Anion induced binding electrochemical signal transduction in ferrocenyl benzolimidazolium podands

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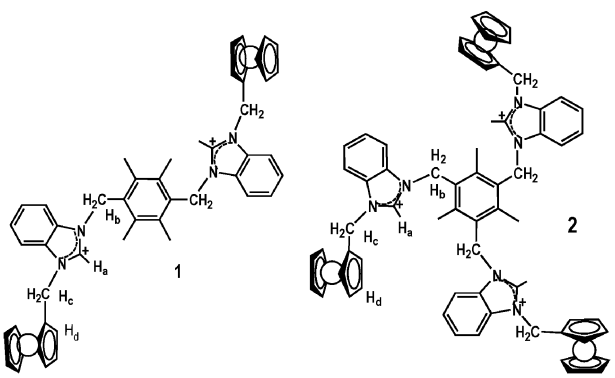
Benzene-based bipodal and tripodal electrochemical-responsive receptors with ferrocenyl arms comprising benzoimidazolium moieties were synthesized and structurally characterized. The two-arm *para* compound **1** · 2Br exhibited a cisoid conformation with the two ferrocene moieties positioned in the same side and a templating bromide anion sited inside. The cisoid form was stabilized not only by the $(C–H)^+\cdots Br^-$ hydrogen bond, but also cooperated by the $C–H\cdots Br^-$ hydrogen bonding related to the Cp rings of the ferrocenyl moieties and the CH_2 groups, respectively. The association constants of the receptor **1** for Cl^-, Br^- and I^- were determined using ^1H NMR titration in d_6-DMSO as 600 M^{-1}, 440 M^{-1} and 350 M^{-1}, respectively. The *meta* three-arm compound **2** · 3Br adopted a *cone* conformation with a bromide anion sited inside the molecular cavity and three ferrocene-containing arms positioned on the same side. The cationic heterocycle interacted with the bromide anion through the three-fold $C–H\cdots Br^-$ hydrogen bonding. ^1H NMR titrations in d_6 DMSO revealed that the association constants of **2** for Cl^-, Br^- and I^- were 9.7×10^3 M^{-1}, 6.8×10^3 M^{-1} and 120 M^{-1}, respectively. Electrochemical measurements demonstrated that directed hydrogen bonding between the ferrocenyl moiety and the anion was important for the two-arm receptor **1** exhibiting more efficient binding electrochemical signal transduction.

Introduction

The selective recognition and sensing of anions by artificial host molecules have emerged recently as a key research theme within the generalized area of supramolecular chemistry.[1,2] So far, the focus has been mainly on the supramolecular chemistry of a receptor. This approach, however, suffers from shortcomings such as the high cost of synthesis and the loss of real-time response.[3] Therefore, for anion-sensing applications, the challenge faced by chemists goes beyond the achievement of strong and highly selective anion coordination chemistry and becomes one of detecting and amplifying an anion binding event to produce a measurable output.[4,5] Thus a general effective chemosensor should contain at least two units, each one displaying a precise function, the binding site and the signalling unit. Generally, receptors designed to electrochemically recognize guest molecules should couple the complexation process to a redox active metallocenyl signalling unit.[6,7] Recently, Steed *et al.* reported a new approach for binding-electrochemical signal transduction through the designed podands based on two or three hydrogen bonding 'arms' containing ferrocenyl species. The conformational change resulting from anion binding caused electrochemical sensing.[8]

In the contribution, we outline our initial work[9] on a simple approach to construct ferrocene-based podands comprising benzoimidazolium hydrogen bonding moieties (Scheme 1) and investigate the factors influencing the binding electrochemical signal transduction. The recognition of the host is introduced by the presence of directional hydrogen-bonding $(C–H)^+$ functionality as well as the electrostatic force between the benzoimidazolium moieties and the anion.[10] Charged hydrogen bonding is very intriguing in comparison with many other types of hydrogen bonding,[11] and provides the possibility of moderating the host geometry by placing the binding sites into a suitable orientation.[12] In fact, the related imidazolium-based receptors have been used for fluorescent and electrochemical sensing through conformational changes on binding.[13]



