Entrapment of ferrocenes within supramolecular, deep-cavity resorcin[4]arenes†

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Using a template-based method to molecular self-assembly, the ability of ferrocene (FcH) and two of its acetylated derivatives [FcAc, 1,1′-Fc(Ac)₂] to induce formation of a supramolecular deep cavity based upon *C*-methylcalix[4]resorcinarene 1 and 4,4′-bipyridine 2, 1·2(2), 3, is revealed; equatorial inclusion of 1,1′-Fc(Ac)₂ within 3 promotes a change in conformation of the guest.

Ferrocenes are attractive guests for studies involving facets of second sphere coordination in which molecular receptors serve as hosts.[1,2] The cyclopentadienyl (Cp) rings of such complexes can be readily derivatized and, upon interacting with the surface of a receptor, may adopt a conformation not exhibited by the free molecule which, in turn, may influence properties of the guest (*e.g.* reactivity).[3] Despite this realization, it is surprising that little structure information exists concerning the interaction of ferrocene (FcH) with most receptors designed to date, an observation likely related to the relatively large size of the complex. α-Cyclodextrin was the first receptor shown to assemble with FcH in the solid state, in the form of a 2:1 assembly [2(α-CD)·FcH],[4] while a hemicarcerand has been recently illustrated to encapsulate the molecule in a 1:1 host–guest complex (HC·FcH).[5] In each case, the included FcH is located within a symmetric cavity such that the Cp rings of the molecule are surrounded by identical chemical environments, which, in effect, prohibits any degree of discrimination, in terms of recognition, among the rings.[6]

Our approach to the construction of a host able to recognize FcH, and its derivatives (FcR), involves the use of a supramolecular cavity based upon Högberg's resorcin[4]arenes.[7] In particular, extensive work has demonstrated that co-crystallization of *C*-methylcalix[4]resorcinarene 1 with 4,4′-bipyridine 2 typically yields a one-dimensional, wave-like polymer, 1·2(2), 3, in which the cavity of 1 is deepened supramolecularly,[8] interacting with four stacking pyridine units of 2 by way of four O–H···N hydrogen bonds.[9] The cavity created by the five molecules, which may be induced to form by way of guest templation,[10] is flexible, being able to accommodate either single or multiple guests by way of a conformational reorganization of the network 3.[9]

With the observation that hemicarcerands recognize FcH realized,[5] we sought to determine whether 3 may be exploited in a similar manner. In contrast to the cavities cited above, the cavity of 3 is polar and, therefore, may be used to control the orientation, and possibly the conformation, of a ferrocene guest in which the structure of the guest is dictated by the electron-rich, bowl-shaped cavity of 1.[6] Here, we reveal the ability of 3 to serve as a host for FcR. In particular, using a template-based method to molecular self-assembly,[10] we demonstrate the ability of FcH in 3·FcH, and its mono- (FcAc) and 1,1′-di-acetylated [Fc(Ac)₂] derivatives in 3·FcAc and 3·Fc(Ac)₂, respectively, to assemble within 3 such that each FcH guest interacts with the cavity of 1 in a 'side-on', or equatorial fashion. For 3·Fc(Ac)₂, the Cp rings of the complex adopt a 1,1′-eclipsed conformation[11] which contrasts a 1,3′-staggered struc-

ture for the free molecule.[12] To our knowledge, 3·FcH, 3·FcAc and 3·Fc(Ac)₂ represent the first examples in which metallocenes have been isolated within a resorcin[4]arene in the solid state.‡

Addition of FcH (0.020 g) to a boiling aliquot of EtOH (5 mL) in the presence of an equimolar amount of 1 (0.058 g) and two molar equivalents of 2 (0.033 g) yielded, upon slow cooling, a microcrystalline powder with yellow–orange crystals of 3·FcH suitable for X-ray analysis within a day. The formulation of 3·FcH was confirmed by single crystal X-ray analysis§ and ¹H NMR spectroscopy.

