_4H_6$[B] unit of **18** are listed in Table 2. A comparison with the respective NMR signals of the complexes **2** and **19**, previously obtained from the addition reaction of (butadiene)zirconocene with 9-BBN[2] and $B(C_6F_5)_3$,[16][17] respectively, show a number of subtle differences, but a similar overall spectroscopic environment.[18] This indicates the occurrence of an analogous product structure in the $HB(C_6F_5)_2$ + (butadiene)$ZrCp_2$ addition reaction. We must assume that the H−B functional group of the reagent **3** has also added the electrophilic boron center to the butadiene terminus and the hydride to the zirconium center to give the metallacyclic (π-allyl)Zr(μ-H)B complex **18**.

Table 2. A comparison of selected $^1H$- and $^{13}C$-NMR data of the (butadiene)zirconocene borane adducts **18**, **2**, and **19**

| | **18**[a] | **2**[a,b] | **19**[c] |
|---|---|---|---|
| 1-H | 1.81 | 2.56 | 2.25 |
| 1-H′ | 1.69 | 1.40 | 1.85 |
| 2-H | 5.15 | 3.81 | 5.88 |
| 3-H | 4.38 | 4.48 | 5.23 |
| 4-H | 3.64 | 2.01 | 2.56 |
| 4-H′ | 1.46 | 1.29 | 1.47 |
| μ-H | −3.3 | −4.5 | − |
| C1 | 49.1 | 44.8 | 52.7 |
| C2 | 120.1 | 95.7 | 131.8 |
| C3 | 96.2 | 112.4 | 123.8 |
| C4 | 25.5 | 28.3 | 28.5 |

[a] $^1H/^{13}C$ NMR in [D$_6$]benzene. − [b] From ref.[2] − [c] $^1H$ NMR in [D$_6$]benzene, $^{13}C$ NMR in [D$_8$]toluene, from ref.[16]



Scheme 3. Reaction of (butadiene)zirconocene with $HB(C_6F_5)_2$ and related electrophilic borane reagents

## Conclusions

We conclude that the electrophilic borane $H-B(C_6F_5)_2$ has probably added to (butadiene)zirconocene in an analogous way as has 9-BBN. In the reaction with the ($\eta^2$-formaldehyde)zirconocene dimer there was the attractive alternative reaction possibility of $HB(C_6F_5)_2$ to add in a similar fashion as had been observed for the $H-AlR_2$ reagent or $H-ZrCp_2^+$,[8][10] namely by addition of the H−M unit to the dipolar Zr−O edge of the metallaoxirane template. However, our experiment has shown that the electrophilic boron center in the reagent **3** shows no tendency to add to the nucleophilic metallaoxirane oxygen atom to form such an adduct. Instead, insertion of the HB moiety into the $Zr-CH_2$[O] bond of the metallacyclic three-membered ring of **8** is observed, leading to the formation of the respective five-membered heterocycle, as was observed in the analogous case of the 9-BBN addition to ($\eta^2$-formaldehyde)zirconocene (**8**).[11] From these experiments, it appears that $HB(C_6F_5)_2$ behaves as an example of an ordinary borane reagent, just as 9-BBN or $HBEt_2$,[3b] despite the presence of two strongly electron-withdrawing $-C_6F_5$ substituents at the boron atom.

## Experimental Section

Reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For more general information including a list of spectrometers and instruments used for the physical characterization of the compounds see ref.[8] The starting materials $HB(C_6F_5)_2$ (**3**),[3a] ($\eta^2$-formaldehyde)zirconocene dimer (**8**),[9] and ($\eta^4$-butadiene)zirconocene (**1**)[1] were prepared according to literature procedures.

