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Oxidation of $[M(\eta\text{-}C_5H_5)_2]$, M = Cr, Fe or Co, by the new Brønsted acid $H_2O{\cdot}B(C_6F_5)_3$ yielding the salts $[M(\eta\text{-}C_5H_5)_2]^+A^-$, where $A^- = [(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]^-$ or $[(C_6F_5)_3BOH\cdots H_2OB(C_6F_5)_3]^-$ †

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The Brønsted acids $H_2O{\cdot}B(C_6F_5)_3$ and $D_2O{\cdot}B(C_6F_5)_3$ have been synthesized. Reaction of neutral divalent metallocenes $[M(\eta\text{-}C_5H_5)_2]$, M = Cr, Fe or Co, with two equivalents of $H_2O{\cdot}B(C_6F_5)_3$ **2a** resulted in metallocene oxidation and formation of salts containing $[M(\eta\text{-}C_5H_5)_2]^+$ cations together with the hydroxoborate anion $[HOB(C_6F_5)_3]^-$ which is hydrogen bonded to the second acid equivalent, namely $[M(\eta\text{-}C_5H_5)_2][(F_5C_6)_3\text{-}BOH\cdots H_2OB(C_6F_5)_3]$, M = Cr **3a**, Fe **4a** or Co **5a**. Treatment of one equivalent of **2a** and one equivalent of $B(C_6F_5)_3$ **1** with $[M(\eta\text{-}C_5H_5)_2]$ yielded salts containing the same metallocene cations but now with μ-OH bridged anions, as in $[M(\eta\text{-}C_5H_5)_2][(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]$, where M = Cr **3b** or Co **5b**. All products have been characterised by NMR spectroscopy, elemental analysis, and the single-crystal structures of **2a**, **3a**, **4a**, and **5a** have been determined.

Introduction

The strong Lewis acid $B(C_6F_5)_3$ **1** is currently of interest as a methyl abstracting agent and thereby activator of early transition-metal Ziegler–Natta polymerisation systems.[1,2] The compound $B(C_6F_5)_3$ was known to react with water[3–6] but systematic study of the reactions had not been reported.

Recently the water adduct $2H_2O{\cdot}H_2OB(C_6F_5)_3$ has been described[7] and characterised in the solid state. This Lewis acid–base adduct was found to protonate the compound $[Ir(\eta\text{-}C_5H_5)\text{-}(1,5\text{-}COD)]$ to give the hydridoiridium(III) cation $[Ir(\eta\text{-}C_5H_5)\text{-}(1,5\text{-}COD)H][(F_5C_6)_3B\text{-}\mu\text{-}OH\text{-}B(C_6F_5)_3]$.[7] The compound $2H_2O{\cdot}H_2OB(C_6F_5)_3$ is sufficiently stable for the determination of the crystal structure but it did not prove to be a useful reagent for synthetic chemistry. Several papers have reported HC_6F_5 and $HOB(C_6F_5)_2$ as decomposition products from systems containing water and $B(C_6F_5)_3$.[6,8,9] Here we report a synthesis of the monoaqua adduct $H_2O{\cdot}B(C_6F_5)_3$ **2a**, and we have found that this molecule can be used as a stoichiometric source of H^+ for the protonation and thereby oxidation of the metallocenes $[M(\eta\text{-}C_5H_5)_2]$, M = Cr, Fe or Co.

Results and discussion

Syntheses

The compound $H_2O{\cdot}B(C_6F_5)_3$ **2a** or $D_2O{\cdot}B(C_6F_5)_3$ **2b** was prepared by addition of one equivalent of water or D_2O respectively to a suspension of $B(C_6F_5)_3$ in pentane at −78 °C. Upon warming the mixture to room temperature the organoborane $B(C_6F_5)_3$ dissolves and reacts and the adducts, **2a** or **2b**, then precipitate from the pentane. Compounds **2a** and **2b** when stored under dinitrogen at room temperature showed no perceptible change.

Treatment of the compound $[Cr(\eta\text{-}C_5H_5)_2]$ with two equivalents of **2a** in CH_2Cl_2 at −78 °C rapidly results in an orange-brown solution of $[Cr(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ **3a**. Crystallographic characterisation definitively shows the $[Cr(\eta\text{-}C_5H_5)_2]^+$ cation together with the $[HOB(C_6F_5)_3]^-$ anion which is hydrogen bonded to the second equivalent of **2a**.