A space-filling view of the X-ray crystal structure of 3·FcH is shown in Fig. 1. The FcH guest, which lies across a crystallographic mirror plane, has assembled within the wave-like framework 3 [polymer wavelength (λ) 25.4 Å; amplitude (ampl.) 19.3 Å],[9] which is propagated along the crystallographic *b*-axis [O···N separations (Å): O(1)···N(1) 2.74(11), O(2)···N(2) 2.68(13)], such that the sandwich complex interacts with 1 in an equatorial fashion. In this arrangement, the Cp–Fe–Cp axis of the iron complex is pointed in a direction that runs approximately parallel to the direction of the hydrogen bonds of 3 such that the Cp ligands of the guest, which adopt an approximate eclipsed D_{5h} conformation,[13] interact with 1 and 2 by way of C–H···π interactions.[14] Notably, the fit displayed by 1 and FcH markedly contrasts that of HC·FcH in which the sandwich complex is included axially,[5] the principal rotation axes of host and guest being approximately coincident. In both 2(α-CD)·FcH[4] and HC·FcH,[5] the Cp rings of the FcH guest adopt a staggered D_{5d} conformation.[13]

The observation that 3 may host FcH in the solid state suggested that 3 may be used to host derivatives of the complex. Indeed, 3 has been shown to accommodate guests of various size by modifying the relative orientations of the components of the host which results in a conformational change of the network.[9] If achieved, we anticipated that it may be possible to control stereochemical features of a ferrocene guest in which the substituents of the Cp ligands, owing to their electronic nature, may be directed either in or out of the cavity of 1.[6]

To test this hypothesis, 1 (0.040 g) was co-crystallized with two molar equivalents of 2 (0.023 g) from a boiling aliquot of EtOH (5 mL) in the presence of a molar equivalent of either
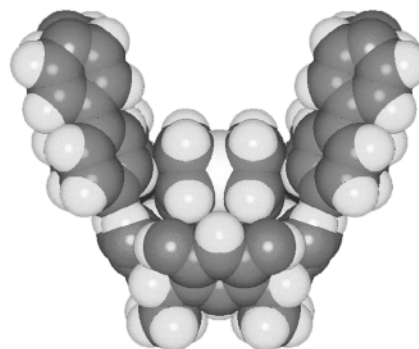

Fig. 1 Space-filling view of guest inclusion in the X-ray crystal structure of 3·FcH.

FcAc or Fc(Ac)$_2$. Yellow and red crystals of **3**·FcAc and **3**·Fc(Ac)$_2$, respectively, suitable for X-ray analysis grew within a day. The formulations of **3**·FcAc and **3**·Fc(Ac)$_2$ were confirmed by single crystal X-ray analysis§ and ^{1}H NMR spectroscopy.

An ORTEP perspective of the X-ray crystal structure **3**·Fc(Ac)$_2$ is shown in Fig. 2(a). In a similar way to **3**·FcH, the guests have assembled within **3** such that both complexes lie within **1** in an equatorial fashion and the Cp rings of the guests, which run in a direction parallel to the hydrogen bonds of **3** [O···N separations for **3**·FcAc and **3**·Fc(Ac)$_2$ (Å): O(1)···N(1) 2.660(3), 2.705(3), O(2)···N(3) 2.710(3), 2.683(3), O(5)···N(2) 2.649(3), 2.762(3), O(6)···N(4) 2.758(3), 2.633(3), respectively], interact with **1** and **2** by way of C–H···π forces [**3**·FcAc and **3**·Fc(Ac)$_2$: polymer λ (Å): 27.0, 26.6; ampl. (Å): 18.4, 18.5, respectively]. In this arrangement, the electron-rich carbonyl substituents of the guests are directed away from the cavity of **1** such that the substituents, which, as in the free molecules,[12,18] are approximately co-planar with the Cp rings, lie above the wider rim of **1**. For **3**·Fc(Ac)$_2$, the acetyl groups of the disubstituted complex, in contrast to free Fc(Ac)$_2$ and most 1,1′-disubstituted ferrocenes which tend to crystallize in a 1,3′-conformation,[19] adopt a 1,1′-conformation such that the substituents are eclipsed [Fig. 2b].¶ Indeed, this latter observation may be attributed, in part, to the electron-rich nature of the cavity of **3** which, upon maximizing attractive non-covalent forces between host and guest, has induced the molecule, by way of second sphere coordination,[1,2] to adopt a structure of a less preferred conformer.[12,19]

