# Study of the Reaction of Tridentate Ligands with Ferrocenyl Boronic Acid

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Evaluation of the reactivity of eight tridentate ligands derived from amino alcohols and salicylaldehyde, 2-hydroxyacetophenone, or 2-hydroxybenzophenone with ferrocenyl boronic acid has shown that the reaction leads to both monomeric and dimeric ferrocenyl boronates. A coordinative N–B bond is essential to give the tetrahedral boron atoms that are responsible for the formation of heterobicyclic structures containing six, seven and ten members. The purity and identity of all compounds were unequivocally established by analytical and multinuclear ($^1$H, $^{11}$B, $^{13}$C) magnetic resonance spectroscopic data. Furthermore, the structures of the dimeric (**2a**) and monomeric (**5b**) boron complexes were established by X-ray diffraction analyses. The dimeric compound contains a ten-membered ring in a *boat–chair–boat* conformation, while the monomeric compound has a seven-membered ring with a *chair* conformation.


## Introduction

The synthesis and study of ferrocenyl boron derivatives has generated considerable interest due to their interesting properties and potential applications.[1−6] The boryl group attached to the Cp fragment exerts an interesting influence, attributed to $p_\pi-p_\pi$ interactions between the cyclopentadienyl system and the boron $p_z$ orbital. Additionally, the through-space Fe−B interaction seen in (dibromoboryl)ferrocenes and (bispentafluorophenyl)boryl ferrocenes is favored because the occupied d orbitals on the iron center have the appropriate symmetry to interact with the empty p orbital of the boron center.[6b,7] Borylated ferrocenes are isoelectronic with stable ferrocenyl carbocations.[7,8] Due to possible applications of their unusual properties to electronic materials, boron compounds containing ferrocenyl units have recently been examined as charge-transfer complexes.[9−12]

Moreover, boronic acids are potentially useful for selective recognition of sugars as they can form strong boronic acid−diol interactions.[10,13,14] In addition, the complexation of boronic acids with sugars affords a fluorescence intensity that is affected by complexation.[15] Ferrocenyl boronic acid derivatives have also been used in the electrochemical detection of saccharides[13,14] and the selective recognition of fluoride, whereby the boron atom acts as a hard acid and fluoride as the hard base.[16]

Recently, ferrocenyl boron macrocycles have been prepared by the reaction of 1,1′ diborylated ferrocene [1,1′-{$C_5H_4$[B(R)Br]}$_2$] with tetrafunctional Lewis bases such as 2,5-di(pyrazol-1-yl)hydroquinone and quaterpyridine.[17,18] Here, formation of the dative N−B bond facilitates cyclization leading to cyclic oligomers. However, the reaction of difunctional Lewis bases such as pyrazine or 4,4′-bipyridine with 1,1-diborylated ferrocene led to polymeric materials only.[19]

Relatively few detailed studies have been performed on the coordination chemistry of ferrocenyl boronic acid. Previously, we reported the synthesis of monomeric,[20,21] dimeric,[21,22] trimeric,[23] and tetrameric[24] boron compounds by reaction of boronic acids with Schiff bases where the formation of dative N−B bonds is very important in their cyclization.[25] Here we describe the reactivity of ferrocenyl boronic acids with different tridentate ligands using simple condensation reactions.

## Results and Discussion

We have investigated the reaction of boronic acids with different ligands to establish the factors involved in the formation of macrocyclic structures. To further evaluate electronic and steric factors we selected $CpFeC_5H_4B(OH)_2$, as the ferrocenyl group is bulkier and more electrophilic than a phenyl group.[22] Thus, we discuss here the reactivity of various tridentate ligands with ferrocenyl boronic acid in order to prepare new macrocyclic boron compounds.

The reaction of tridentate ligand **1a** derived from salicylaldehyde and ethanolamine with ferrocenyl boronic acid was carried out under reflux of THF to yield, after 60 min, a red solid that is stable to air (Scheme 1). The EI mass

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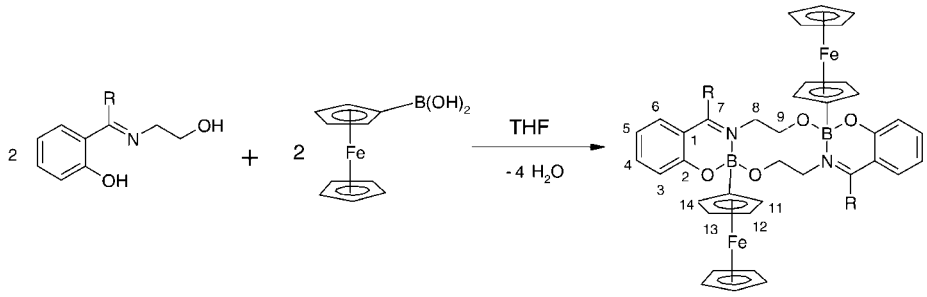



**1a**: R = H, **1b**: R = Me, **1c**: R = Ph

**2a**: R = H, **2b**: R = Me, **2c**: R = Ph

Scheme 1. Dimeric boron compounds from tridentate ligands

spectrum has a highest peak at $m/z$ = 718, establishing the dimeric composition of compound **2a**.