In contrast, upon mixing one equivalent of compound **2a**, a further one equivalent of $B(C_6F_5)_3$ and $[Fe(\eta\text{-}C_5H_5)_2]$ in pentane at −78 °C no immediate colour change is apparent. After several days at room temperature, however, the initial yellow of the ferrocene solution gradually becomes dark green. When the initial reaction mixture is exposed to air a dark green colour develops rapidly. A blue, crystalline product is obtained after recrystallisation from CH_2Cl_2–pentane and the crystal structure shows the compound to be $[Fe(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2\text{-}OB(C_6F_5)_3]$ **4a**, in which a $[HOB(C_6F_5)_3]^-$ anion is hydrogen bonded to an $H_2O{\cdot}B(C_6F_5)_3$ molecule. We assume that the water molecule derives from the air.

Reaction of the compound $[Co(\eta\text{-}C_5H_5)_2]$ with two equivalents of **2a** in pentane at −78 °C and warming to room temperature caused a steady change to yellow and the reaction appeared to be complete within 3 h. The resulting pale yellow solid was purified in the same manner as above. The crystal structure showed the product to be the compound $[Co(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ **5a**. The crystal structures of all three compounds **3a**, **4a** and **5a** have closely similar cell parameters.

Treatment of the metallocenes $[M(\eta\text{-}C_5H_5)_2]$, M = Cr or Co, with a 1:1 mixture of **2a** and $B(C_6F_5)_3$ gave the salts $[M(\eta\text{-}C_5H_5)_2][(F_5C_6)_3B\text{-}\mu\text{-}OH\text{-}B(C_6F_5)_3]$, M = Cr **3b** or Co **5b**. The principal difference in the reaction conditions used for the **3b** and **5b** syntheses *versus* those for **3a** and **5a** was the presence of one less equivalent of water in the former and it appears that the formation of A^- in $[M(\eta\text{-}C_5H_5)_2]^+A^-$ can be controlled as desired. We note that the (μ-OH) bridged anions $[(F_5C_6)_3B\text{-}\mu\text{-}OH\text{-}B(C_6F_5)_3]^-$ in **3b** and **5b** are much more sensitive to water than the hydrogen bonded anions $[(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]^-$ in **3a**, **4a**, and **5a**. Attempts to synthesize **3b**, **4b**, and **5b** from $[M(\eta\text{-}C_5H_5)_2]$ and two equivalents of $B(C_6F_5)_3$ and one equivalent of water resulted in only low yields of **3a**, **4a**, and **5a**.

In solution compound **2a** behaves as the Brønsted acid $[H]^+[HOB(C_6F_5)_3]$. Controlled oxidation of neutral $[M^{II}(\eta\text{-}C_5H_5)_2]$ by $[H]^+$ to give the $[M^{III}(\eta\text{-}C_5H_5)_2]^+$ cations is presumed

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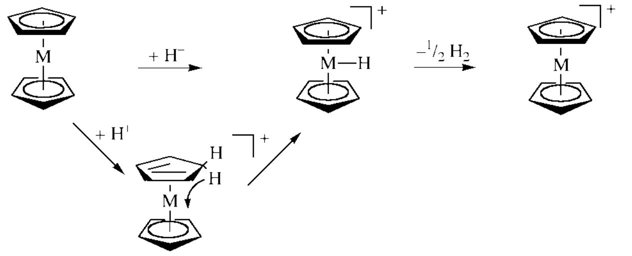
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http//www.rsc.org/suppdata/dt/1999/4325/

to proceed by formation of intermediate metallocene hydride cations $[M^{IV}(\eta\text{-}C_5H_5)_2H]^+$.[10] These may be formed either by a direct protonation of the metal centre or indirectly by initial *exo*-proton addition to a η-cyclopentadienyl ring to give a η-cyclopentadiene ligand followed by migration of an *endo* hydrogen from the methylene group to the metal centre. The intermediate hydride cations $[M(\eta\text{-}C_5H_5)_2H]^+$ could then liberate H_2, to give the cations $[M(\eta\text{-}C_5H_5)_2]^+$. These proposed pathways are shown in Scheme 1. After oxidation of the metallocene with **2a** the product anion always contains the anion $[HOB(C_6F_5)_3]^-$. The syntheses of the new compounds **2**–**5** are shown in Scheme 2.

