

Novel Organometallic Building Blocks for Molecular Crystal Engineering. 2. Synthesis and Characterization of Pyridyl and Pyrimidyl Derivatives of Diboronic Acid, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)_2]$, and of Pyridyl Boronic Acid, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)]$

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The synthesis and structural characterization of the ferrocenyl diboronic acid complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)_2]$ (**1**) and of its products of monosubstitution, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)]$ (**2**) in three polymorphic modifications, **2a–c**, and of disubstitution, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{N})_2]$ (**4**), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}_6\text{H}_4\text{-4-C}_5\text{H}_4\text{N})_2]$ (**6**), and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-5-C}_4\text{H}_3\text{N}_2)_2]$ (**7**), are reported together with an investigation of the mode of supramolecular bonding in the solid state. The competition between the hydrogen-bonding interactions of the $(\text{B})\text{O}-\text{H}\cdots\text{O}(\text{B})$ and $(\text{B})\text{O}-\text{H}\cdots\text{N}$ types in the cases of crystalline **1** and **2** has been investigated. The $\text{B}(\text{OH})_2$ group provides two hydrogen bonding donor groups and two acceptors, forming mainly cyclic hydrogen-bonded systems in topological analogy with a primary amido group. Compounds **4**, **6**, and **7** are examples of neutral disubstituted pyridyl and pyrimidyl ferrocenyl complexes with potentials as supramolecular ligands. The compounds $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NH})(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)]$ [**3a**], $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NH})(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)]$ [**3b**], and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NH})_2]$ [**5**] have been obtained by treatment with acids of compounds **2** and **4**, respectively. The interionic hydrogen bonds have also been investigated.

Introduction

The investigation of the bonds between molecules involves all areas of chemistry, in particular the thriving areas of supramolecular and materials chemistry.¹ The goal is that of reaching an intelligent control of the recognition and assembly processes that lead from molecular or ionic components to superstructures: hence, from individual to collective (chemical and physical) properties. All these ideas also apply to molecular crystal engineering,² the area of supramolecular chemistry devoted to the design and bottom-up construction of functional crystalline materials. As noncovalent interactions are responsible for the existence and functioning of supermolecules, intermolecular and/or inter-

ionic interactions are responsible for cohesion and solid-state properties of molecular crystals.³

A major issue in modern crystal engineering is that of exploiting the topological, electronic, and spin properties of metal atoms to construct molecular materials in which metal centers are joined by ligands⁴ and can communicate via coordination bonds or noncovalent interactions, such as hydrogen bonds.^{3b} We are contributing,⁵ together with others,⁶ to the efforts to open an organometallic avenue to molecular crystal engineering. Organometallic molecules and ions combine the supramolecular bonding capacity of organic molecules with

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the presence of metal atoms, which bring about an almost combinatorial mixture of valence, spin, and charge states together with coordination geometries.

While many organic compounds utilized by the crystal engineer are commercially available and can be used directly in the supramolecular assembly (cocrystallization, charge transfer, inclusion, host–guest, etc.) this is not so with organometallic species, which need, most often, to be synthesized on purpose. With this idea in mind, we have begun to prepare, also in collaboration with others, novel organometallic building blocks with adequate supramolecular bonding functionalities for the construction of desired architectures.⁷ We have focused our strategy on the possibility of adding hydrogen-bonding donor/acceptor groups, such as $-\text{COOH}$, $-\text{OH}$, and $-\text{CHO}$, to robust sandwich complexes. The rationale for this choice is that the hydrogen bond is the strongest of the noncovalent interactions and best combines strength and directionality.⁸ Strength is a synonym for cohesion and stability, while directionality implies topological control and selectivity, which are fundamental prerequisites for successful control of the aggregation processes.

In previous studies, we have shown that carboxylic $-\text{COOH}$, $-\text{OH}$, primary $-\text{CONH}_2$, and secondary $-\text{CONHR}$ amido groups form essentially the same type of hydrogen-bonding interactions whether as part of organic molecules or as metal-coordinated ligands.⁹ This is not surprising, as hydrogen bonds formed by such strong donor and acceptor groups are at least 1 order of magnitude stronger than most noncovalent interactions. Dicarboxylic acid molecules, for example, offer the possibility of supramolecular networking because of the twin hydrogen bonding function. We have extensively exploited this feature in the construction and/or utilization of the sandwich acids $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]$,¹⁰ $[\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]^+$,^{5a} and $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{COOH})_2]$.⁷ The cobalt cationic complex, in particular, has proved to be extremely versatile for the selective trapping of alkali-metal ions and for use in solid–gas reactions with vapors of acids and bases.¹¹

The aim of this paper is essentially 2-fold. First, we will expand our chemistry and crystal engineering

efforts toward a different supramolecular bonding functionality, namely the boronic acid group $-\text{B}(\text{OH})_2$, and investigate the intermolecular hydrogen-bonding patterns formed by the diboronic acid ferrocenyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)_2]$ (**1**), whose solid-state structure was unknown, and by the three polymorphic modifications of the monosubstituted pyridyl derivative $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)]$ (**2**). Second, we exploit the boronic acid group $-\text{B}(\text{OH})_2$ as a chemical intermediate in the synthesis of disubstituted pyridyl and pyrimidyl derivatives through a modified Suzuki coupling protocol (used also to obtain **2**; see below). The bis-(pyridyl) derivative $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{N})_2]$ (**4**), the bis(phenylpyridyl) derivative $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}_6\text{H}_4\text{-4-C}_5\text{H}_4\text{N})_2]$ (**6**), and the bis(pyrimidyl) complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-5-C}_4\text{H}_3\text{N}_2)_2]$ (**7**), as well as the monosubstituted species **2**, have been synthesized and structurally characterized. While the interest in compounds **1** and **2** is mainly in the hydrogen-bonding capacity of the diboronic acid unit(s), compounds **4**, **6**, and **7** are interesting as sophisticated supramolecular ligands toward late-transition-metal atoms in the formation of larger complexes or coordination networks. A preliminary study of compound **4** has shown that it can be successfully used to prepare heterobimetallic metalla macrocycles with metals such as Ag(I), Cu(II), and Zn(II).¹² For the sake of completeness, the salts $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NH})(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)][\text{NO}_3]$ (**3a**), $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NH})(\eta^5\text{-C}_5\text{H}_4\text{-B}(\text{OH})_2)][\text{SO}_4]\cdot 3\text{H}_2\text{O}$ (**3b**), and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NH})_2][\text{Cl}]_2\cdot 4\text{H}_2\text{O}$ (**5**) have also been prepared by treatment with acids of compounds **2** and **4**, respectively.