To determine if a larger substituent could influence the imine bond and alter the course of the reaction, we prepared ligands derived from 2-hydroxyacetophenone (**1b**) and 2-hydroxybenzophenone (**1c**); however, these ligands react with ferrocenyl boronic acid to give dimeric boronates **2b** and **2c** in moderate yields (Scheme 1).

The dimeric composition of these compounds was established by spectroscopic analyses whereby the EI mass spectra have highest peaks at $m/z$ = 746 and 870, which correspond to the molecular weight of **2b** and **2c**, respectively. In all cases, the base peak corresponds to the loss of one ferrocenyl moiety. NMR analyses of **2a** and **2c** could not be obtained due the compounds' insolubility in common solvents. In the NMR spectra of **2b** only a single set of signals is observed, owing to the $C_2$ fold axis present in the molecule. The $^{11}B$ NMR spectrum of **2b** shows a singlet at $\delta$ = 7.8 ppm, which is in the range expected for tetracoordinate boron atoms containing a dative N−B bond.[26]

The stretching band for the C=N group in the IR spectra is shifted to 1640, 1610, and 1606 $cm^{-1}$ for **2a**, **2b**, and **2c**, respectively. The lower shift showed by **2b** and **2c** can be attributed to electronic and inductive effects of the methyl and phenyl groups present.

The crystal structure of **2a** confirms the dimeric nature of this compound (Figure 1). Crystallographic data and selected distances and bonds are listed in Tables 1 and 2, respectively. In analogy to the dimeric compounds previously described,[22,24,25] the structure has an inversion center at the center of the ten-membered ring. Ferrocenyl substituents on each boron atom are *trans* disposed with regard to the ten-membered macrocycle, which may be attributed to the bulkiness of the ferrocenyl moieties. A dative N−B bond, together with the required tetrahedral geometry of the boron atoms, is responsible for the dimeric form of these compounds.

Thus, B(1)−N(1) [1.632(5) Å] in **2a** is very similar to that of the boron-phenyl derivative [1.624(3) Å[24]] and accords with analogous systems.[27] The C(10)−B(1) [1.595(6) Å] is slightly shorter than in the phenyl derivative [1.601(3) Å] because the ferrocenyl group is a stronger electron donor than the phenyl group.

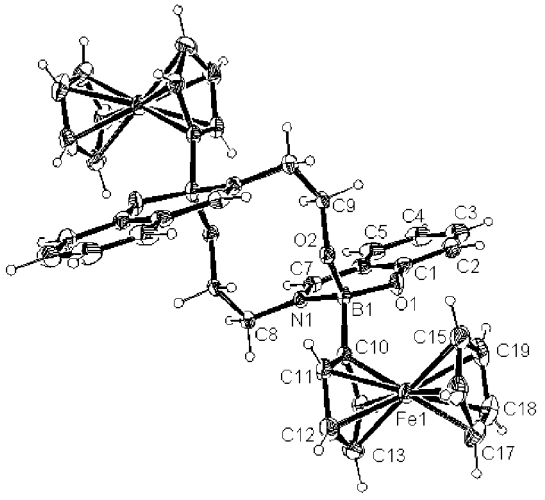



Figure 1. Molecular structure of solid-state **2a**

The tetrahedral geometry for the boron atom is evident from the bond angles, which are in the range 106.9(3)−111.5(3)°, the largest being O(1)−B(1)−C(10), which in the boron-phenyl derivative[24] is 109.4(2)°. This difference in bond angles may be attributed to the steric effect of the bulkier ferrocene unit, compared to the phenyl group. As expected, the inverse effect is observed on comparing the N(1)−(B1)−(C10) angle, which is slightly smaller [107.0(3)°] in the ferrocene derivative than in the phenyl [108.1(2)°] one.[24] The six-membered heterocycle is nearly planar, as evidenced by the O(1)−B(1)−N(1)−C(7) torsion angle (10.2°). The ten-membered heterocycle presents a *boat−chair−boat* conformation. The structure shows a relatively short transannular H···O interaction (2.47 Å) between the oxygen atom on one side of the ring with a hydrogen atom from the $CH_2$ group on the opposite side.

In contrast, the reaction of ligands **1d** and **1e**, obtained from salicylaldehyde and 1-aminomethylcyclohexanol, with two equivalents of ferrocenyl boronic acid provided exclusively complexes **3a** and **3b** (Scheme 2). The different reactivity, compared to **1a** and **1c** ligands, may be attributed to the cyclohexyl group at the β position relative to the nitrogen