Scheme 1

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Results and discussions

Synthesis and crystal structures

The compounds **1** · 2Br and **2** · 3Br were achieved by reaction of 1-ferrocenylmethyl-1-benzoimidazole[14] and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene or 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene using the literature method, respectively.[10] The compounds **1** · 2BPh_4 and **2** · 3BPh_4 used for ^{1}H NMR and electrochemistry titrations of anions were afforded by general anion exchange reactions. Fig. 1 shows the molecular structure of the bromide salt **1** · 2Br. As can be expected, the receptor **1** exhibited the cisoid formation with the two ferrocenyl arms sited on the same side of the podand and one of the bromide anions captive inside. The cisoid form of the receptor was stabilized by the chelating of the guest anion through the $(C–H)^+\cdots Br^-$ hydrogen bond (H_a). The C···Br separations were 3.565(6) and 3.540(5) for C(9)···Br(1) and C(29)···Br(1) with C–H···Br^- angles being 150.3(1) and 151.4(1)° for C(9)–H(9A)···Br(1) and C(29)–H(29A)···Br(1), respectively. Interestingly, the hydrogen atoms in the unsubstituted Cp rings of the ferrocenyl moieties and the CH_2 groups interacted with the bromide anion through the C–H···Br^- hydrogen bonding. The C···Br separations were 3.769(6), 3.780(6) and 3.756(5) Å for C(10)···Br(1) and C(30)···Br(1), C(15)···Br(1) with C–H···Br^- angles being 143, 145 and 150° for C(10)–H(10A)···Br(1), C(30)–H(30B)···Br(1), C(15)– H(15A)···Br(1), respectively. The bond communication, provided typically by conjugated chemical bond linkage between the redox center(s) and the binding cavity, was one of the main pathways for guest-binding coupling in the electrochemical recognition,[15] the directed hydrogen-bonding between the ferrocene moiety and the anion provided an opportunity to exhibit efficiency binding electrochemical signal transduction.

The cationic receptor **2** did adopt a *cone* conformation with a bromide anion inside the molecular cavity and three ferrocenyl arms positioned on the same side of the benzene ring

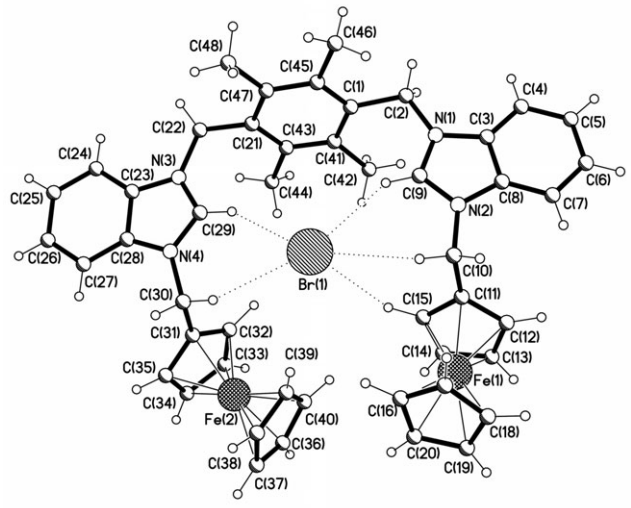

Fig. 1 Molecular structure of compound **1** · 2Br with the atomic numbering scheme showing the *cis*-conformation.

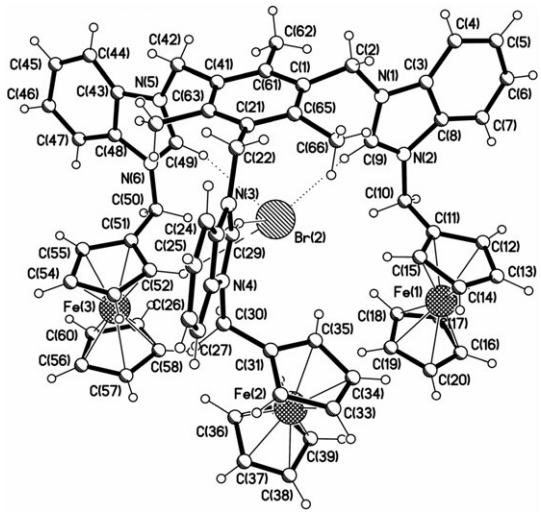

Fig. 2 Molecular structure of compound **2** · 3Br with the atomic numbering scheme showing the *cone* conformation.