It is worth recalling that boronic acids, which are known to form covalently bonded complexes with diols, have been attracting much attention and are currently studied as a tool for carbohydrate sensors and as potential substitutes for commercial enzyme-based sensors;^{13a–d} molecules containing $\text{R-B}(\text{OH})_2$ groups attached to a ferrocene unit have also been designed and synthesized and their properties analyzed with techniques such as circular dichroism^{13e} and electrochemistry.^{13f,g}

Chart 1 shows how the boronic acid group can form hydrogen-bonding interactions similar to those observed with primary amides and carboxylic acids.^{14a} With respect to the carboxylic ring, both amido and boronic acid groups have the possibility for lateral bonds in addition to the formation of octaatomic rings ($\text{R}_2^2(8)$ in graph-set terminology^{14b,c}). Moreover, the boronic acid group may present the advantage, over groups containing $\text{C}=\text{O}$, of an expectedly smaller tendency to coordi-

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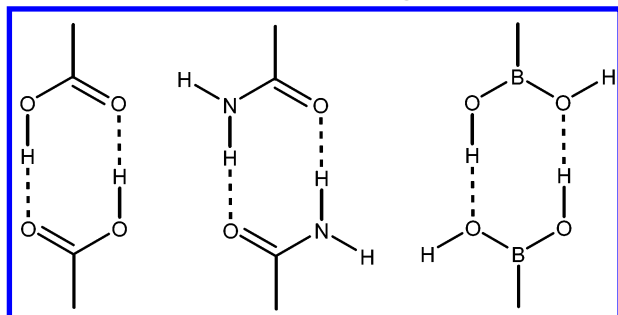
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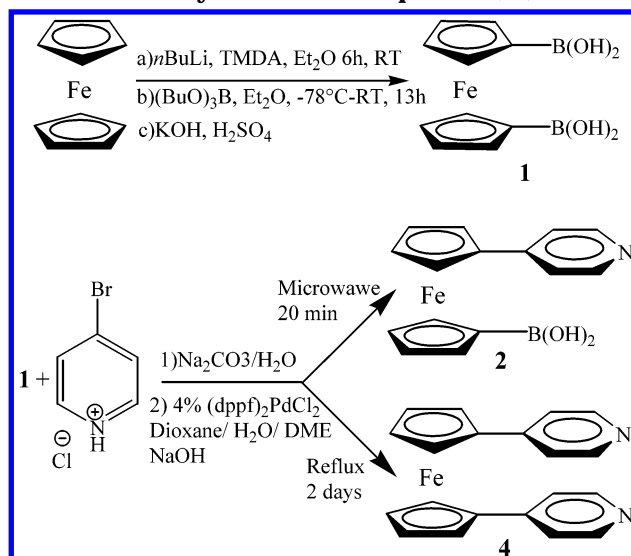
Chart 1. Comparison between Hydrogen-Bonding Ring Motifs Involving Carboxylic (Left), Amido (Middle), and Boronic (Right) Groups

nate to metal centers. The presence of two boronic acid groups in **1** and of the pyridyl ligand and of one boronic acid group in **2** and the convolution of these features with the conformational freedom around the coordination axis of the Cp ligands in both compounds may have interesting consequences on the way these molecules can interact in the solid state.

We were also intrigued by the possible competition between interactions of (B)O–H...N hydrogen bonds and N...B intermolecular bonds in compound **2**, which carries *both* the boronic acid group and the pyridyl group. The two ligands have different acid–base properties: while the pyridine N atom is a Lewis base, the boronic acid group behaves as a Brønsted acid because of the polarized –OH groups. Thus compound **2** can form, at least in principle, *both* intermolecular hydrogen bridges in the solid state via the boronic acid groups *and* intermolecular N...B coordination bonds with the pyridyl Lewis base, as in H₃B...NH₃.¹⁵ On the other hand, the fact that compound **2** has been characterized as two anhydrous polymorphic modifications, **2a** and **2c**, as well as the hydrated form [Fe(η^5 -C₅H₄-4-C₅H₄N)(η^5 -C₅H₄-B(OH)₂)]·0.5H₂O (**2b**) will provide information on the competition between (B)O–H...N and (B)O–H...O(B) intermolecular interactions in the solid state. The study of the relationship between polymorphic and pseudo-polymorphic modifications often offers valuable insight into the factors controlling supramolecular bonding.¹⁶

Results and Discussion

Ferrocene-1,1'-diboronic acid (**1**) was prepared by a reported procedure^{17a} from 1,1'-dilithioferrocene and tri-*n*-butyl borate, followed by hydrolysis of the resulting dibutylboronate. The mono(pyridyl) boronic acid **2a** and the 1,1'-bis(4-pyridyl)ferrocene (**4**) were obtained from **1** through a modified Suzuki coupling protocol,^{17b,c} as depicted in Scheme 1. Prolonged heating of a mixture

Scheme 1. Synthesis of Complexes 1, 2, and 4

of **1** and 4-bromopyridine, in the presence of 4 mol % (dppf)PdCl₂ catalyst, afforded the bis(pyridine) derivative **3** in 53% yield after chromatographic purification. On the other hand, from the same reaction mixture irradiated for a short period (20 min) in a microwave oven, the monosubstituted product **2a** was obtained in 57% yield. Similar reaction procedures were used to prepare compounds **6** and **7** (see Experimental Section). All compounds have been characterized by single-crystal X-ray diffraction, and their structural features and supramolecular bonding are discussed in the following.

Boronic Acid Complexes [Fe(η^5 -C₅H₄-B(OH)₂)₂] (1**) and [Fe(η^5 -C₅H₄-4-C₅H₄N)(η^5 -C₅H₄-B(OH)₂)] (**2**) and the Nitrate (**3a**) and Sulfate (**3b**) Salts of **2**.** Relevant intermolecular hydrogen bonding parameters for all compounds discussed herein are reported in Table 1. Compound **1** shows all the potentials of the boronic acid group as a hydrogen-bonding linker. The principal motif is represented in Figure 1a as chains of hydrogen-bonded ferrocenyl moieties in a transoid conformation. Both boronic acid groups form R₂²(8) rings (in graph set terminology) with adjacent molecules along the chains,¹⁴ which are reminiscent of the chains formed by the dicarboxylic acid sandwich complex [Co^{III}(C₅H₄-COOH)₂]₂¹⁺^{5a} and by the two forms of [Cr^I(C₆H₅COOH)₂]₂¹⁺.⁷