Table 1. Crystal data and structure refinement for **2a** and **5b**

| | **2a** | **5b** |
|---|---|---|
| Empirical formula | $C_{19}H_{18}BNFeO_2$ | $C_{22}H_{24}BNFeO_2$ |
| Molecular mass | 359.01 | 410.08 |
| Crystal size [mm$^3$] | 0.20 × 0.24 × 0.50 | 0.48 × 0.30 × 0.21 |
| Temperature [K] | 293 | 293 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| Unit cell dimensions | | |
| $a$ [Å] | 7.7230(10) | 8.5644(6) |
| $b$ [Å] | 10.5580(10) | 11.3609(7) |
| $c$ [Å] | 10.7290(10) | 19.1696(12) |
| α [°] | 103.660(10) | 90.00 |
| β [°] | 95.000(10) | 91.5850(10) |
| γ [°] | 109.610(10) | 90.00 |
| $V$ [Å$^3$] | 787.44 (15) | 1864.5(2) |
| $Z$ | 2 | 4 |
| Density (calculated) [g/cm$^3$] | 1.51 | 1.429 |
| Absorption coefficient [mm$^{-1}$] | 0.968 | 0.826 |
| Index ranges | −8/9, −12/0, −12/13 | −10/10, −13/13, 0/23 |
| Reflections collected | 3117 | 17467 |
| Independent reflections | 2951 | 3283 |
| parameters | 217 | 246 |
| Final $R$ indices [$I>2\sigma(I)$] | 0.049 | 0.0487 |
| $R$ indices (all data) | $wR2$ = 0.1597 | $wR2$ = 0.1058 |
| GOOF | 1.005 | 1.219 |
| Largest diff. peak and hole [e/Å$^3$] | 0.437/ −0.309 | 0.302 / −0.297 |

Table 2. Selected bond lengths [Å] and angles [°] for **2a** and **5b**

| | **2a** | **5b** |
|---|---|---|
| Bond lengths [Å] | | |
| O(1)−B(1) | 1.491(5) | 1.481(4) |
| O(1)−C(1) | 1.324(5) | 1.333(3) |
| O(2)−B(1) | 1.432(6) | 1.426(4) |
| O(2)−C(9)[a] | 1.413(5) | 1.424(3) |
| B(1)−N(1) | 1.632(5) | 1.641(3) |
| B(1)−C(10)[b] | 1.595(6) | 1.596(4) |
| N(1)−C(7) | 1.286(5) | 1.290(4) |
| N(1)−C(8)[c] | 1.459(5) | 1.473(3) |
| Bond angles [°] | | |
| B(1)−O(1)−C(1) | 125.9(4) | 119.6(2) |
| B(1)−O(2)−C(9)[a] | 119.0(3) | 119.0(2) |
| O(1)−B(1)−O(2) | 111.5(4) | 111.1(2) |
| O(1)−B(1)−N(1) | 106.9(3) | 105.0(2) |
| O(2)−B(1)−N(1) | 109.1(3) | 107.8(2) |
| O(1)−B(1)−C(10)[b] | 111.5(3) | 111.1(2) |
| O(2)−B(1)−C(10)[b] | 110.6(4) | 111.8(2) |
| N(1)−B(1)−C(10)[b] | 107.0(3) | 107.5(2) |
| B(1)−N(1)−C(7) | 121.8(3) | 122.7(2) |
| B(1)−N(1)−C(8)[c] | 119.2(3) | 115.0(2) |
| C(7)−N(1)−C(8)[c] | 119.0(4) | 122.3(2) |

[a] For **5b** is C(12). [b] For **5b** is C(13). [c] For **5b** is C(9).

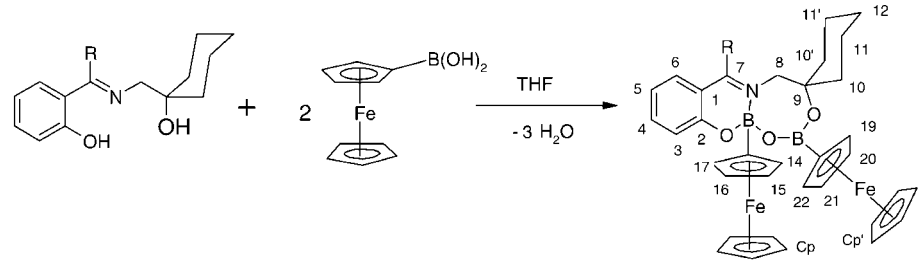
atom in ligands **1d** and **1e**, which could cause strong intramolecular interactions upon formation of either a dimeric structure or a monomeric compound containing five- and six-membered rings. Consequently, bicyclic structures are preferred. The six- and seven-membered rings contain two boron atoms, one tetrahedral and the other tricoordinate. When only one equivalent of ferrocenyl boronic acid is used, **3a** and **3b** are also formed, but in lower yields. Attempts to form the dimeric compound from this ligand by using different reaction conditions as well as other boronic acids were unsuccessful.

Bicyclic structures for **3a** and **3b** were established by MS, where the molecular peaks appear at $m/z$ = 639 and 653, respectively. $^{11}$B NMR spectra show two signals at δ = 34.8 and 8.2 ppm for **3a** and 38.3 and 7.2 ppm for **3b**, corresponding to trigonal and tetrahedral boron atoms, respectively. $^1$H NMR shows an AB system for the $NCH_2C$ group, due to the formation of the seven-membered heterocycle.