**Reaction of ($\eta^2$-Formaldehyde)zirconocene Dimer (8) with $HB(C_6F_5)_2$ (3) in a 1:1 Ratio. − Formation of 16 (NMR Experiment):** Complex **8** (15.0 mg, 29.6 μmol) and the borane **3** (10.3 mg, 29.8 μmol) were suspended in 1 mL of [D$_6$]benzene. Within 5 min, the starting materials had dissolved to give a pale yellow solution. NMR-spectroscopic analysis revealed the formation of **16**. − $^1H$ NMR (200.1 MHz, [D$_6$]benzene): $\delta$ = 5.79, 5.52 (s, each 10 H, Cp), 4.27 (br., 2 H, $B-CH_2$), 2.81 (s, 2 H, $Zr-CH_2$), B−*H* signal not observed. − $^{11}B$ NMR (64.2 MHz, [D$_6$]benzene): $\delta$ = −13.0 (br., d). − The reaction was analogously carried out in [D$_2$]dichloromethane to also generate **16**: $^1H$ NMR (200 MHz, [D$_2$]dichloromethane): $\delta$ = 6.23, 5.99 (s, each 10 H, Cp), 4.26 (br., 2 H, $B-CH_2$), 3.22 (s, 2 H, $Zr-CH_2$), B−*H* signal not observed. − $^{13}C$ NMR (50.3 MHz, [D$_2$]dichloromethane): $\delta$ = 148.2, 139.3, 137.5 [each d, $^1J_{CF}$ = 240 Hz, *o*-, *p*-, *m*-$B(C_6F_5)_3$], 113.8, 108.9 (Cp), 78.2 (br., $B-CH_2$), 72.0 ($Zr-CH_2$), *ipso*-C resonance of $C_6F_5$ not observed. − $^{11}B$ NMR (64.2 MHz, [D$_2$]dichloromethane): $\delta$ = −13.5 (d, $^1J_{BH}$ = 65 Hz).

**Reaction of 8 with 3 in a 1:2 Stoichiometry. − Preparation of 17:** The addition reaction was carried out as an NMR experiment in both [D$_6$]benzene and [D$_2$]dichloromethane, and on a preparative scale. Typical NMR experiment: Complex **8** (15.0 mg, 29.6 μmol) and $HB(C_6F_5)_2$ (20.6 mg, 58.1 μmol) were suspended in 1 mL of [D$_6$]benzene. The mixture was stirred for 5 min, then the precipitated product was collected by filtration and characterized by NMR spectroscopy in a 1:1 [D$_6$]benzene/[D$_8$]toluene mixture [$^1$H

NMR: δ = 6.21 (s, 20 H, Cp), 4.36 (br., 4 H, B−$CH_2$−Zr), B−H resonance not observed; $^{11}$B NMR: δ = −13.0 (br., $\nu_{1/2} \approx 210$ Hz]. The reaction between **8** and **3** in a 1:2 ratio was also carried out in [$D_2$]dichloromethane: $^1$H NMR (200.1 MHz): δ = 6.43 (s, 20 H, Cp), 4.45 (br., 4 H, B−$CH_2$−Zr), B−H resonance not observed; $^{13}$C NMR (50.3 MHz): δ = 115.5 (Cp), other signals not detected due to the low solubility of **17**; $^{11}$B NMR (64.2 MHz): δ = −13.2 (br., $\nu_{1/2} \approx 170$ Hz).

**Reaction of 8 with 3 on a Preparative Scale:** (Formaldehyde)zirconocene dimer (**8**, 60 mg, 119 μmol) and $HB(C_6F_5)_2$ (**3**, 85 mg, 246 μmol) were introduced as solids into a Schlenk tube. Toluene (3 mL) was added at ambient temperature and the mixture vigorously stirred. The solid reagents dissolved within ca. 1 min, and within a reaction time of ca. 5 min a precipitate of the product **17** formed. It was allowed to settle, the supernatant liquid was decanted, the remaining solid was washed with toluene (1 mL) and dried in vacuo to give 78 mg (51%) of **17**. The product contained one equivalent of toluene, m.p. 99 °C, 178 °C (decomp.). − $C_{46}H_{26}B_2F_{20}O_2Zr_2 \cdot C_7H_8$ (1286.9): calcd. C 49.47, H 2.66; found: C 49.47, H 3.36.