The chains criss-cross in the crystal structure (Figure 1b) and establish hydrogen-bonding cross links with lateral protons, forming 16-atom rings (R₆⁶(16)); the O...O separation within the R₂²(8) ring is shorter than in the larger R₆⁶(16) ring (2.81(1) vs 2.89(1) Å). It is also noteworthy that the R₂²(8) distance is longer than in the dicarboxylic acids [Fe^{II}(C₅H₄COOH)₂] (O...O = 2.621(1), 2.643(1) Å and 2.593(4), 2.635(4) Å in the triclinic^{10a} and monoclinic^{10b} forms, respectively), [Co^{III}(C₅H₄COOH)₂]₂¹⁺ (O...O = 2.600(2) Å),^{5e} [Cr(C₆H₅COOH)₂]₂¹⁺ (O...O ranging from 2.558(2) to 2.643(2) Å) and [Cr^I(C₆H₅-COOH)₂]₂¹⁺ (O...O ranging from 2.618(2) to 2.634(2) Å);⁷ this difference probably arises from the much stronger nucleophilicity of the C=O system with respect to the B–O(H) one. As a matter of fact, the O...O separations between neutral molecules, listed in Table 1, are closer to the values of intermolecular distances in solid alcohols and water than to those usually observed between –COOH groups.¹⁸

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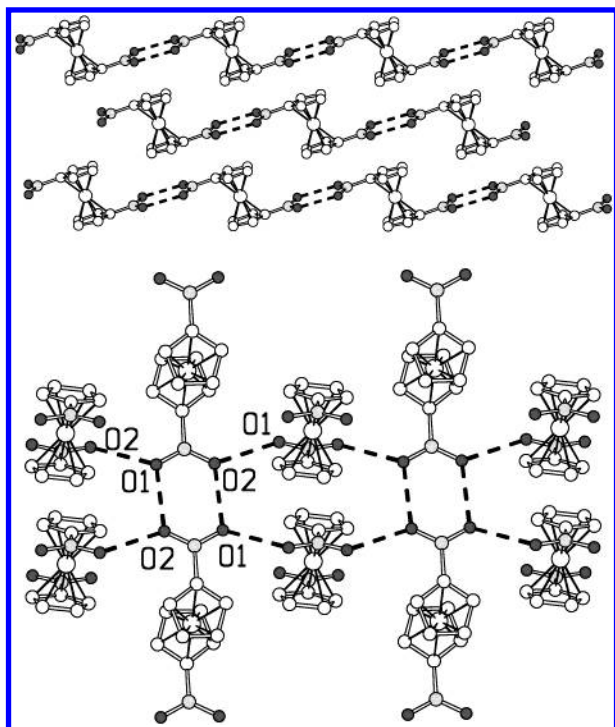


Figure 1. Two views of compound **1**: (a, top) chains of hydrogen-bonded ferrocenyl moieties in a transoid conformation, forming $R_2^2(8)$ rings; (b, bottom) criss-crossing of the chains in the crystal structure and establishment of hydrogen-bonding cross-links with lateral protons, forming larger 16-atom rings ($R_6^6(16)$). H_{CH} atoms are not shown for clarity; H_{OH} atoms are not observed (see the Experimental Section).

Table 1. Relevant Hydrogen Bonding Distances (Å) for Compounds 1, 2a–c, 3a,b, and 5

compd	O(H)⋯X	N(H)⋯X
1	O(1)⋯O(2)	2.81(1)
	O(1)⋯O(2)	2.89(1)
2a	O(1)⋯O(2)	2.97(1)
	O(2)⋯N(1)	2.70(1)
2b	O(1)⋯O(2)	2.782(5)
	O(1)⋯N(1)	2.745(9)
2c	O(2)⋯O(4)	2.855(5)
	O(4)⋯O(3)	2.764(5)
	O(1)⋯N(1)	2.844(5)
	O(3)⋯N(2)	2.790(5)
3a	O(1)⋯O(4) _{nitrate}	2.83(1)
	O(2)⋯O(3) _{nitrate}	2.75(1)
3b	O(1)⋯O(6) _{sulfate}	2.725(4)
	O(2)⋯O(7) _{sulfate}	2.718(5)
	O(3)⋯O(9) _{water}	2.730(5)
	O(4)⋯O(11) _{water}	2.717(5)
	O(9)⋯O(8) _{water}	2.944(5)
	O(10) _{water} ⋯O(7) _{sulfate}	2.837(5)
	O(10) _{water} ⋯O(8) _{sulfate}	2.903(5)
	O(11) _{water} ⋯O(5) _{sulfate}	2.757(5)
	O(11) _{water} ⋯O(6) _{sulfate}	2.772(5)
	O(1) _{water} ⋯O(4) _{water}	2.69(2)
5	O(2) _{water} ⋯O(3) _{water}	2.72(2)
	O(3) _{water} ⋯O(4) _{water}	2.72(2)
	O(1) _{water} ⋯Cl(1)	3.08(2)
	O(1) _{water} ⋯Cl(2)	3.12(2)
	O(2) _{water} ⋯Cl(1)	3.05(2)
	O(2) _{water} ⋯Cl(2)	3.15(1)
	O(4) _{water} ⋯Cl(2)	3.13(2)
	N(1)⋯O(4) _{nitrate}	2.74(1)
	N(1)⋯O(10) _{water}	2.800(6)
	N(1)⋯O(10) _{water}	2.921(6)
	N(2)⋯O(3) _{water}	2.69(2)
	N(1)⋯Cl(1)	3.01(2)
	N(2)⋯O(3) _{water}	2.69(2)

Compound **2** carries both a $B(OH)_2$ unit and a C_5H_4N unit. In terms of molecular structure, the complex represents the intermediate in the formation of the bis-(pyridine) complex **4**. The simultaneous presence of one boronic acid group and one pyridyl group generates

several “supramolecular bonding options” for this molecule, since the $B(OH)_2$ unit is capable of multiple hydrogen-bonding donations as seen above with **1**, and the pyridyl ligand can donate an electron pair to a suitable Lewis acid or accept hydrogen bond formation from a suitable proton donor. Compound **2** has been isolated in three forms, the two anhydrous forms **2a** and **2c** and the monohydrated *pseudo*-polymorphic form **2b**.¹⁶

The family of crystals **2** provides some insight on the “options” mentioned above:

(i) Intermolecular $(B)O-H\cdots N$ interactions are present in all crystals; hence, the pyridyl N atom favors hydrogen-bonding acceptance from the O–H group over electron donation toward the empty orbital on the B atoms.

(ii) Although all three crystals show the simultaneous occurrence of both $(B)OH\cdots O(B)$ and $(B)OH\cdots N$ hydrogen bonds, the patterns are different. This is a consequence of the high conformational freedom of complex **2** around the Fe atom coordination axis, which generates different *relative* orientations of the hydrogen-bonding groups.