We then examined the ligand containing three carbon atoms between the OH and C=N groups to evaluate the effect upon ring closure. **1f** reacted with ferrocenyl boronic acid under reflux in THF (40 min) to yield a red solid that was characterized as monomeric compound **4** (Scheme 3). In accordance with previous reports,[20,28] the six-membered ring is favored (monomer) over a twelve-membered ring (dimer) in this type of ligands. The $^{11}$B NMR spectrum shows a signal significantly up-field (δ = 5.0 ppm) with respect to ferrocenyl boronic acid, due to the formation of a tetrahedral boron atom. In $^1$H NMR, an AB system appears at δ = 4.82 and 4.89 ppm, corresponding to the $CH_2$ group. The iminic proton is shifted to down field (9.21 ppm) in comparison with the ligand (8.57 ppm) due to formation of the dative N−B bond. All boron compounds described herein shown diastereotopic signals for the $C_5H_4$ moiety attached to the boron atoms, in accordance with the literature data.[2]

We also prepared ligands **1g** and **1h** from 4-aminobutanol and salicylaldehyde or 2-hydroxyacetophenone, respectively. **1g** and **1h** reacted with ferrocenyl boronic acid to give the

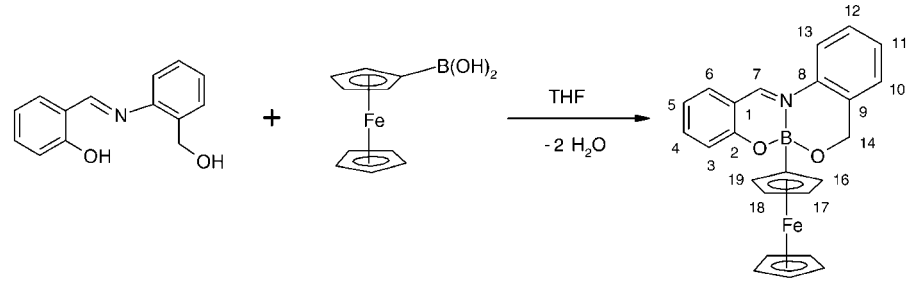
  




**1d**: R = H, **1e**: R = Me

**3a**: R = H, **3b**: R = Me

Scheme 2. Boron complexes having two boron atoms with different geometry




**1f**

**4**

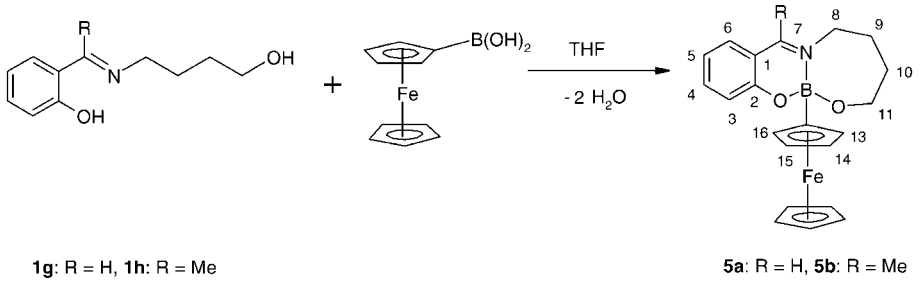
Scheme 3. Monomeric boron compound from an aromatic tridentate ligand

monomeric compounds **5a** and **5b** with six- and seven-membered-rings (Scheme 4). Only a monomeric product was isolated, in contrast to using phenylboronic acid,[30] where both monomeric and dimeric compounds were isolated; a possible explanation is that the bulky ferrocenyl group prevents formation of the dimeric compound. Tetracoordination of the boron atom is evident in the $^{11}B$ NMR spectra, with signals at $\delta = 9.6$ ppm and 8.7 ppm for **5a** and **5b**, respectively, as a result of dative N−B bond formation.

Compound **5b** was characterized by X-ray crystal structure analysis (Figure 2). Selected bond lengths and angles are summarized in Table 2. The corresponding bond lengths and angles in the six-membered rings of **2a** and **5b** are indistinguishable within experimental error. Insignificant variations were found in the dative bond, for **5b** N−B bond is 1.641(3) Å and is very similar to **2a** [1.632(5) Å]. In **5b**, B−O is longer in the six-membered [1.481(4) Å] than in the seven-membered [1.426(4) Å] heterocycle, and the O−B−N bond angle is smaller in the six-membered [105.0(2)°] than in the seven-membered ring [107.8(2)°] as a result of the annular tension and planarity of the ring. The seven-membered ring has a chair conformation in the solid state (Figure 2).

## Conclusions

Ferrocenyl boronic acid reacts with different tridentate ONO ligands to provide, in one step, novel dimeric and monomeric structures depending on the ligand used. Neither different groups in the imine position nor a bulky group such as ferrocenyl influence the formation of the structure. The new chemistry reported here may be useful in macrocyclic syntheses, and ferrocene derivatives could find interesting applications for molecular recognition. Current work in our laboratory involves the reactivity of analogous compounds.