(Fig. 2). The cationic heterocycle interacted strongly with bromide anions through not only electrostatic forces but also the three-fold C–H···Br^- hydrogen bonds between the electron-deficient carbon atoms of the benzoimidazolium rings and the bromide anion with C···Br separations of 3.500(4), 3.522(5), and 3.733(5) for C(9)···Br(2) and C(29)···Br(2), C(49)···Br(2) and C–H···Br^- angles being *ca.* 162° on average, respectively. Since there was no obvious hydrogen-bonding between the ferrocene moiety and the anion in the tripodand, it was suggested that the *cone* conformation of receptor **2** was poor for binding electrochemical signal transduction.

Electrochemistry. Solid-state differential pulse voltammograms were displayed[16,17] to monitor the electrochemical signalling transduction of the two anion-containing crystalline compounds **1** · 2Br and **2** · 3Br. As shown in Fig. 3, while the compound **1** · 2BPh_4 exhibited a broad peak at about 0.65 V, the compound **1** · 2Br and the solid-state species containing templating anions Cl^- and I^- showed broad peaks at about

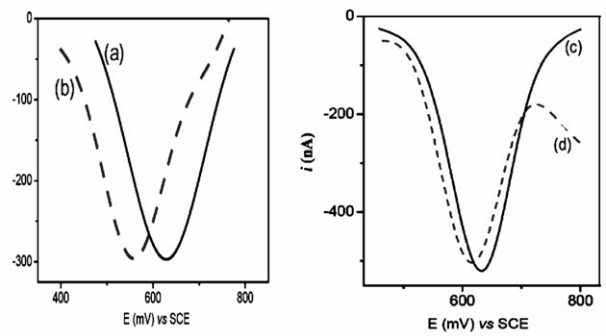

Fig. 3 DPV for receptor **1** · 2BPh_4 in the solid state (left) and in solution (right) (a) **1** · 2BPh_4, (b) **1** · 2Br; (NBu_4)Br; (c) **1** · 2BPh_4; (d) **1** · 2BPh_4 + 5 equiv. bromide.

0.54, 0.57, and 0.60 V, respectively. Clearly the presence of templating anions induced a cathodic shift of about 100 mV. These results demonstrated that the presence of directed anion–ferrocene hydrogen bonding was important for **1** to exhibit effective binding electrochemical signal transduction. To further investigate the binding signal transduction in solution, the electrochemical response of compound $\mathbf{1}\cdot 2BPh_4$ in solution was measured upon addition of Cl^-, Br^- and I^-. As shown in Fig. 3c, the compound $\mathbf{1}\cdot 2BPh_4$ in DMF solution displayed a single reversible ferrocene-based redox couple centered on 0.55 V (*vs.* Ag/AgCl). After addition of up to 5 mole equivalents of Br^-, a cathodic shift in the $E_{1/2}$ value was observed, reaching 30 mV (Fig. 3d). Analogous titration with Cl^- gave a similar cathodic shift of 50 mV. The addition of iodide gave almost no significant change in the redox potential. Upon addition of a large excess (more than 20 times the stoichiometric ratio) of Cl^-, Br^- and I^-, a further cathodic shift in the $E_{1/2}$ was observed and reached 70 mV, 50 mV and 20 mV, respectively.