X-Ray crystallography

An ORTEP[11] diagram of compound **2a** is shown in Fig. 1. Only one equivalent of water is present and it is bound directly to $B(C_6F_5)_3$. Both hydrogen atoms were found in the difference map and their positions refined. The B1–O1 distance is 1.597(2) Å, the mean O–H distance is 0.74(3) Å, the mean B–C distance is 1.629(4) Å and the H1–O1–H2 angle is 91.9(31)°. No other solvent molecules are present and the closest intermolecular contact is 2.206 Å between H1 and F35 in an adjacent molecule in which the F35–H1–O1 angle is 147°. The next shortest intermolecular distance is 2.286 Å between H2 and F25 and the F25–H2–O1 angle is 132°. These distances are relatively short for XH···F intermolecular contacts and consistent with an H···F hydrogen bonding interaction in the solid state.[12]

All crystals of the cations $[M(\eta\text{-}C_5H_5)_2]^+$ were dichroic, a well known characteristic of metallocenium cations. In the asymmetric unit of these crystal structures there is one half of the metallocenium cation and one $[HOB(C_6F_5)_3]^-$ unit, as well as one half of a methylene chloride molecule. Fig. 2 shows an ORTEP for the asymmetric unit of $[Fe(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ **4a**. The presence of one $[HOB(C_6F_5)_3]^-$ anion and one neutral acid–base adduct **2a** is inferred from the charge balance required by the $[M(\eta\text{-}C_5H_5)_2]^+$ cation and supported by location of the hydroxyl hydrogen atom in the difference map. The complete cation and anion are shown for **5a** in Fig. 3. The structures of **3a**, **4a** and **5a** are all analogous and therefore all three will be discussed together. In each case the $[M(\eta\text{-}C_5H_5)_2]^+$ cation has a staggered conformation and is unexceptional compared to other structurally characterised metallocenium salts. The Cp_{cent}–M distances are 1.849, 1.713, and 1.644 Å for Cr, Fe, and Co respectively. The O1···O1