**1g**: R = H, **1h**: R = Me

**5a**: R = H, **5b**: R = Me

Scheme 4. Monomeric boron compounds from tridentate ligands derived from 4-aminobutanol

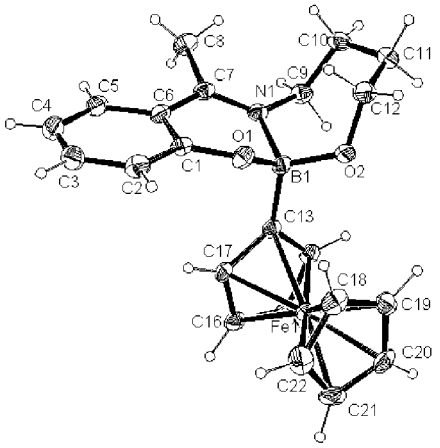



Figure 2. Molecular structure of solid-state **5b**

## Experimental Section

**Materials and Methods:** All reagents were purchased from Aldrich and were used without further purification. NMR spectra were recorded at room temperature using the following spectrometers: Jeol GSX 270, Bruker 300, and Jeol eclipse+400. Chemical shifts are given in ppm. Infrared spectra were recorded on a Perkin−Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were obtained with a HP 5989-A mass spectrometer operating in electron impact mode. Melting points were determined with a Gallenkamp MFB-595 apparatus. Elemental microanalyses were performed by Oneida Research Services (Whitesboro, NY. 13492).

**Crystal Structure Determination:** Single Crystals of **2a** suitable for X-ray diffraction were obtained when the reaction was performed in THF at 25 °C without stirring; crystals of **5b** suitable for X-ray structure analysis were grown by slow evaporation of a THF/$CH_2Cl_2$ solution of the complex. Intensity data were collected at 293 K with an Enraf−Nonius CAD4 diffractometer for compound **2a** and a Bruker-AXS APEX diffractometer with a CCD area detector for **5b**; Mo-*K*α-radiation, λ = 0.71073 Å, graphite monochromator, ω = 2θ scan. Empirical absorption corrections (DIFABS) were applied. The structures were solved by direct methods (SHELXS-86)[30] and refined using SHLXS-97.[31] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. Crystallographic data for the structures have been deposited at the Cambridge Crystallographic Data Center as supplementary material No. 211441 for complex **2a** and 210542 for **5b**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

**General Method for the Preparation of Tridentate Ligands 1a−1h:** The ligands were obtained by condensation of an aldehyde or ketone with the corresponding amino alcohol under reflux in methanol for 45 min. The water formed and part of the solvent was removed using a Dean−Stark trap and the product was then dried under high vacuum. Ligands **1a**,[24] **1b**,[29] **1f**,[20] and **1g**[30] have been described previously.

**General Syntheses for Boron Complexes:** An equimolar solution of **1a−1h** and ferrocenyl boronic acid in THF (60 mL) was prepared and then boiled under reflux for 60 min (two equivalents of the boronic acid were used to prepare **3a** and **3b** complexes). Part of the solvent was then removed with a Dean−Stark trap so as to favor precipitation. The product was then filtered off and washed with small amounts of the same solvent.

**Complex 2a:** Compound **2a** was prepared from **1a** (0.50 g, 3.02 mmol) and ferrocenyl boronic acid (0.70 g, 3.02 mmol). A red solid was obtained, in 72% yield (0.78 g, 1.08 mmol), that is insoluble in all common solvents, m.p. 280−282 °C. IR ṽ = (KBr): 3412, 2930, 2850, 1640 (C=N), 1608, 1560, 1480, 1438, 1316, 1308, 1234, 1214, 1148, 1126, 1110, 1104, 1054, 1044, 1026, 1010, 970, 794, 752 $cm^{-1}$. EM (15 eV): *m*/*z* (%) = 718 (1) [$M^+$] 570 (2), 361 (25), 359 (100), 358 (35), 357 (10), 356 (3), 334 (4), 333 (2), 330 (2), 294 (6), 293 (6), 292 (4), 291 (8), 290 (3), 255 (3), 187 (7), 186 (51), 184 (4), 175 (7), 174 (50), 173 (20), 121 (2). $C_{38}H_{36}B_2Fe_2N_2O_4$: calcd. C 63.06, H 4.97, N 3.87; found C 63.38, H 5.33, N 3.84 (%).

**Complex 2b:** Compound **2b** was prepared from **1b** (0.50 g, 2.79 mmol) and ferrocenyl boronic acid (0.64 g, 2.79 mmol) as an orange solid, in 77% yield (0.80 g, 1.06 mmol) that is slightly soluble in chloroform, m.p. 204−206 °C. IR ṽ = (KBr): 2918, 2850, 1610 (C=N), 1550, 1456, 1444, 1332, 1276, 1214, 1144, 1134, 1118, 1106, 1004, 814, 758 $cm^{-1}$. MS (15 eV): *m*/*z* (%) = 746 (5) [$M^+$], 745 (2), 585 (3), 584 (1), 399 (3), 398 (2), 375 (3), 374 (18), 373 (74), 372 (20), 371 (5), 370 (2), 359 (2), 358 (9), 357 (2), 308 (2), 296 (2), 212 (1), 189 (11), 188 (100), 187 (43), 186 (75), 185 (5), 184 (4), 174 (5), 121 (2), 72 (4), 71 (5), 43 (3), 42 (11), 41 (4). $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.84 (s, 3 H, Me), 4.10−3.93 (m, 4 H, 8-, 9-H), 4.22 (s, 5 H, Cp-H), 4.36 (m, 2 H, 12-, 13-H), 4.44 (m, 2 H, 11-, 14-H), 6.92 (t, *J* = 7.7 Hz, 1 H, 5-H), 7.08 (d, *J* = 7.7 Hz, 1 H, 3-H), 7.54 (t, *J* = 7.7 Hz, 1 H, 4-H), 7.76 (d, *J* = 7.7 Hz, 1 H, 6-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 16.7 (Me), 51.1 (C-8), 61.4 (C-9), 71.9 (C-Cp), 77.2 (C-11, 14), 77.6 (C-12, 13), 118.7 (C-1, 5), 120.5 (C-3), 128.5 (C-6), 136.7 (C-4), 161.4 (C-2), 175.3 (C-7) ppm. $^{11}$B NMR (96 MHz, $CDCl_3$): δ = 7.8 ppm ($h_{1/2}$ = 228 Hz). $C_{40}H_{40}B_2Fe_2N_2O_4$: calcd. C 63.91, H 5.32, N 3.72; found C 63.96, H 5.78, N 3.54 (%).