DPV of compounds $\mathbf{2}\cdot 3BPh_4$ and $\mathbf{2}\cdot 3Br$ both showed a ferrocene-based half-wave potential ($E_{1/2}$) at 0.53 V and 0.52 V, indicating that the presence of templating anions did not induce a significant cathodic shift, although the +3 charged three-arm tripodal hosts have been reported to exhibit a modest electrochemical response.[7a] Upon addition of 20 equivalents of NBu_4X (aliquots of 1 equivalent at a time, X = Cl^-, Br^- or I^-) there were no obvious electrochemical changes (smaller than 15 mV) in the solution, despite the large association constants of the receptor **2** for the anions. The poor binding electrochemical signal transduction should be ascribed to the absence of directed anion–ferrocene hydrogen bonding.

^{1}H NMR titration

To further investigate the anion-binding properties of the receptors **1** and **2** in solution, ^{1}H NMR titrations of the anion of tetrabutylammonium salts in DMSO-d_6 solution were displayed. As shown in Fig. 4, the ^{1}H NMR spectrum of the compound $\mathbf{1}\cdot 2BPh_4$ exhibited a narrow peak at 9.29 ppm for the proton H_a of benzoimidazolium, two peaks at about 5.70 (H_b) and 5.48 ppm (H_c) for the CH_2 groups and two peaks at about 4.51 (H_d) and 4.24 ppm for the substituted Cp rings and one peak at about 4.21 ppm for the unsubstituted Cp rings of the ferrocene moieties, respectively. Upon addition of 1 equivalent of chloride anion to the solution of **1**, a significant downfield shift ($\Delta\delta > 1.25$ ppm) was observed for H_a, suggesting the complexation of the anion by CH hydrogen bonds. The H_b and H_d protons also showed downfield shifts with $\Delta\delta$ about 0.32 ppm and $\Delta\delta$ about 0.23 ppm upon addition of 1 equivalent of Cl^-. The downfield shifts of the three proton signals indicated the presence of three kinds of directional interactions between the receptor **1** and the anion, which was in excellent agreement with the results from the X-ray crystal structure analysis. The association constants (K) determined from the ^{1}H NMR titration curves by using a nonlinear curve fitting program are listed in Table 1.[18]

Table 1 Association constants (K_a/M^{-1}) and the free energy gains for anions with receptor **1** and **2** in DMSO-d_6 from ^{1}H NMR titrations

Receptor	Anion[a]	K_a/M^{-1}[b]	$-\Delta G^\circ_{298}$/kJ mol^{-1}
$\mathbf{1}\cdot 2BPh_4$	Cl^-	6.0×10^2	15.8
$\mathbf{1}\cdot 2BPh_4$	Br^-	4.4×10^2	15.1
$\mathbf{1}\cdot 2BPh_4$	I^-	3.5×10^2	14.5
$\mathbf{2}\cdot 3BPh_4$	Cl^-	9.7×10^3	22.7
$\mathbf{2}\cdot 3BPh_4$	Br^-	6.8×10^3	21.9
$\mathbf{2}\cdot 3BPh_4$	I^-	1.2×10^2	11.9

[a] Anions exist as their tetrabutylammonium salts. [b] Errors in K_a were $\leq 10\%$.

The ^{1}H NMR spectrum of compound $\mathbf{2}\cdot 3BPh_4$ also exhibited a narrow peak at 10.49 ppm for the proton H_a of benzoimidazolium, two peaks at about 5.88 (H_b) and 5.82 ppm (H_c) for the CH_2 groups and two peaks at about 4.84 (H_d) and 4.23 ppm for the substituted Cp rings and one peak at about 4.36 ppm for the substituted Cp rings of the ferrocene moieties, respectively (Fig. 5). Upon addition of chloride anion to the solution of $\mathbf{2}\cdot 3BPh_4$, a downfield shift only for the H_a proton ($\Delta\delta > 0.3$ ppm) was observed, suggesting the complexation of the anion by (C–H)···X (X = halide anion) hydrogen bonding. As expected, no obvious changes in