Scheme 1

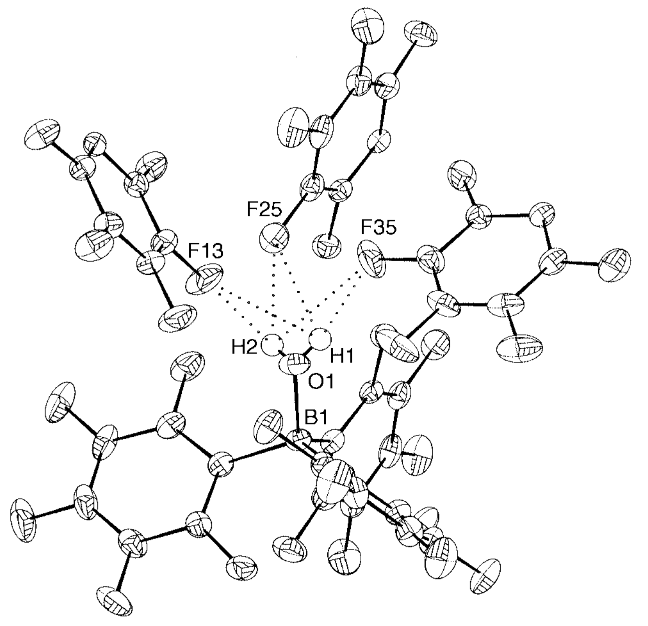
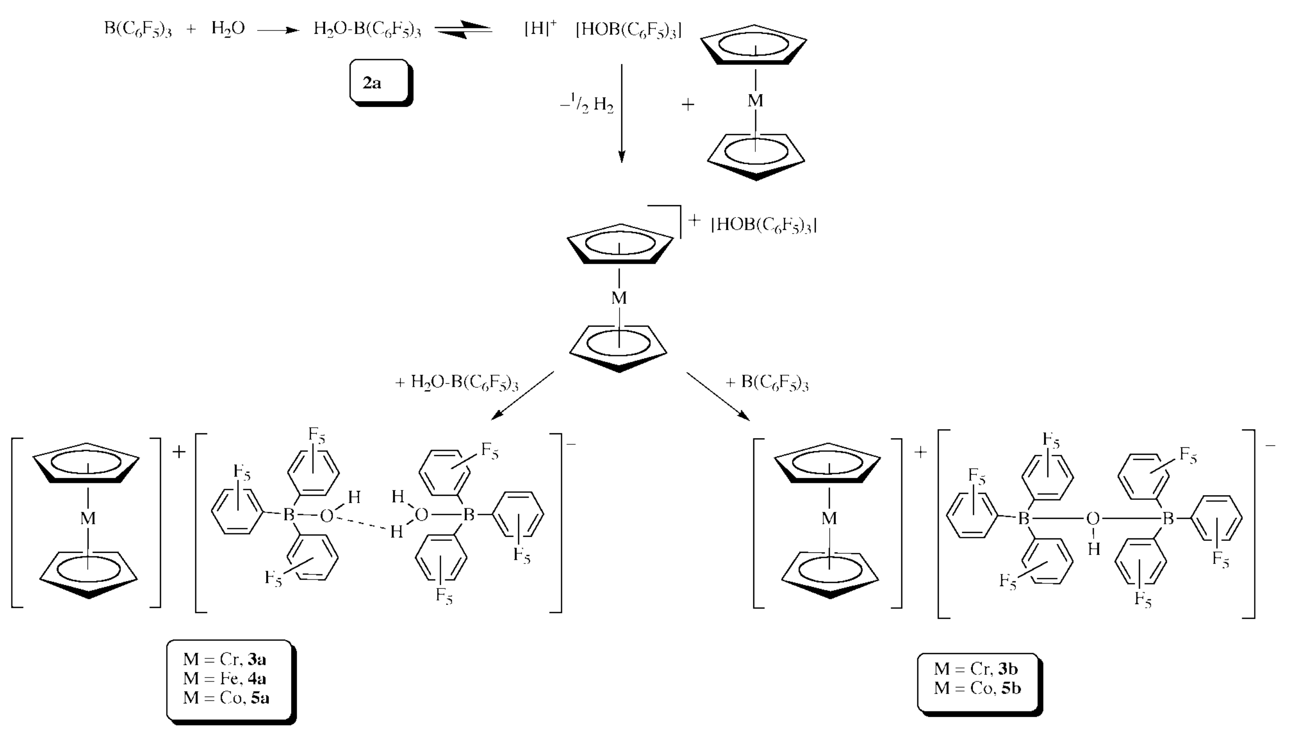


Fig. 1 An ORTEP diagram of $H_2O{\cdot}B(C_6F_5)_3$ **2a** with hydrogen-bonding contacts to adjacent molecules in the unit cell.



Scheme 2

Table 1 NMR data in CD_2Cl_2 at room temperature

	Compound	^{1}H OH	^{1}H Cp	^{11}B	^{19}F		
					ortho	*para*	*meta*
	$B(C_6F_5)_3$	—	—	59 (br)	−131.4	−147.1	−164.3
2a	$H_2O{\cdot}B(C_6F_5)_3$	6.75	—	6.65	−134.8	−154.2	−163.0
2b	$D_2O{\cdot}B(C_6F_5)_3$	−1.83[a]	—	4.50	−135.4	−155.5	−163.3
3a	$[Cr(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$	7.30	Not observed	−3.52	−134.14	−158.3	−162.51
4a	$[Fe(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$	7.08	36.1	−4.00	−137.6	−161.4	−167.3
5a	$[Co(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$	6.45	5.65	−3.64	−136.9	−160.5	−165.7
3b	$[Cr(\eta\text{-}C_5H_5)_2][(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]$	8.76	Not observed	−3.48	−135.7	−159.0	−163.3
5b	$[Co(\eta\text{-}C_5H_5)_2][(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]$	8.46	5.66	−3.44	−136.5	−160.5	−166.0

[a] ^{2}H NMR spectrum.