In crystalline **2a** the molecules form dimers via $(B)-OH\cdots N$ bonds ($O\cdots N = 2.70(1)$ Å), as shown in Figure 2a. These dimers are then linked in a secondary pattern by the $(B)OH\cdots O(B)$ lateral bonds ($O\cdots O = 2.97(1)$ Å). This arrangement leads to eclipsing of the $B(OH)_2$ group over the C_5H_4N group. In **2b**, on the other hand, the primary motif appears to be the boronic acid ring based on $(B)OH\cdots O(B)$ bonds ($O\cdots O = 2.782(5)$ Å), which is reminiscent of the carboxylic ring (see Chart 1), while dimers are formed by the lateral O–H groups with the pyridyl acceptors ($(B)OH\cdots N$ bonds, $O\cdots N = 2.745(9)$ Å). The conformation of the two ligands is *cisoid*. In crystalline **2c** a third, almost intermediate, topology is observed (see Figure 2c), even though the molecule adopts the same conformation as in **2b**. In **2b** there are boronic rings based on $(B)OH\cdots O(B)$ bonds ($O\cdots O = 2.764(5)$ Å) and lateral $(B)OH\cdots N$ bonds ($O\cdots N = 2.790(5)$ and $2.844(5)$ Å) but there are also lateral $(B)-OH\cdots O(B)$ bonds as in **2a** ($O\cdots O = 2.855(5)$ Å) leading to the complex pattern shown in Figure 2c.

These differences and analogies concur to indicate that the $(B)OH\cdots N$ and the $(B)OH\cdots O(B)$ donor–acceptor systems have comparable strength and do not lead to a strong topological preference. This characteristic, coupled with the structural nonrigidity of the ferrocenyl complexes, could justify the observation of different crystal forms obtained in relatively similar crystallization conditions (see the Experimental Section).

Compound **2b** is a hydrated form. The water molecules do not seem to play any particular role in the packing; the distances from the neighboring atoms are fairly long (shortest $O\cdots O_{water} = 3.13(1)$ Å) and indicative of the fact that the water molecules are loosely held in the packing. On the other hand, the thermogravimetric (TGA) treatment of **2b** indicates that water can be fully removed only when the temperature reaches 183 °C. Importantly, powder X-ray diffraction measurements before and after dehydration show an almost unchanged pattern, which indicates that the crystal **2b**

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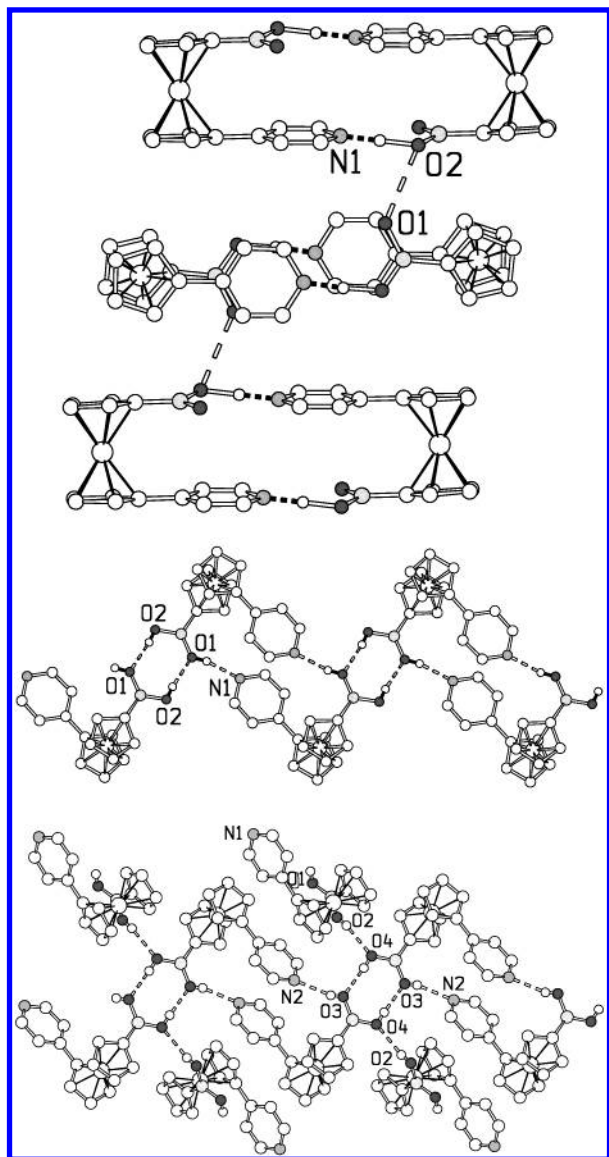


Figure 2. (a, top) Hydrogen-bonded dimers formed by (B)-OH \cdots N interactions in crystalline **2a**. Note how the dimers are connected via (B)OH \cdots O(B) interactions. The H atom bound to O(1) was not observed (see the Experimental Section). (b, middle) Hydrogen-bonding pattern in crystalline **2b**. Note how the ligand conformation has changed from eclipsed in **2a** to cisoid in **2b**. (c) Hydrogen-bonding pattern in crystalline **2c**. Note the similarity of the ligand conformation to that in **2b** and the presence of lateral (B)-OH \cdots O(B) interactions as in **2a**. H_{CH} atoms are not shown for clarity.

retains the hydrogen-bonded network structure upon water removal.

Protonation of **2** with HNO₃ leads to formation of the cationic salt [Fe(η^5 -C₅H₄-4-C₅H₄NH)(η^5 -C₅H₄-B(OH)₂)]⁺[NO₃]⁻ (**3a**). Three independent hydrogen bonds are observed, all involving the [NO₃]⁻ anion: two O \cdots O hydrogen bonds between the boronic acid group and O atoms of the anion (2.83(1), 2.75(1) Å) and the charge-assisted ⁺N-H \cdots O⁻ interaction (N \cdots O = 2.741(1) Å). No link between the cations is present; thus, the preference appears to go to charge-assisted interactions between ions of opposite charge. The hydrogen-bonding interactions are shown in Figure 3a. Protonation with H₂SO₄ leads to formation of the hydrated salt [Fe(η^5 -