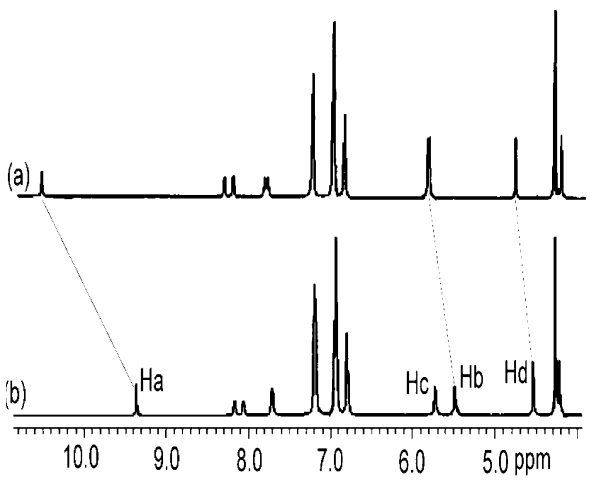

Fig. 4 ^{1}H NMR spectra of host $\mathbf{1}\cdot 2BPh_4$ before (b) and after (a) the addition of 1 equivalent of chloride anion in DMSO-d_6.

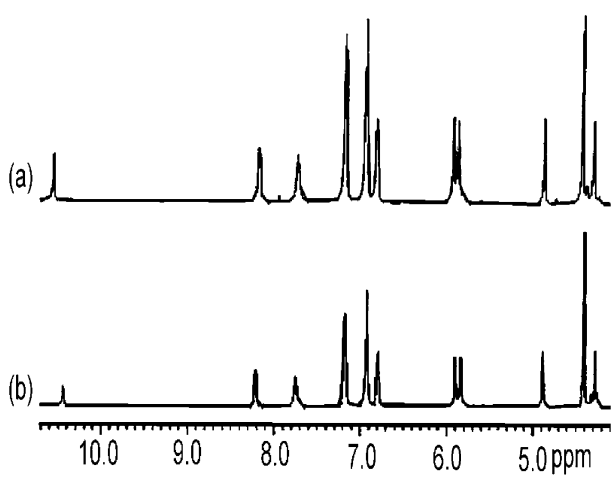

Fig. 5 ^{1}H NMR spectra of host $\mathbf{2}\cdot 3BPh_4$ before (b) and after (a) the addition of 1 equivalent of chloride anions in DMSO-d_6.

chemical shifts were observed for the other protons. This result confirmed the absence of auxiliary hydrogen bonding between the other protons and the chloride anion. The association constants (K) are also listed in Table 1.

It can be seen that while the two-arm receptor **1** shows poorer selectivity, binding-induced conformational change in these species results in more efficient electrochemical signalling than in the three-arm receptor **2**. Clearly, the presence of direct hydrogen bonding between the ferrocene and the halide anion is important for the receptor **1** exhibiting more effective binding electrochemical signal transduction.

Experimental

Materials and methods

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. 1-Ferrocenylmethyl-1-benzoimidazole was synthesized according to the literature method.[13] Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240 analytical instrument. ^{1}H NMR spectroscopic measurements were recorded on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference at room temperature. ^{1}H NMR titration was recorded on a Bruker AM-500 NMR spectrometer using DMSO-d_6 solution (8×10^{-3} M). Differential pulse voltammetry (DPV) was recorded with an EG and GPAR model 273 instrument. Solution state measurements were performed in DMF with n-Bu_4NClO_4 (0.1 mol dm^{-3}) as supporting electrolyte in a three-electrode cell with a pure Ar gas inlet and outlet. A sweep rate of 20 mV s^{-1} was used in all pulse experiments. The cell comprised a platinum wire working electrode, a platinum auxiliary electrode and an Ag/AgCl wire reference electrode. The ferrocene (1.0×10^{-3} mol dm^{-3}) was used as external standard. Solid-state voltammograms were measured by using a carbon-paste working electrode; well-ground mixture of each bulk sample and carbon paste (graphite and mineral oil) were set in the channel of a glass tube and connected to a copper wire. A platinum-wire counter electrode and an Ag/AgCl reference electrode were used. Measurements were performed by using a three-electrode system in 0.1 mol dm^{-3} $NaClO_4$ aqueous solutions at a scan rate of 20 mV s^{-1}, in the range 0–1.0 V. The ferrocene in solid state was also used as external standard with $E_{1/2} = 0.25$ V *vs.* Ag/AgCl electrode.