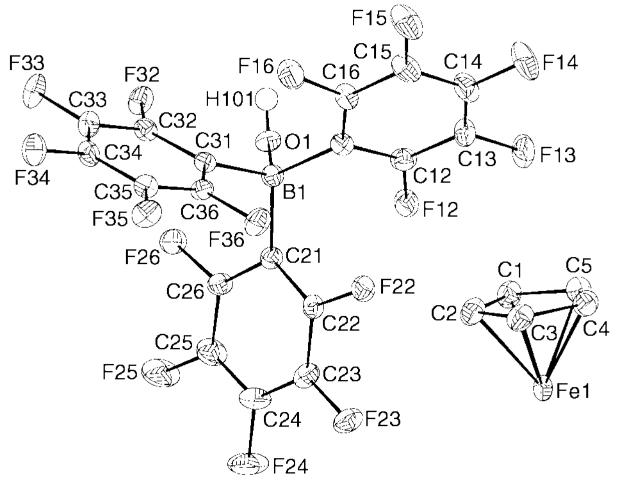


Fig. 2 An ORTEP diagram showing the asymmetric unit of $[Fe(\eta\text{-}C_5H_5)][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ **4a**. Carbon-bound hydrogen atoms and the methylene chloride solvate molecule have been removed for clarity.

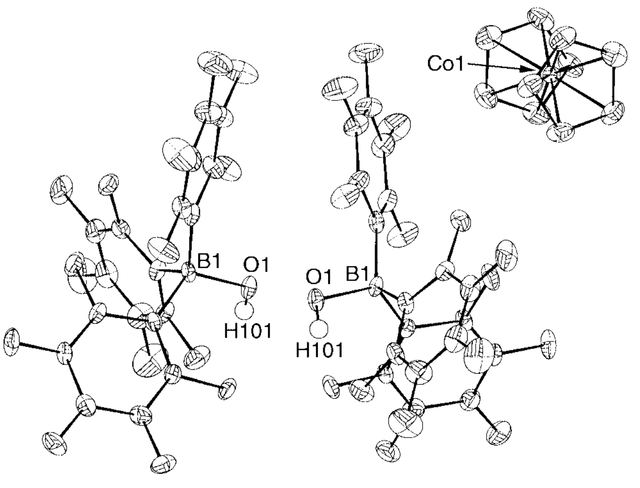


Fig. 3 An ORTEP diagram of $[Co(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ **5a**. Details as in Fig. 2.

distances of 2.403–2.416 Å are reasonable for hydrogen bonding.[13–15] The second hydrogen atom of the water molecule was not found in the difference map and the lattice symmetry indicates that it is localised closer to neither one oxygen nor the other, but rather is, on average, equidistant from both. The ions $[Fe(\eta\text{-}C_5H_5)_2]^+$ and $[Co(\eta\text{-}C_5H_5)_2]^+$ are common in organometallic chemistry but the only other structurally characterised chromocenium compound is $[Cr(\eta\text{-}C_5H_5)_2]^+[Cr(\eta\text{-}C_5H_5)(CO)_3]^-$.[16] The cation in this structure and that in **3a** are virtually identical.

Several low quality X-ray diffraction data sets were collected for compound **3b** that were sufficient to establish connectivity, but not suitable for publication. Crystals were consistently very small and with significant methylene chloride solvent disorder. The structure of the μ-OH bridging anion has been well determined previously.[7]

NMR Spectroscopy

The ^{1}H, ^{11}B, and ^{19}F NMR data for the new compounds are collected in Table 1. The ^{1}H resonance of H_2O shifts from δ 2.16 to 6.75 upon co-ordination to $B(C_5F_5)_3$. One observed ^{1}H resonance for the hydroxide and water groups in **3a**, **4a**, and **5a** is consistent with a rapid proton exchange or a hydrogen-bonding interaction in solution, supported by solid state studies discussed below. The ^{1}H resonances for **3a**–**5a** are distinct from those of **3b** and **5b** which are shifted significantly downfield. Exposure to the oxidatively stable **3b** and **5b** to air leads to ^{1}H spectra similar to those of **3a**–**5a**, showing gradual absorption of H_2O by the system. The ^{1}H NMR resonances for the η-cyclopentadienyl rings are consistent with those reported earlier for analogous $[Fe(\eta\text{-}C_5H_5)_2]^+$ [17] and $[Co(\eta\text{-}C_5H_5)_2]^+$ [18] systems. No corresponding resonance was observed for the paramagnetic $[Cr(\eta\text{-}C_5H_5)_2]^+$ cation. The variable temperature magnetic moment study of **3a** gives a moment of 3.8 μ_B, as predicted for an $S = 3/2$ spin-only system, as previously reported for the compound $[Cr(\eta\text{-}C_5H_5)_2]^+$.[19]