**Complex 2c: 2c** was prepared from **1c** (0.50 g, 2.07 mmol) and ferrocenyl boronic acid (0.48 g, 2.07 mmol). A red solid was obtained, in 83% yield (0.74 g, 0.84 mmol), that is insoluble in all common solvents, m.p. 288−298 °C. IR ṽ = (KBr): 3094, 3066, 2934, 2916, 1606 (C=N), 1548, 1474, 1456, 1444, 1338, 1214, 1148, 1118, 1112, 1102, 1026, 1012, 1002, 802, 752 $cm^{-1}$. MS (15 eV): *m*/*z* (%) = 870 (15) [$M^+$], 435 (24), 311 (17), 239 (13), 368 (20), 296 (16), 250 (100), 236 (24), 186 (21), 148 (15), 98 (27), 84 (32), 44 (79). $C_{50}H_{44}B_2Fe_2N_2O_4$: calcd. C 68.56, H 5.02, N 3.20; found C 68.89, H 5.29; N 3.20 (%).

**Complex 3a: 3a** was prepared from **1d** (0.30 g, 1.28 mmol) and ferrocenyl boronic acid (0.30 g, 1.28 mmol) as a red solid, in 73% yield (0.60 g, 0.93 mmol), that is slightly soluble in chloroform, m.p. 228 °C. IR ṽ = (KBr): 3504, 2928, 2850, 1638 (C=N), 1552, 1474, 1458, 1446, 1406, 1390, 1382, 1270, 1260, 1214, 1176, 1148, 766 $cm^{-1}$. MS (15 eV): *m*/*z* (%) = 639 (100) [$M^+$], 595 (1), 478 (2), 427 (17), 362 (5), 320 (11), 242 (81), 212 (27), 186 (44), 148 (30), 121 (21), 95 (8), 67 (9), 56 (9). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.81−1.17 (m, 10 H, 10-, 10′-, 11-, 11′-, 12-H), 3.24 (d, *J* = 12.9 Hz, 1 H, $8_b$-H), 3.68 (m, 1 H, 16-H), 4.01 (m, 1 H, 15-H), 4.12 (m, 1 H, 17-H), 4.18 (s, 5 H, Cp-H $B_{tetra}$), 4.19 (d, *J* = 12.9 Hz, 1 H, $8_a$-H), 4.29 (s, 5 H, Cp-H $B_{tri}$), 4.33 (m, 1 H, 14-H), 4.37 (m, 1 H, 21-H), 4.42 (m, 1 H, 20-H), 4.54 (m, 1 H, 22-H), 4.61 (m, 1 H, 19-H), 6.86 (t, *J* = 8.6 Hz, 1 H, 5-H), 7.13 (d, *J* = 8.6 Hz, 1 H, 3-H), 7.27 (d, *J* = 8.6 Hz, 1 H, 6-H), 7.56 (t, *J* = 8.6 Hz, 1 H, 4-H), 7.85 (s, 1 H, 7-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 21.8 (C-11′), 21.9 (C-11), 26.0 (C-12), 34.8 (C-10′), 38.4 (C-10), 66.5 (C-8), 68.3

(C-Cp $B_{tetra}$), 68.5 (C-Cp $B_{tri}$), 68.7 (C-16), 69.4 (C-15), 70.3 (C-21), 71.2 (C-17), 71.4 (C-14), 72.4 (C-20), 73.9 (C-9), 74.1 (C-22), 74.8 (C-19), 115.9 (C-1), 118.6 (C-5), 119.8 (C-3), 131.5 (C-6), 138.2 (C-4), 161.3 (C-2), 161.6 (C-7) ppm. $^{11}$B NMR (96 MHz, $CDCl_3$): δ: $B_{tri}$ = 34.8 ppm ($h_{1/2}$ = 260.3 Hz), $B_{tetra}$ = 8.2 ppm ($h_{1/2}$ = 130.3 Hz). $C_{34}H_{35}B_2Fe_2NO_3$: calcd. C 63.34, H 5.43, N 2.17; found C 63.07, H 5.85, N 2.20 (%).