Caution! Although no problems were encountered in this work, the perchlorate is potentially explosive and should be handled with care.

Syntheses

Compound 1·2Br. 1,4-Bis(bromomethyl)-2,3,5,6-tetramethylbenzene (0.80 g, 2.50 mmol) and 1-ferrocenylmethyl-1-benzoimidazole (1.59 g, 5.00 mmol) were dissolved in CH_2Cl_2 and sealed and left undisturbed in darkness at room temperature for 2 days. During this time, a yellow precipitate formed. This was filtered off and washed with CH_2Cl_2 and Et_2O to give the desired product as a yellow powder (1.53 g, 64%) giving compound **1** as the bromide salt. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 10.19 (s, 3H, H_a), 8.25 (d, 2H, ArH), 8.14 (d, 2H, ArH), 7.72 (q, 4H, ArH), 5.79 (s, 4H, CH_2), 5.76 (s, 4H, CH_2), 4.72 (s, 4H, CpH), 4.27 (s, 10H, CpH), 4.20 (s, 4H, CpH), 2.26 (s, 12H, CH_3). Anal. Calcd (%) for $C_{48}H_{48}N_4Fe_2Br_2$: C, 60.5; H, 5.1; N, 5.9. Found: C, 60.4; H, 5.1; N, 5.8. Crystals suitable for X-ray work were obtained by evaporating a methanol–ethanol (1 : 1) solution in air.

Compound 1·2BPh$_4$. Compound **1**·2Br (0.70 g, 0.74 mmol) was dissolved in methanol (40 mL), and a methanolic solution of $NaB(C_6H_5)_4$ (0.76 g, 2.22 mmol) was added to the bromide salt solution and left to stir at room temperature for 6 h. Over this time, the tetrabenzeneborate salt precipitated. The yellow powder was filtered, washed with methanol and diethyl ether, and dried *in vacuo*, yielding 1.33 g, 91%. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 9.29 (s, 3H, H_a), 8.16 (d, 2H, ArH), 8.13 (d, 2H, ArH), 7.72 (q, 4H, ArH), 7.17 (s, 16H, ArH), 6.92 (t, 16H, ArH), 6.78 (t, 8H, ArH), 5.80 (s, 4H, CH_2), 5.46 (s, 4H, CH_2), 4.50 (s, 4H, CpH), 4.23 (s, 10H, CpH), 4.20 (s, 4H, CpH), 2.25 (s, 12H, CH_3). Anal. Calcd (%) for $C_{96}H_{84}N_4Fe_2B_2 \cdot 2H_2O$: C, 78.6; H, 6.3; N, 3.8. Found: C, 78.5; H, 6.3; N, 3.8.

Compound 2·3Br. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (1.0 g, 2.5 mmol) and 1-ferrocenylmethyl-1-benzoimidazole (2.38 g, 7.5 mmol) were dissolved in CH_2Cl_2 and sealed and left undisturbed in darkness at room temperature for 2 days. During this time, a yellow precipitate formed. This was filtered off and washed with CH_2Cl_2 and Et_2O to give the desired product as a yellow powder (2.09 g, 62%) of compound **2** as the bromide salt. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 10.57 (s, 2H, H_a), 8.26 (d, 3H, ArH), 8.23 (d, 3H, ArH), 7.77 (q, 6H, ArH), 5.92 (s, 6H, CH_2), 5.84 (s, 6H, CH_2), 4.87 (s, 6H, CpH), 4.37 (s, 15H, CpH), 4.23 (s, 6H, CpH), 2.36 (s, 9H, CH_3). Anal. Calcd (%) for $C_{66}H_{63}N_6Fe_3Br_3$: C, 58.8; H, 4.7; N, 6.2. Found: C, 58.8; H, 4. 7; N, 6.3. Crystals suitable for X-ray work were obtained by evaporating a methanol/ethanol 1 : 1 solution in air.