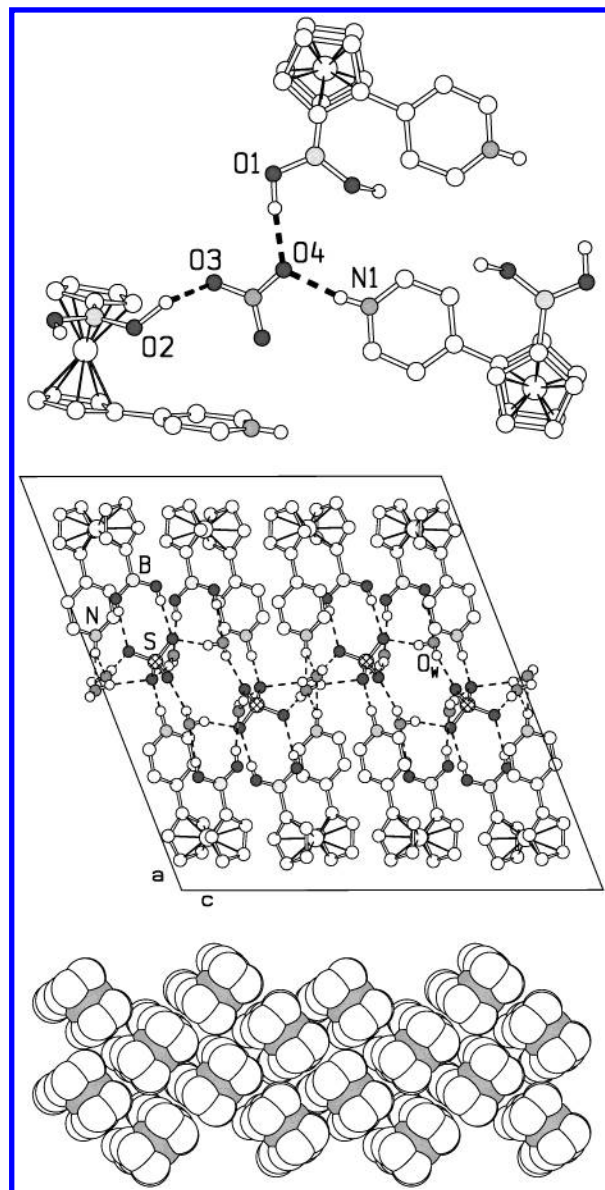


Figure 3. Hydrogen-bonding patterns in the nitrate **3a** (a, top) and sulfate **3b** (b, middle) salts of [Fe(η^5 -C₅H₄-4-C₅H₄NH)(η^5 -C₅H₄-B(OH)₂)]⁺ and (c, bottom) projection in the *bc* plane of the van der Waals ferrocenyl moiety "wall" in **3b**. H_{CH} atoms not shown for clarity.

C₅H₄-4-C₅H₄NH)(η^5 -C₅H₄-B(OH)₂)]₂[SO₄] \cdot 3H₂O (**3b**). Two independent hydrogen bonds are observed between the B(OH)₂ group and the [SO₄]²⁻ anion (O \cdots O = 2.725(4) and 2.718(5) Å) (see Figure 3c). The shortest, charge-assisted intermolecular H bond is between the ⁺N-H group and the [SO₄]²⁻ anion (N \cdots O = 2.654(5) Å). The three molecules interact via hydrogen bonding with the boronic acid, the ⁺N-H group, and the sulfate anion (see Table 1). As can be appreciated from Figure 3b, the hydrogen-bonding functions are all segregated between two "walls" of ferrocenyl moieties, which are in van der Waals contact with adjacent rows along the direction of the *c* axis. A projection of the van der Waals "walls" in the *bc* plane is shown in Figure 3c.

Disubstituted Derivatives [Fe(η^5 -C₅H₄-4-C₅H₄N)₂] (**4**), [Fe(η^5 -C₅H₄-C₆H₄-4-C₅H₄N)₂] (**6**), and [Fe(η^5 -C₅H₄-5-C₄H₃N₂)₂] (**7**). Compound **4** is the first of a series of bipyridine-type ferrocenyl molecules and has

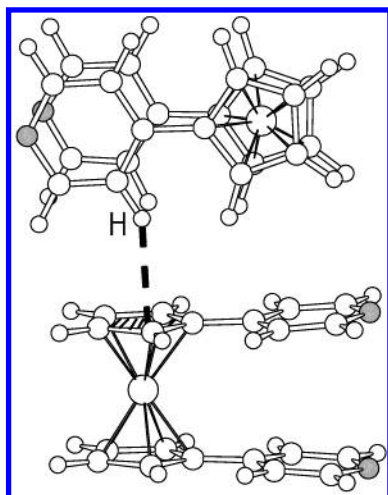


Figure 4. $\text{CH}\cdots\pi$ interaction ($(\text{C})\text{H}\cdots\pi = 2.66 \text{ \AA}$, $\text{C}-\text{H}\cdots\pi = 146.3^\circ$) observed in crystalline **4**. The broken line represents the distance from the H atom to the plane of the aromatic ring on the adjacent molecule.

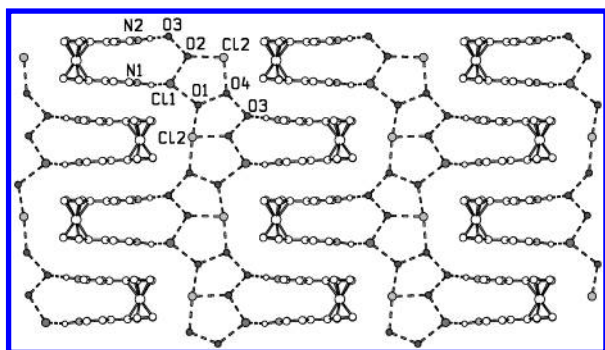


Figure 5. Formation of hydrogen-bonding interactions of the $^+\text{N}-\text{H}\cdots\text{O}_{\text{water}}$ and of the $^+\text{N}-\text{H}\cdots\text{Cl}^-$ type by the $\text{N}-\text{H}$ donors on each complex in crystalline **5**. The cations are arranged in piles and are connected to cations on adjacent piles via a network of $\text{O}(\text{H})_{\text{water}}\cdots\text{O}_{\text{water}}$ and $\text{O}(\text{H})_{\text{water}}\cdots\text{Cl}^-$ hydrogen-bonding interactions.

been used already to synthesize heterobimetallic metalla macrocycles.¹² In the absence of stronger hydrogen-bonding interactions, crystal cohesion is guaranteed by van der Waals interactions and by $\text{CH}\cdots\pi$ interactions ($(\text{C})\text{H}\cdots\pi = 2.66 \text{ \AA}$, $\text{C}-\text{H}\cdots\pi = 146.3^\circ$) (see Figure 4). To evaluate $\text{CH}\cdots\pi$ interactions, $\text{C}-\text{H}$ distances were normalized to the neutron derived value of 1.08 \AA ; the distance reported is taken from the H atom to the plane of the aromatic ring.¹⁹ It is noteworthy that, although the transoid structure ought to be preferred for steric reasons, the complex adopts an eclipsed conformation in the solid state, very likely as a consequence of packing optimization.

When **4** is treated with HCl , the hydrated dichloride salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NH}_2)_2][\text{Cl}]_2\cdot 4\text{H}_2\text{O}$ (**5**) is obtained. The two $\text{N}-\text{H}$ donors on each complex form two types of hydrogen-bonding interactions, namely an $^+\text{N}-\text{H}\cdots\text{O}$ bond with water ($\text{N}\cdots\text{O} = 2.69(2) \text{ \AA}$) and $^+\text{N}-\text{H}\cdots\text{Cl}^-$ bond with the chloride anion ($\text{N}\cdots\text{Cl} = 3.01(2) \text{ \AA}$), as shown in Figure 5. The system crystallizes in the chiral space group $P2_12_12_1$, with the dications arranged in piles along the a axis. The organometallic cations belonging to adjacent piles are all interconnected

via a network of $\text{O}(\text{H})_{\text{water}}\cdots\text{O}_{\text{water}}$ and $\text{O}(\text{H})_{\text{water}}\cdots\text{Cl}^-$ hydrogen bonding interactions ($\text{O}_{\text{water}}\cdots\text{O}_{\text{water}}$ and $\text{O}_{\text{water}}\cdots\text{Cl}$ distances in the ranges $2.69(2)-2.72(2)$ and $3.05(2)-3.15(1) \text{ \AA}$, respectively).