**Complex 3b: 3b** was prepared from **1e** (0.30 g, 1.21 mmol) and ferrocenyl boronic acid (28 g, 1.21 mmol) as an orange solid in 78% yield (0.62 g, 0.94 mmol), m.p. 219 °C. IR ṽ = (KBr): 2922, 1612 (C=N), 1550, 1458, 1438, 1420, 1380, 1348, 1330, 1270, 1208, 1192, 1178, 1154, 1104, 762 cm$^{-1}$. MS (15 eV): *m/z* (%) = 653 (97) [M$^+$], 639 (2), 467 (38), 441 (11), 426 (4), 398 (7), 376 (2), 257 (17), 256 (100), 240 (3), 212 (6), 186 (18), 162 (2). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.80−1.10 (m, 10 H, 10-, 10′-, 11-, 11′-, 12-H), 2.50 (s, 3 H, Me), 3.52 (d, *J* = 14.9 Hz, 1 H, $8_b$-H), 3.75 (s, 1 H, 16-H), 3.93 (s, 1 H, 15-H), 4.10 (s, 1 H, 17-H), 4.20 (s, 5 H, Cp-H $B_{tetra}$), 4.24 (s, 1 H, 14-H), 4.25 (d, *J* = 14.9 Hz, 1 H, $8_a$-H), 4.29 (s, 5 H, Cp-H $B_{tri}$), 4.33 (s, 1 H, 21-H), 4.36 (s, 1 H, 20-H), 4.56 (s, 1 H, 22-H), 4.63 (s, 1 H, 19-H), 6.89 (td, *J* = 7.8, 1.5 Hz, 1 H, 5-H), 7.00 (dd, *J* = 7.8, 1.5 Hz, 1 H, 3-H), 7.55 (td, *J* = 7.8, 1.5 Hz, 1 H, 4-H), 7.76 (dd, *J* = 7.8, 1.5 Hz, 1 H, 6-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.3 (Me), 21.8 (C-11), 22.1 (C-11′), 26.0 (C-12), 35.3 (C-10′), 36.1 (C-10), 59.3 (C-8), 68.3 (C-16), 68.4 (C-15), 68.5 (C-21), 68.6 (C-20), 68.7 (C-Cp $B_{tetra}$), 68.9 (C-Cp $B_{tri}$), 71.4 (C-17), 71.6 (C-14), 74.2 (C-22), 74.7 (C-19), 74.9 (C-9), 118.6 (C-1), 118.8 (C-5), 119.3 (C-3), 131.1 (C-6), 136.9 (C-4), 160.7 (C-2), 168.9 (C-7) ppm. $^{11}$B NMR (96 MHz, $CDCl_3$): δ: $B_{tri}$ = 38.3 ($h_{1/2}$ = 905 Hz), $B_{tetra}$ = 7.2 ppm ($h_{1/2}$ = 148 Hz). $C_{35}H_{37}B_2Fe_2NO_3$: calcd. C 63.80, H 5.62, N 2.13; found C 64.10, H 6.08, N 2.91 (%).

**Complex 4: 4** was prepared from **1f** (0.30 g, 1.32 mmol) and ferrocenyl boronic acid (0.30 g, 1.32 mmol) as a red solid in 75.5% yield (0.42 g, 1.00 mmol), m.p. 236−238 °C. IR ṽ = (KBr): 3080, 3056, 2916, 1618 (C=N), 1548, 1474, 1452, 1438, 1388, 1302, 1240, 1210, 1192, 1104, 1094, 1008, 952, 938, 816, 762 cm$^{-1}$. MS (15 eV): *m/z* (%) = 421 (100) [M$^+$], 420 (44), 419 (12), 418 (4), 357 (1), 356 (6), 355 (4), 354 (3), 353 (5), 352 (1), 317 (1), 312 (2), 300 (4), 299 (2), 298 (2), 297 (4), 296 (2), 290 (2), 238 (2), 237 (20), 236 (84), 235 (55), 234 (9), 225 (2), 187 (2), 186 (20), 184 (2). $^1$H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 5 H, Cp-H), 3.79 (m, 1 H, 18-H), 3.88 (m, 1 H, 17-H), 3.93 (m, 1 H, 19-H), 4.05 (m, 1 H, 16-H), 4.82 (d, *J* = 15.5 Hz, 1 H, $14_b$-H), 4.89 (d, *J* = 15.5 Hz, 1 H, $14_a$-H), 6.96 (t, *J* = 7.9 Hz, 1 H, 5-H), 7.01 (d, *J* = 7.9 Hz, 1 H, 3-H), 7.28 (d, *J* = 7.5 Hz, 1 H, 10-H), 7.40 (t, *J* = 7.5 Hz, 1 H, 11-H), 7.46 (t, *J* = 7.5 Hz, 1 H, 12-H), 7.60 (t, *J* = 7.9 Hz, 1 H, 4-H), 7.68 (d, *J* = 7.9 Hz, 1 H, 6-H), 7.97 (d, *J* = 7.5 Hz, 1 H, 13-H), 9.21 (s, 1 H, 7-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 62.3 (C-14), 67.6 (C-Cp), 67.9 (C-18), 68.0 (C-17), 70.6 (C-19), 71.0 (C-16), 117.9 (C-1), 118.9 (C-13), 119.1 (C-3), 119.6 (C-5), 125.8 (C-11), 127.8 (C-12), 128.4 (C-10), 132.9 (C-6), 134.9 (C-9), 137.9 (C-4), 138.2 (C-8), 156.8 (C-7), 160.2 (C-2) ppm. $^{11}$B NMR (96 MHz, $CDCl_3$): δ = 5.0 ppm ($h_{1/2}$ = 555 Hz). $C_{24}H_{20}B_1Fe_1N_1O_2$: calcd. C 67.99, H 4.72, N 3.30; found C 67.69, H 4.70, N 3.42 (%).