The ^{11}B NMR spectra are particularly diagnostic for these compounds because the resonances differ dramatically between three-co-ordinate boranes and the four-co-ordinate boron in the Lewis acid–base adducts. The former resonance is broad, whereas those for **2a** and **2b** are quite sharp and shifted upfield by more than 50 ppm. The upfield shift and marked sharpening of the ^{11}B resonance are reliable indicators in boron chemistry that a fourth ligand has been bound to boron.[20–27] Furthermore, the boron centre is sensitive to charge in that the neutral four-co-ordinate species have resonances further downfield than the anionic borates. It is not possible to distinguish between the two anions, in **3a** and **3b** for example, with ^{11}B NMR because boron is insensitive to the degree of protonation at oxygen.

The ^{19}F spectra of compounds **2a** and **2b** show resonances broadly similar to those of $B(C_6F_5)_3$ but the *para*-fluorine has shifted slightly upfield. This resonance is the most sensitive of the aromatic fluorine shifts and is a good indicator for reactivity of $B(C_6F_5)_3$.[28] The ^{19}F data for the $[M(\eta\text{-}C_5H_5)_2]^+A^-$ complexes are distinct from those of the free borane but also do not permit distinction between the two different types of anions in, for example, **3a** and **3b**.

In conclusion, the synthesis of the Lewis acid–base adduct $H_2O{\cdot}B(C_6F_5)_3$ **2a** is described and acts as an oxidising agent of the metallocenes $[M(\eta\text{-}C_5H_5)_2]$ to form the salts $[M(\eta\text{-}C_5H_5)_2]^+A^-$ as shown in Scheme 2.

Experimental

All reactions were carried out under dinitrogen, either in a glove-box or using conventional Schlenk techniques. The compounds $B(C_6F_5)_3$,[29] $[Cr(\eta\text{-}C_5H_5)_2]$,[30] and $[Co(\eta\text{-}C_5H_5)_2]$[31] were prepared according to the literature. The compound $B(C_6F_5)_3$ was freshly sublimed before use. Water and D_2O were distilled and purged with nitrogen prior to use. The NMR spectra were recorded on either a 300 MHz Varian Mercury (^{1}H, ^{11}B, and ^{19}F at 300.13, 96.25, and 282.36 MHz respectively) or a 500 MHz Varian Unity Plus spectrometer (^{1}H, ^{11}B, and ^{19}F at 499.87, 160.38, and 470.28 MHz respectively) in CD_2Cl_2 at room temperature. Protio spectra were referenced internally using residual protio-solvent and Me_4Si (δ 0). Heteronuclei were referenced externally to $BF_3{\cdot}Et_2O$ (^{11}B, δ 0) and $CFCl_3$ (^{19}F, δ 0). Elemental analyses were performed by the Inorganic Chemistry Laboratory Microanalytical Services. Magnetic susceptibility data were collected on a Quantum Design SQUID Susceptometer.

Syntheses

Compound $H_2O{\cdot}B(C_6F_5)_3$ 2a. A 900 mg portion (1.76 mmol) of $B(C_6F_5)_3$ was dissolved in 40 mL of pentane at room temperature. The solution was cooled to −78 °C which caused some of the borane to precipitate. One equivalent (32 µL) of distilled water was added at low temperature and the solution allowed to warm to room temperature whilst stirring. Initially upon warming all reagents dissolved, but after 2 h a white precipitate had appeared. The solution volume was reduced to 15 mL, the supernatant filtered off, and the residual white powder dried *in vacuo*. The powder was recrystallised from a saturated solution of CH_2Cl_2 layered with pentane to give a crystalline product. Yield: 0.75 g, 80%. Analysis: % Calculated (% found) C 40.8 (41.0), H 0.5 (0.4), B 2.0 (2.1).