The synthetic route that leads to **4** has been utilized to generate the bis(phenylpyridyl) complex **6**. In contrast to **4**, which adopts an eclipsed conformation in the solid state, compound **6** adopts a fully transoid structure (see Figure 6). The $\text{C}_5\text{H}_4\text{-C}_6\text{H}_4\text{-4-C}_5\text{H}_4\text{N}$ system is not flat, but twisted: the phenyl ring and the pyridyl rings form angles of ca. 14.1 and 5.3° with the Cp ligand, respectively. The molecules form ring dimers in their crystals via $\text{C}-\text{H}\cdots\text{N}$ interactions ($\text{C}\cdots\text{N}$ distance $3.457(5) \text{ \AA}$), and the dimers are arranged in infinite chains extending along the b axis direction (see Figure 6).

The eclipsed conformation is found again in the ferrocene pyrimidyl complex **7** (see Figure 7a). The pyrimidyl group forms a twist angle of ca. 28.7° with the Cp ligand. The crystals of **7** are affected by an interesting type of structural disorder with the molecular piles shifted in the crystals by a pitch of "half a molecule" along the a axis. This is due to the fact that the inter-ring separation is almost the same whether the ligands are in van der Waals contacts or are bound via the metal atoms, so that the average crystal structure shows metal atoms with 50% occupancy between every Cp ring along the molecular piles. It is noteworthy that one of the hydrogen atoms of the pyrimidyl ligands points toward the iron metal center of the adjacent pile ($\text{Fe}\cdots\text{H} = 3.20 \text{ \AA}$ for a normalized H atom position), as can be observed in Figure 7b.

Conclusions

The main scope of the present study has been that of synthesizing and characterizing a series of new organometallic molecules that could add to the storehouse of building blocks available to the "organometallic crystal engineer". A second objective has been that of exploring less common hydrogen-bonding functionalities that could provide alternatives, in terms of robustness and transferability, to the strong hydrogen-bonding groups usually employed to link organometallic building blocks in molecular crystals.

Polycarboxylic acids are being widely utilized for the bottom-up preparation of supramolecular aggregates and crystalline materials based on molecular or ionic building blocks.²⁰ The $-\text{COOH}$ group is, in fact, capable of forming strong intermolecular hydrogen bonds and the presence of several $-\text{COOH}$ groups with different orientations in space allows construction of one-, two-, and three-dimensional aggregates. This also applies to organometallic acids, although they are much less common than polycarboxylic organic acids, which often are commercially available. The $-\text{COOH}$ functional group, however, can easily give coordination to metal centers when employed together with coordination complexes. In many instances, there is a competition between metal atoms accepting electron donation from

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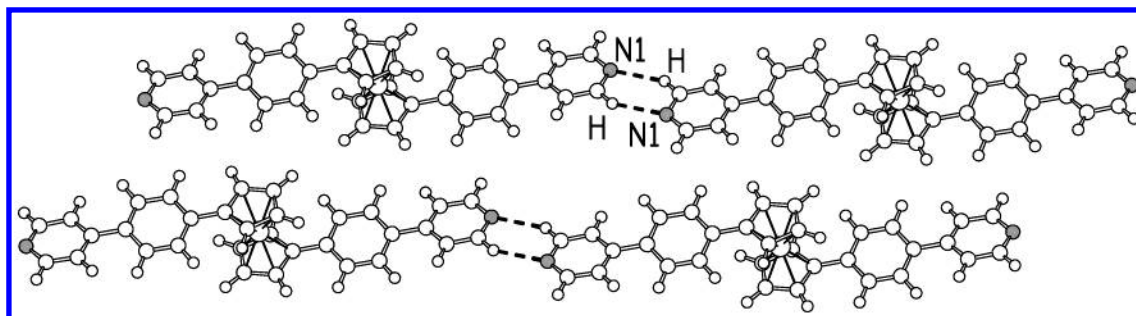


Figure 6. Transoid conformation of the two ligands in crystalline **6**, allowing formation of infinite chains of ring dimers, linked via C–H···N interactions.

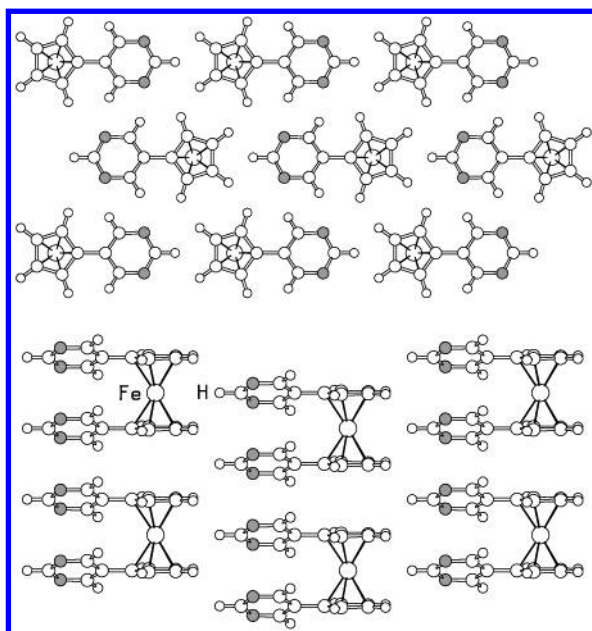


Figure 7. (a, top) Eclipsed conformation of the ferrocene pyrimidyl complex **7**. (b, bottom) Molecular piles along the *a* axis. Only one of the two disordered positions of iron is shown. Note how one of the pyrimidyl hydrogen atoms points toward an iron metal center on the adjacent pile.

the lone pairs on the O atoms and the capacity of forming intermolecular hydrogen-bonding interactions. This competition may prevent formation of supramolecular metal-containing networks based on hydrogen-bonding linkers.

In this study we have explored the hydrogen-bonding capacity of a less conventional acid, namely the boronic acid group --B(OH)_2 . In terms of Brønsted acidity the B(OH)_2 group is weaker than the --COOH group, in view of the reduced polarization of the O–H bond, because the O atom is bound to the electron-deficient boron atom rather than to an electron-rich carbon atom. In terms of nucleophilicity, on the other hand, the O atom of the --O--H groups is much weaker than the --C=O system. Altogether the $\text{B(OH)}_2\cdots\text{B(OH)}_2$ interaction is weaker than the $\text{OH}\cdots\text{O}$ interaction between two --COOH groups. This is also reflected in the O···O separations. On the basis of this parameter one could say that the interaction recalls the $\text{OH}\cdots\text{O}$ bond observed in alcohols.¹⁸ On the other hand, the study of compounds **1** and **2** shows that the possibility of “lateral” hydrogen bonds, afforded by the additional --OH units, can be exploited to extend the hydrogen bond network by linking hydrogen-bonded chains together, as in primary amides.