**X-ray Crystal Structure Analysis of 17:** Single crystals were obtained from [$D_2$]dichloromethane solution at room temperature. Formula $C_{46}H_{26}B_2F_{20}O_2Zr_2 \cdot 2\,CD_2Cl_2$, $M$ = 1368.58, light yellow crystal, 0.25 × 0.20 × 0.05 mm, $a$ = 14.295(1), $b$ = 15.430(1), $c$ = 11.513(1) Å, β = 103.12(1)°, $V$ = 2473.2(3) Å$^3$, $\rho_{calcd.}$ = 1.832 g cm$^{-3}$, $F(000)$ = 1344 e, μ = 7.55 cm$^{-1}$, absorption correction by SORTAV (0.834 ≤ $T$ ≤ 0.963), $Z$ = 2, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, $T$ = 198 K, ω and φ scans, 22325 reflections collected (±$h$, ±$k$, ±$l$), [(sinθ)/λ] = 0.71 Å$^{-1}$, 7495 independent and 5756 observed reflections [$I \geq 2\,\sigma(I)$], 365 refined parameters, $R$ = 0.049, $wR^2$ = 0.134, max. residual electron density 1.93 (−1.46) e Å$^{-3}$ in the region of the solvent molecule, hydrogen atoms at boron atoms from difference Fourier map and refined free, all other hydrogen atoms calculated and refined as riding atoms. The data set was collected with a Nonius KappaCCD diffractometer, placed on a Nonius rotating anode generator FR591.[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120189. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat. + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

**Reaction of (Butadiene)zirconocene (1) with $HB(C_6F_5)_2$ (3). − Preparation of 18:** A mixture of (butadiene)zirconocene (**1**) (199 mg, 0.72 mmol) and of $HB(C_6F_5)_2$ (**3**) (250 mg, 0.72 mmol) in toluene (10 mL) was stirred for 30 min at room temperature. Solvent was removed from the red-brown solution. The resulting solid was stirred up in pentane (10 mL). The solid product was collected by filtration, washed with 10 mL of pentane and dried in vacuo to give 335 mg (75%) of **18**, m.p. 162 °C (decomp.) − $^1$H NMR (360.1 MHz, [$D_6$]benzene): δ = 5.23, 5.08 (s, each 5 H, Cp), 5.15 (m, 1 H, 2-H), 4.38 (m, 1 H, 3-H), 3.64 (m, 1 H, 4-H), 1.81 (m, 1 H, 1-H), 1.69 (m, 1 H, 1-H′), 1.46 (m, 1 H, 4-H′), −3.3 (br., 1 H, B-*H*). − $^{13}$C NMR (90.6 MHz, [$D_6$]benzene): δ = 149.3 and 148.3, 140.3 and 139.9, 137.7 and 137.5 [each d, $^1J_{CF}$ = 240 Hz, *o*-, *p*-, *m*-$B(C_6F_5)_3$], 120.1 (C-2), 107.8, 106.9 (Cp), 96.2 (C-3), 49.1 (C-1), 25.5 (br., C-4). − GCOSY (360.1 MHz, [$D_6$]benzene): δ = 5.15/4.38 (2-H/3-H), 5.15/1.81 (2-H/1-H), 5.15/1.69 (2-H/1-H′), 4.38/3.64 (3-H/4-H), 4.38/1.46 (3-H/4-H′), 3.46/1.46 (4-H/4-H′), 1.81/1.69 (1-H/1-H′). − HETCOR (360.1 MHz, [$D_6$]benzene): δ = 120.1/5.15 (C-2), 107.8/5.08 (Cp), 106.9/5.23 (Cp), 96.2/4.38 (C-3), 49.1/1.81 (C-1/1-H), 49.1/1.69 (C-1/1-H′). − $^{11}$B NMR (64.2 MHz, [$D_6$]benzene): δ = −32.4. − $^{19}$F NMR (282.4 MHz, [$D_6$]benzene): δ = −131.1, −131.8 [*o*-$B(C_6F_5)_3$], −156.9, −159.0 [*p*-$B(C_6F_5)_3$], −162.7, −163.5 [*m*-$B(C_6F_5)_3$]. − IR (KBr): $\tilde{\nu}$ = 3128, 2962, 2916, 2875, 2843, 1782, 1643, 1515, 1464, 1376, 1278, 1207, 1096, 1017, 971, 816, 734 cm$^{-1}$. − $C_{26}H_{17}BF_{10}Zr$ (621.44): calcd. C 50.25, H 2.76; found C 48.99, H 2.87.

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