The compound $D_2O{\cdot}B(C_6F_5)_3$ 2b. A portion of $B(C_6F_5)_3$ (390 mg, 0.76 mmol) in 30 mL of pentane was treated as for the synthesis of compound **2a** with 14 µL of D_2O. A similar white powder precipitated from solution upon completion of the reaction, which proved to be analytically pure. Yield: 0.30 g, 77%. Analysis: % Calculated (% found) C 40.8 (40.4), H 0.8 (0.8).

The compound $[Cr(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ 3a. A portion of $[Cr(\eta\text{-}C_5H_5)_2]$ (137 mg, 0.75 mmol) was dissolved in 40 mL CH_2Cl_2 and cooled to −78 °C. In a separate flask, $B(C_6F_5)_3$ (770 mg, 1.5 mmol) in 20 mL CH_2Cl_2 was cooled to −78 °C, 13.5 µL of water were added using a syringe and the resulting mixture was subsequently added to the $[Cr(\eta\text{-}C_5H_5)_2]$ solution *via* a cannula. The initially dark red metallocene solution became orange-brown over 30 min. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. The solvents were removed *in vacuo*, the crude orange-brown powder was washed with pentane, and the product recrystallised from a saturated CH_2Cl_2 solution layered with pentane. Orange-yellow crystals analysing for compound **3a**$\cdot CH_2Cl_2$ were isolated and the presence of CH_2Cl_2 in the crystals was confirmed by X-ray diffraction. Yield: 0.23 g (25%). Analysis: % Calculated (% found) C 42.6 (42.8), H 1.1 (1.2), Cr 3.9 (4.5). Selected IR data (cm^{-1}, KBr): for **3a**: 3635.5 sharp weak ν(O–H), 3131 sharp v. weak ν(C–H) of C_5H_5; for $H_2O{\cdot}B(C_6F_5)_3$ 3384 v. strong, v. broad ν(O–H).

The compound $[Fe(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ 4a. A portion of $[Fe(\eta\text{-}C_5H_5)_2]$ (162 mg, 0.87 mmol) in 25 mL of pentane at room temperature was treated with a solution of compound **2a** (900 mg, 1.76 mmol) in 25 mL of pentane *via* cannula. After 2 h stirring under N_2 the yellow reaction mixture was opened to air and after 8 h a large amount of blue powder had precipitated. The pentane supernatant was removed *via* filtration and the powder recrystallised from CH_2Cl_2 layered with pentane to give blue-red crystals analysing as **4a**$\cdot\frac{1}{2}CH_2Cl_2$, which stoichiometry was confirmed crystallographically. Yield: 0.42 g (42%). Analysis: % calculated (% found) C 43.4 (42.8), H 1.1 (1.3), Fe 4.3 (4.6). Selected IR data (cm^{-1}, KBr): 3634 sharp weak ν(O–H), 3120 sharp v. weak ν(C–H) of C_5H_5.

The compound $[CO(\eta\text{-}C_5H_5)_2][(F_5C_6)_3BOH\cdots H_2OB(C_6F_5)_3]$ 5a. A 32 mg (0.17 mmol) portion of $[Co(\eta\text{-}C_5H_5)_2]$ was dissolved in 20 mL of CH_2Cl_2 and cooled to −78 °C. Two equivalents of compound **2a** were dissolved in 30 mL of CH_2Cl_2 and added to the metallocene solution *via* cannula. The blue-black colour immediately began to change to pale yellow. After one hour at −78 °C the solution was allowed to warm to room temperature. After 16 h solvents were removed *in vacuo* to yield a pale yellow powder that was recrystallised from CH_2Cl_2 and pentane to give pale yellow microcrystals analysing as **5a**. Yield: 0.11 g (53%). Recrystallisation from CH_2Cl_2 layered with pentane provided crystals large enough for X-ray diffraction. Analysis: % calculated (% found) C 44.9 (44.1), H 1.0 (1.5). Selected IR data (cm^{-1}, KBr): 3634 sharp weak ν(O–H), 3126 sharp v. weak ν(C–H) of C_5H_5.