Compound **2** provides also insight into the competition between the pyridyl nitrogen and the boronic oxygen as hydrogen-bonding acceptors. The three crystals differ in the patterns of hydrogen-bonding intermolecular interactions. The comparison of the hydrogen bond networks in the three forms of compound **2** indicates that the $\text{(B)OH}\cdots\text{N}$ and the $\text{(B)OH}\cdots\text{O(B)}$ donor–acceptor systems have comparable strength and do not lead to strong topological preferences.

In terms of chemical behavior, we have shown that one or both boronic acid groups in **1** can be substituted for pyridyl and other groups, opening up the route to the preparation of a plethora of novel mono- and bidentate ligands. The pyridyl boronic complex **2** is potentially useful for the simultaneous use as a ligand toward a metal center and as an intermolecular linker via the remaining B(OH)_2 unit. Preliminary results have been extremely encouraging and will be the subject of future reports.

Disubstitution of the --B(OH)_2 unit from **1** has allowed preparation of the bis(pyridyl), bis(phenylpyridyl), and bis(pyrimidyl) derivatives **4**, **6**, and **7**. Thanks to the possibility of metal coordination via the N atom lone pairs, these molecules can be exploited as sophisticated supramolecular ligands toward late-transition-metal atoms in the formation of larger complexes or of coordination networks. While we have not yet succeeded in the preparation of coordination networks based on **4**, **6**, and **7**, we have been able to prepare heterobimetallic metalla-macrocycles adducts of compound **4** with Ag^{I} , Cu^{II} , and Zn^{II} , confirming the potentials of the system.¹²

Experimental Section

General Information. All the starting materials were purchased from Aldrich and used as such without further purification. The starting material ferrocene-1,1'-diboronic acid, $[\text{Fe}(\eta^5\text{--C}_5\text{H}_4\text{--B(OH)}_2)_2]$ (**1**), was prepared according to the literature procedure.¹⁷ Compound **1** (10 mg, 0.036 mmol) was dissolved in water–acetone (1:1) (7 mL). Suitable single crystals for X-ray studies were obtained by slow evaporation of the solution at room temperature.

Synthesis of $[\text{Fe}(\eta^5\text{--C}_5\text{H}_4\text{--4-C}_5\text{H}_4\text{N})(\eta^5\text{--C}_5\text{H}_4\text{--B(OH)}_2)]$ (2a**).** An aqueous solution of Na_2CO_3 solution (1 M, 2.2 mL) was added to a solution of 4-bromopyridinium hydrochloride (0.088 g, 0.45 mmol) in dioxane (6.5 mL) under Ar, to generate 4-bromopyridine; the suspension was heated to 50 °C. The catalyst $\text{PdCl}_2[1,1'\text{--bis(diphenylphosphino)ferrocene}]$ (0.012 g, 0.014 mmol) was added, followed by a mixture of boronic acid (0.123 g, 0.45 mmol) and NaOH (3 M, 0.24 mL) in DME (3 mL). The reaction was refluxed for 20 min in a conventional microwave (power 650 kW). After hydrolysis with ice–water

Table 2. Crystal Data and Details of Measurements for Compounds 1, 2a–c, 3a,b, and 5–7

	1	2a	2b	2c	3a	3b	5	6	7
formula	C ₁₀ H ₁₂ B ₂ FeO ₄	C ₁₅ H ₁₄ BF ₂ FeNO ₂	C ₁₅ H ₁₅ BF ₂ FeNO _{2.5}	C ₁₅ H ₁₄ BF ₂ FeNO ₂	C ₁₅ H ₁₅ BF ₂ FeNO _{2.5}	C ₃₀ H ₃₆ B ₂ Fe ₂ N ₂ O ₁₁ S	C ₂₀ H ₂₄ Cl ₂ FeN ₂ O ₄	C ₃₂ H ₂₄ FeN ₂	C ₁₈ H ₁₄ FeN ₄
M _w	273.67	306.93	315.94	306.93	369.95	765.99	483.16	492.38	342.18
space group	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
a (Å)	7.429(6)	8.838(2)	17.330(3)	9.370(1)	14.080(5)	21.954(4)	13.810(9)	8.088(1)	3.533(1)
b (Å)	7.011(4)	9.385(4)	13.121(3)	11.583(2)	8.443(5)	7.362(2)	9.270(5)	8.033(3)	19.178(5)
c (Å)	10.031(5)	15.937(3)	15.996(3)	13.076(4)	14.343(5)	20.871(4)	17.360(5)	17.907(3)	10.350(3)
α (deg)	90	90	90	101.61(2)	90	90	90	90	90
β (deg)	90.62(5)	96.40(1)	131.08(2)	101.84(2)	116.15(2)	111.35(3)	90	98.42(1)	96.48(3)
γ (deg)	90	90	90	96.84(1)	90	90	90	90	90
V (Å ³)	522.4(6)	1313.7(7)	2741.8(9)	1341.5(5)	1198(1)	3142(1)	2222(2)	1148.0(5)	696.8(4)
Z	2	4	8	4	4	8	4	2	2
F(000)	280	632	1304	632	760	1584	1000	512	352
μ(Mo Kα) (mm ⁻¹)	1.438	1.146	1.103	1.122	1.014	1.055	0.947	0.682	1.086
no. of measd rflns	1915	2393	2503	4930	2797	5576	6858	3334	1002
no. of unique rflns	944	2307	2411	4707	2685	5426	2044	2015	485
no. of params	71	92	194	341	196	445	152	161	57
GOF on F ²	0.986	0.928	0.769	0.988	0.859	1.137	1.079	1.071	1.037
R1 (on F (I > 2σ(I)))	0.0913	0.0682	0.0378	0.0423	0.0598	0.0396	0.0840	0.0479	0.0650
wR2 (on F ² , all data)	0.2598	0.2642	0.1245	0.1252	0.2265	0.1175	0.2414	0.1309	0.1736

the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with an NH₄Cl solution followed by water, dried on Na₂SO₄, and concentrated. The residue was chromatographed on silica gel with CH₂Cl₂/EtOH (95:5) to give 0.083 g of the product as a bright red solid. The solid was dissolved in acetone and filtered; the solution was evaporated in a rotary evaporator, yielding 0.079 g of pure product (yield 57%). Yellow single crystals of **2a** were obtained by slow evaporation at +4 °C of a solution obtained by dissolution of 11 mg of compound **2** in 12 mL of a CH₂Cl₂–CH₃OH (9:1) mixture. Anal. Calcd for **2a**: C, 58.70; H, 4.60; N, 4.56. Found: C, 58.51; H, 4.46; N, 4.57.