Compound 2·3BPh$_4$. Compound **2**·3Br (1.00 g, 0.74 mmol) was dissolved in methanol (40 mL), and a methanolic solution of $NaB(C_6H_5)_4$ (0.76 g, 2.22 mmol) was added to the bromide salt solution and left to stir at room temperature for 6 h. Over this time, the tetrabenzeneborate salt precipitated. The yellow powder was filtered, washed with methanol and diethyl ether, and dried *in vacuo*, yielding 1.43 g, 93%. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 10.4 ppm (s, 2H, H_a), 8.22 (d, 6H, ArH), 7.75 (t, 6H, ArH), 7.16 (s, 24H, ArH), 6.90 (t, 24H, ArH), 6.77 (t, 12H, ArH), 5.88 (s, 6H, CH_2), 5.82 (s, 6H, CH_2), 4.84 (s, 6H, CpH), 4.36 (s, 15H, CpH), 4.23 (s, 6H, CpH), 2.30 (s, 9H, CH_3). Anal. Calcd (%) for $C_{138}H_{123}N_6B_3Fe_3 \cdot H_2O \cdot CH_3OH$: C, 78.9; H, 6.1; N, 4.0. found: C, 78.1; H, 6.1; N 4.1.

Crystallography

Intensities of compounds **1** and **2** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromatic Mo-Kα radiation (λ = 0.710 73 Å) using SMART and SAINT[19] programs. The structures was solved by direct methods and refined on F^2 by using full-matrix least-squares methods with SHELXTL version 5.1.[20] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were

Table 2 Crystal data and structure refinements for compound **1** · 2Br and compound **2** · 3Br

Compound	**1** · 2Br	**2** · 3Br
Empirical formula	$C_{48}H_{52}Fe_2N_4Br_2O_2$	$C_{67}H_{69}Br_3Fe_3N_6O_2$
M_r	988.46	1397.56
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	11.274(1)	12.011(1)
b/Å	12.881(1)	21.169(2)
c/Å	15.144(2)	27.819(3)
α/°	88.71(2)	
β/°	89.25(3)	98.45(2)
γ/°	85.25(2)	
V/Å^3	2190.9(4)	6996.6(1)
Z	2	4
D_c/g cm^{-3}	1.498	1.327
$F(000)$	1004	2832
μ/mm^{-1}	2.529	2.37
T/K	293(2)	293(2)
No. reflections measured	11 046	29 461
No. unique reflections	7608	11 953
R_{int}	0.084	0.161
R_1	0.063	0.076
wR_2	0.110	0.144
Gof	1.020	0.988

localized in their calculated positions and refined using a riding model. Parameters for data collection and refinement of **1** and **2** were summarized in Table 2. For the compound **1** · 2Br, one Cp ring was refined disordered with the site occupancy factor (s.o.f.) of each disordered atom fixed at 0.5. The anisotropic parameters for the disordered parts were also constrained to which the thermal parameters of each atom in one Cp ring were similar. Hydrogen atoms of the lattice water molecules were found from the Fourier Map, however, refined using the riding model by fixed bond distances and isotropic parameters. Since the quality of the single crystal of **2** · 3Br was not satisfactory, the observed/unique reflection ratio was only 20%. To make the refinement stable, 518 restraints were used to constrain the anisotropic parameters of the two ferrocene arms to which the thermal parameters of each atom in one arm were similar. One of the bromide anions was disordered into three positions with the site occupancy factor (s.o.f.) refined as 0.666 67, 0.166 67 and 0.166 67, respectively. The water and methanol molecules in the crystal were refined disordered. There were two positions with the s.o.f each being 0.5 for the disordered methanol molecule, and the s.o.f was about 0.55 and 0.45 for the two disordered positions being occupied by the oxygen atoms of the water molecules. No hydrogen atoms of the disordered solvent molecules were added and refined.†

Acknowledgements

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† CCDC reference numbers 286334 and 286335. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b508173d

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