The compound $[Cr(\eta\text{-}C_5H_5)_2][(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]$ 3b. A 1 : 1 : 1 ratio of $[Cr(\eta\text{-}C_5H_5)_2]$ (0.566 mmol, 103 mg), compound **2a** (0.566 mmol, 300 mg), and $B(C_6F_5)_3$ (0.566 mmol, 290 mg) was mixed in the solid state in a flask and cooled to −78 °C, 40 mL of CH_2Cl_2 were added and an immediate change from dark red to orange was observed. After 30 min the solution was warmed to room temperature, stirred for 2 h and the solvent removed *in vacuo*. The resulting orange powder was recrystallised from CH_2Cl_2 and pentane to give orange-yellow crystals analysing as **3b**$\cdot CH_2Cl_2$. Yield 0.11 g (23%). Analysis: % Calculated (% found) C 43.2 (43.0), H 1.0 (1.4), Cr 4.0 (3.6).

The compound $[Co(\eta\text{-}C_5H_5)_2][(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]$ 5b. A similar procedure to that for compound **3b** was followed except that pentane was used as the solvent. Upon warming to room temperature a pale yellow powder precipitated. The supernatant was removed *via* filtration and pale yellow crystals were obtained *via* recrystallisation from CH_2Cl_2 and pentane. Yield: 0.04 g (10%). Analysis: % calculated (% found): C 42.9 (43.1), H 1.0 (1.25), Co 4.5 (4.4).

X-Ray crystallography

All crystals were selected under an inert atmosphere, covered with Paratone-N oil, and mounted on the end of a glass fibre. Data were collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) as summarised in Table 2. The images were processed with the DENZO and SCALEPACK programs[32] and corrections for Lorentz-polarisation effects were performed. All solution, refinement, and graphical calculations were performed using the CRYSTALS[33] and CAMERON[34] software packages. The structures were solved by direct methods using the SIR 92[35] program and refined by full-matrix least squares procedure on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. For compound **2a** both hydrogen atoms were found in the difference map and their positions refined. For **3a**, **4a**, and **5a** in each case one proton bound to oxygen was located in the difference map but its position was not refined. The final proton of the three in the $OH\cdots H_2O$ moiety was not part of the refinement. A Chebychev weighting scheme was applied with the parameters 1.78, 0.414, and 1.36 for **2a**, 1.18, 1.32, and 0.799 for **3a**, 1.22, 1.16, and 0.763 for **4a** and 2.33, 1.11, and 1.61 for **5a**, as well as an empirical absorption correction.[36]

CCDC reference number 186/1707.

See http://www.rsc.org/suppdata/dt/1999/4325/ for crystallographic files in .cif format.

Table 2 Crystallographic data for compounds **2a**, **3a**, **4a** and **5a**

	2a $H_2O{\cdot}B(C_6F_5)_3$	**3a** $[Cr(\eta\text{-}C_5H_5)_2]$-$[(F_5C_6)_3BOH\cdots H_2OB$-$(C_6F_5)_3]{\cdot}CH_2Cl_2$	**4a** $[Fe(\eta\text{-}C_5H_5)_2]$-$[(F_5C_6)_3BOH\cdots H_2OB$-$(C_6F_5)_3]{\cdot}0.5\ CH_2Cl_2$	**5a** $[Co(\eta\text{-}C_5H_5)_2]$-$[(F_5C_6)_3BOH\cdots H_2OB$-$(C_6F_5)_3]{\cdot}CH_2Cl_2$
Formula	$C_{18}H_2BF_{15}O$	$C_{23.5}H_7BClCr_{0.5}F_{15}O$	$C_{23.25}H_7BCl_{0.5}Fe_{0.5}F_{15}O$	$C_{23.5}H_7BClCo_{0.5}F_{15}O$
M	529.99	662.55	643.74	666.01
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$	$C2/c$
a/Å	10.8660(5)	14.231(3)	14.254(3)	14.2530(9)
b/Å	11.5140(3)	24.002(5)	23.887(5)	24.1780(9)
c/Å	14.5910(7)	14.202(3)	14.073(3)	14.1350(8)
β/°	98.092(2)	90.63(3)	90.52	90.00(3)
V/Å^3	1807.3	4850.8	4791.2	4871.0
T/K	150	150	125	150
Z	4	8	8	8
μ(Mo-Kα)/mm^{-1}	0.22	0.510	0.520	0.610
Total data	10685	14096	18572	14459
No. unique data	3900	4972	4638	4385
No. observed data	3624	4765	3445	2619
No. parameters	322	380	383	388
R	0.0765	0.0949	0.0551	0.0792
R'	0.0505	0.0601	0.0629	0.0874

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