In this report, we have revealed the ability of **1**, with a cavity deepened supramolecularly,[8] to entrap FcH, and two of its acetylated derivatives, in the solid state. Owing to the ability of **1** to interact with the complex in an equatorial fashion, we have shown that it is possible to effect the conformation of a ferrocene guest such that, for Fc(Ac)$_2$, the substituents of the complex lie eclipsed. With such observations realized, we plan to determine if more reactive derivatives of FcH may be entrapped within **3** such that the substituents of the Cp rings may undergo reaction in the solid state.[20] We are also investigating whether **3** may be used as a host for other transition-metal-based complexes in which the structure behaviours of such organic–organometallic host–guest materials are expected to be governed by the supramolecular properties of **3** by way of second-sphere coordination.[1,2]
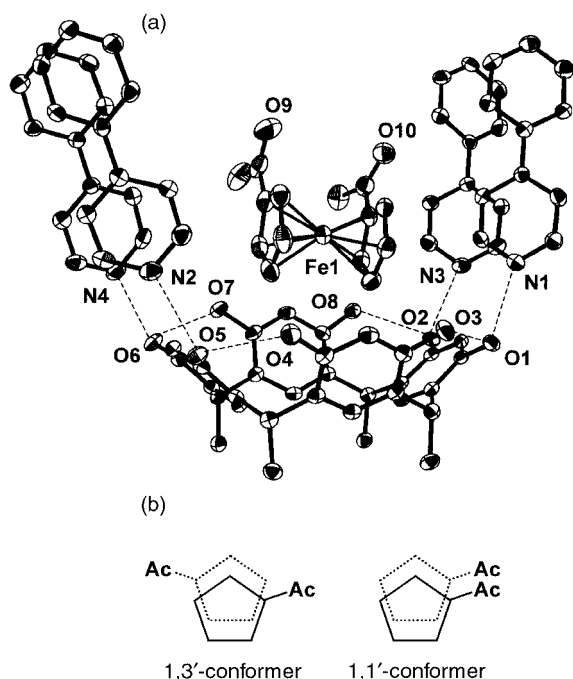

(a)

(b)

1,3′-conformer   1,1′-conformer

Fig. 2 (a) ORTEP perspective of the X-ray crystal structure of **3**·Fc(Ac)$_2$ and (b) schematic representation illustrating the conformation of Fc(Ac)$_2$ within the cavity of **3**. The guest adopts a 1,1′-conformation.

Notes and references

‡ To our knowledge, a metallocene has not been observed to assemble within a calix[4]arene in the solid state.

§ *Crystal data*: for **3**·FcH: monoclinic, space group, $P2_1/m$, $a = 9.730(1)$, $b = 25.440(3)$, $c = 10.825(1)$ Å, $\beta = 110.710(3)°$, $V = 2506.4(6)$ Å^3, $D_c = 1.38$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71070$ Å) for $Z = 2$. Least-squares refinement based on 1527 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 3370 unique reflections) led to a final value of $R = 0.089$.

For **3**·FcAc: monoclinic, space group, $P2_1/n$, $a = 18.477(1)$, $b = 11.742(1)$, $c = 26.086(1)$ Å, $\beta = 107.794(1)°$, $V = 5389.0(4)$ Å^3, $D_c = 1.34$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71070$ Å) for $Z = 2$. Least-squares refinement based on 5416 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 7041 unique reflections) led to a final value of $R = 0.034$.

For **3**·Fc(Ac)$_2$: monoclinic, space group, $P2_1/n$, $a = 18.808(1)$, $b = 11.948(1)$, $c = 25.595(1)$ Å, $\beta = 108.306(1)°$, $V = 5460.4(4)$ Å^3, $D_c = 1.37$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71070$ Å) for $Z = 2$. Least-squares refinement based on 5676 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 7141 unique reflections) led to a final value of $R = 0.044$. Intensity data for **3**·FcH, **3**·FcAc and **3**·Fc(Ac)$_2$ were collected at 173 K using the SMART system. Aromatic, methine, methyl and hydroxy hydrogen atoms were placed by modelling the moieties as rigid groups with idealised geometry, maximizing the sum of the electron density at the calculated hydrogen positions.

Structure solutions were accomplished using SHELXS-86[15] and refinements were conducted using SHELXL93[16] locally implemented on a pentium-based IBM compatible computer. Structure refinements and production of figures were accomplished with the aide of RES2INS.[17]

CCDC 182/1550. See http://www.rsc.org/suppdata/cc/a9/a909745g/ for crystallographic files in .cif format.

¶ We also note that the acetyl groups of free and entrapped Fc(Ac)$_2$ display *transoid* and *cisoid* relationships, respectively, while the Cp ligands in both complexes are eclipsed.

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