**Complex 5a: 5a** was prepared from **1g** (0.50 g, 2.60 mmol) and ferrocenyl boronic acid (0.60 g, 2.60 mmol) as a red solid in 88% yield (0.88 g, 2.26 mmol); it is soluble in chloroform, m.p. 223 °C. IR ṽ = (KBr): 3414, 2924, 2886, 2850, 1642 (C=N), 1608, 1560, 1476, 1460, 1228, 1212, 1114, 1106, 1000, 810, 770, 764 cm$^{-1}$. MS (15 eV): *m/z* (%) = 387 (100) [M$^+$], 386 (31), 385 (8), 384 (2), 322 (3), 321 (3), 203 (9), 202 (71), 201 (20), 200 (20), 187 (2), 186 (15), 148 (2), 78 (2). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.91−1.63 (m, 4 H, 9-, 10-H), 3.69 (t, *J* = 9.0 Hz, 2 H, 8-H), 3.87 (m, 1 H, 16-H), 3.99 (t, *J* = 9.0 Hz, 2 H, 11-H), 4.10 (s, 5 H, Cp-H), 4.12 (m, 1 H, 14-H), 4.17 (m, 1 H, 15-H), 4.20 (m, 1 H, 13-H), 6.83 (td, *J* = 8.5, 1.8 Hz, 1 H, 5-H), 7.11 (d, *J* = 8.5 Hz, 1 H, 3-H), 7.26 (dd, *J* = 8.5, 1.8 Hz, 1 H, 6-H), 7.57 (td, *J* = 8.5, 1.8 Hz, 1 H, 4-H), 8.03 (s, 1 H, 7-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 27.6 (C-10), 32.2 (C-9), 56.2 (C-11), 62.4 (C-8), 68.6 (C-Cp), 68.8 (C-15), 69.1 (C-14), 70.9 (C-16), 72.1 (C-13), 117.3 (C-1), 118.8 (C-5), 119.8 (C-3), 131.4 (C-6), 137.8 (C-4), 161.9 (C-2), 162.4 (C-7) ppm. $^{11}$B NMR (96 MHz, $CDCl_3$): δ = 9.6 ppm ($h_{1/2}$ = 154.8 Hz). $C_{21}H_{22}B_1Fe_1N_1O_2$: calcd. C 64.69, H 5.64, N 3.59; found C 64.99, H 5.59, N 3.95 (%).

**Complex 5b: 5b** was obtained from **1h** (0.50 g, 2.41 mmol) and ferrocenyl boronic acid (0.55 g, 2.41 mmol) as a red solid, in 84.7% yield (0.82 g, 2.03 mmol), that is soluble in chloroform, m.p. 196 °C. IR ṽ = (KBr): 2914, 2894, 2364, 1624 (C=N), 1558, 1458, 1434, 1370, 1348, 1328, 1280, 1210, 1126, 1110, 996, 960, 760 cm$^{-1}$. MS (15 eV): *m/z* (%) = 401 (100) [M$^+$], 400 (29), 386 (5), 336 (1), 217 (11), 216 (80), 215 (22), 186 (57), 162 (4), 146 (2). $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.00−1.30 (m, 4 H, 9-, 10-H), 2.47 (s, 3 H, Me), 3.56 (m, 1 H, 15-H), 3.63 (t, *J* = 9.0 Hz, 2 H, 8-H), 3.91 (m, 1 H, 14-H), 3.93 (t, *J* = 9.0 Hz, 2 H, 11-H), 4.06 (m, 1 H, 16-H), 4.07 (s, 5 H, Cp-H), 4.19 (m, 1 H, 13-H), 6.83 (t, *J* = 7.8 Hz, 1 H, 5-H), 7.08 (d, *J* = 7.8 Hz, 1 H, 3-H), 7.45 (d, *J* = 7.8 Hz, 1 H, 6-H), 7.46 (t, *J* = 7.8 Hz, 1 H, 4-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 15.9 (Me), 28.8 (C-10), 30.6 (C-9), 48.4 (C-11), 61.8 (C-8), 68.3 (C-Cp), 68.4 (C-15), 68.7 (C-14), 70.2 (C-16), 72.1 (C-13), 118.3 (C-5), 118.9 (C-1), 120.3 (C-3), 128.2 (C-6), 136.2 (C-4), 160.8 (C-2), 168.1 (C-7) ppm. $^{11}$B NMR (96 MHz, $CDCl_3$): δ = 8.7 ppm ($h_{1/2}$ = 159 Hz). $C_{22}H_{24}B_1Fe_1N_1O_2$: calcd. C 65.42, H 5.94, N 3.47; found C 65.69, H 6.11, N 3.61 (%).

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