Synthesis of [Fe(η⁵-C₅H₄-4-C₅H₄N)(η⁵-C₅H₄-B(OH)₂)]·0.5H₂O (2b**).** Single crystals of **2b** were obtained by slow evaporation at room temperature of a solution obtained by dissolution of 13 mg of compound **2a** in acetone (5 mL) followed by addition of H₂O (2 mL). Anal. Calcd for **2b**: C, 57.02; H, 4.79; N, 4.43. Found: C, 57.18; H, 4.77; N, 4.44.

Synthesis of [Fe(η⁵-C₅H₄-4-C₅H₄N)(η⁵-C₅H₄-B(OH)₂)] (2c**).** Single crystals of **2c** were obtained by slow evaporation at 4 °C of a solution obtained by dissolution of 17 mg of compound **2a** in acetone (7 mL) followed by addition of 2 mL of an aqueous 0.1 M solution of NH₃. Anal. Calcd for **2c**: C, 58.70; H, 4.60; N, 4.56. Found: C, 58.65; H, 4.47; N, 4.56.

Synthesis of [Fe(η⁵-C₅H₄-4-C₅H₄NH)(η⁵-C₅H₄-B(OH)₂)]·[NO₃] (3a**).** Single crystals of **3a** were obtained by evaporation of an aqueous solution of **2a** (10 mg, 0.0325 mmol) in HNO₃ (0.01 M, 3.5 mL). Anal. Calcd for **3a**: C, 48.70; H, 4.09; N, 7.57. Found: C, 48.57; H, 4.08; N, 7.55.

Synthesis of [Fe(η⁵-C₅H₄-4-C₅H₄NH)(η⁵-C₅H₄-B(OH)₂)]·[SO₄]·3H₂O (3b**).** Single crystals of **3b** were obtained by evaporation of an aqueous solution of **2a** (10 mg, 0.0325 mmol) in H₂SO₄ (0.01 M, 3.5 mL). Anal. Calcd for **3b**: C, 47.04; H, 4.74; N, 3.66. Found: C, 47.20; H, 4.75; N, 3.65.

Synthesis of [Fe(η⁵-C₅H₄-4-C₅H₄NH)₂][Cl]₂·4H₂O (5**).** Single crystals of **5** were obtained by slow evaporation at 25 °C of a solution of **4** (10 mg; 0.0294 mmol, prepared according to the literature procedure¹²) in HCl (0.01 M, 5.8 mL). Anal. Calcd for **5**: C, 49.72; H, 5.01; N, 5.80. Found: C, 49.61; H, 5.00; N, 5.81.

Synthesis of [Fe(η⁵-C₅H₄-C₆H₄-4-C₅H₄N)₂] (6**).** To a solution of 4-(*p*-bromophenyl)pyridine²¹ (0.213 g, 91 mmol) in dioxane (6.5 mL) under Ar was added 1 M aqueous Na₂CO₃ (2.73 mL); the catalyst PdCl₂[1,1'-bis(diphenylphosphino)ferrocene] (0.006 g, 0.007 mmol) was added, followed by a mixture of boronic acid (0.100 g, 0.36 mmol) and 3 M aqueous NaOH (0.24 mL) in DME (15 mL). The reaction was refluxed for 3 days. After hydrolysis with ice–water, the mixture was extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with NH₄Cl solution followed by water and dried on Na₂SO₄ and concentrated. The residue was chromatographed on silica gel with CH₂Cl₂–EtOH (95:5) to give 0.082 g of the product as a bright red solid (yield 46%). Single crystals of **6** were obtained by slow evaporation at 4 °C of a solution obtained by dissolution of 11 mg of compound **6** in 6 mL of CH₂Cl₂. Anal. Calcd for **6**: C, 78.06; H, 4.91; N, 5.69. Found: C, 77.88; H, 4.89; N, 5.68.

Synthesis of [Fe(η⁵-C₅H₄-5-C₄H₃N₂)₂] (7**).** To a solution of 5-bromopyrimidine (0.141 g 0.91 mmol) in DME (5 mL) under Ar was added the catalyst PdCl₂[1,1'-bis(diphenylphosphino)ferrocene] (0.006 g, 0.007 mmol), followed by a mixture of boronic acid (0.100 g 0.36 mmol) and 3 M aqueous NaOH (0.24 mL) in DME (20 mL). The reaction mixture was refluxed for 2 days. After hydrolysis with ice–water, the mixture was extracted with CH₂Cl₂ (3 × 13 mL). The organic layer was washed with NH₄Cl solution followed by water and dried on Na₂SO₄ and concentrated. The residue was chromatographed on silica gel with CH₂Cl₂–EtOH (95:5) to give 0.071 g of the

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product as a bright red solid (yield 61%). Single crystals of **7** were prepared by slow evaporation at 4 °C of a benzene solution of the compound. Anal. Calcd for **7**: C, 63.18; H, 4.12; N, 16.37. Found: C, 63.30; H, 4.13; N, 16.32.

Crystallography. Crystal data and details of measurements for compounds **1**, **2a–c**, **3a,b**, and **5–7** are reported in Table 2. The structure of **4** has been described previously¹² (CCDC-177938). Common to all compounds were the following: X-ray data collected at room temperature on a Nonius CAD-4 diffractometer, graphite monochromator (Mo K α radiation, $\lambda = 0.710\,73\text{ \AA}$), ψ -scan absorption correction. All non-H atoms were refined anisotropically. All H_{OH} and H_{NH} atoms in **2b,c**, **3a,b**, and **5–7** and one H_{OH} atom in **2a** were directly located from Fourier maps and refined; the second H_{OH} atom in **2a** and the two H_{OH} atoms in **1** were not observed. H atoms bound to C atoms were added in calculated positions. In the case of **5**, which crystallizes in the chiral space group $P2_12_12_1$, the absolute structure was attributed to the lowest Flack parameter (0.34(19) vs 0.64(11)). The computer program SHELXL97^{22a} was used for structure solution and refinement. The computer program SCHAKAL99^{22b} was used for all

graphical representations. For the evaluation of hydrogen-bonding parameters the program PLATON was used.^{22c} In all cases, correspondence between the structures determined by single-crystal X-ray diffraction and those of the bulk materials precipitated from solution was confirmed by comparing the experimental powder diffractograms obtained from the bulk material with those calculated on the basis of the single-crystal structures.

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Supporting Information Available: Details about the X-ray crystal structures, including tables of crystal data and structure refinement parameters, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters, TGA for crystalline **2b**, comparison of X-ray powder patterns for crystalline **2b** before and after TGA, and ORTEP figures for all compounds described herein. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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