DOI: 10.1002/ejic.200500551

Experimental and Theoretical Study of the Encapsulation of a Linear Oligo(ferrocenylsilane) Trimer with β-Cyclodextrin

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Keywords: Cyclodextrins / Ferrocene / Inclusion compounds / Oligo(ferrocenes) / Ab initio calculations

An inclusion compound comprising β-cyclodextrin (β-CD) and the trimetallic oligo(ferrocenylsilane) $FcSiMe_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4SiMe_2)]Fc$ [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$] has been prepared and characterised in the solid state by elemental analysis, powder X-ray diffraction, thermogravimetric analysis and magic angle spinning NMR spectroscopy (^{13}C, ^{29}Si). The results are consistent with the formation of a 2:1 (host-to-guest) inclusion complex. Ab initio calculations were carried out in order to investigate the possible inclusion geometries. The best host–guest fit was obtained for a tilted geometry of the ferrocene fragment relative to the β-CD axis (φ = 29°) with a 140-pm inclusion of the corresponding Fe centre below the plane of the rim. The structure of the organometallic trimer allows its inclusion interaction with a second β-CD host, leading to the 2:1 stoichiometry.

Introduction

Ferrocene has captured the interest of chemists, leading to the formation of countless derivatives with applications in areas as diverse as catalysis,[1] nonlinear optics,[2] electrochemistry,[3] medicine and biology.[4] Recently, macromolecular derivatives with luminescent properties have been created, with promising applications in biosciences.[5] Polymers containing ferrocene units either in the side chain or in the main chain have also attracted increasing attention as they may feature new electrical, optical or even magnetic properties.[6] Research into main chain polymers began to really expand with the development of new polymerisation techniques, in particular the discovery of the ring-opening polymerisation (ROP) of strained [1]ferrocenophanes.[7] ROP of silicon-bridged [1]ferrocenophanes gives poly(ferrocenylsilanes), which have been shown to yield magnetic composite ceramics at 500–1000 °C.[8] Poly(ferrocenylsilanes) are thermoplastic materials that become liquid above 150 °C and can be shaped into films, tablets or nanometric fibres.[9] Their thermoplastic properties are a result of the molecular flexibility and of the helix-shaped molecular packing. In order to gain insight into the conformation and packing of these polymers in the solid state, linear oligo(ferrocenes) have been prepared and studied by single-crystal X-ray diffraction and computer modelling.[10,11] The structure observed for the pentamer, $FcSiMe_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4SiMe_2)]_nFc$ [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, n = 3], appears to be a good model for the corresponding prototypical high polymer, poly(ferrocenyldimethylsilane).[10a,10b]

The oligo(ferrocenyldimethylsilanes) with n = 0–7 can be prepared by the anionic ring-opening oligomerisation of (1,1′-ferrocenediyl)dimethylsilane (**1**). The [1]ferrocenophane **1** is also the precursor used to prepare the corresponding high polymers (by ROP). We recently reported on the modification of β-cyclodextrin (β-CD) with ferrocenyl groups by ring-opening of encapsulated molecules of **1**.[12] This work has led us to study the interaction of cyclodextrins with oligo(ferrocenyldimethylsilanes).[13] CDs are cyclic oligosaccharides capable of binding hydrophobic molecules, called guests, noncovalently in the ring cavity. Inclusion of ferrocene in α-, β- and γ-CDs was first described in 1984.[14] Since then, the binding of a broad variety of ferrocene derivatives with CDs has been reported.[15] However, to the best of our knowledge, the only ferrocene–cyclodextrin adduct to be successfully characterised by single-crystal X-ray diffraction is the 2:1 (host-to-guest) α-CD–ferrocene complex.[16] This makes theoretical calculations a very important tool to evaluate the structures of CD–organometallic inclusion compounds. Two possible inclusion geometries of ferrocene derivatives in cyclodextrins were proposed by Harada and Takahashi,[14] namely axial and equatorial inclusion. Molecular mechanics studies in 1988 confirmed Harada's conclusions.[17] In the present work, we describe an experimental and theoretical study of the interaction of the trimer $FcSiMe_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4SiMe_2)]Fc$ (**2**) with β-CD. We anticipated that these

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studies would yield information about the flexibility and conformation of the oligo(ferrocenes), as well as providing a new family of potentially interesting organometallic-cyclodextrin inclusion compounds.

Results and Discussion

Synthesis and Characterisation

A solution of the trimer $FcSiMe_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4SiMe_2)]Fc$ (**2**) in CH_2Cl_2 was added to an aqueous solution of β-CD at 50 °C, in a 2:1 (β-CD:**2**) stoichiometry. A pale orange solid precipitated slowly at the interface between the two solutions. After stirring the mixture for 4 days, the product was isolated by decantation and rinsed with water. Elemental analysis indicated the formation of a 2:1 (host-to-guest) inclusion compound, designated as $(\beta\text{-CD})_2\cdot$**2**. The yield was 36%. Figure 1 shows the powder XRD patterns for pristine β-CD hydrate, the trimer **2** and the product $(\beta\text{-CD})_2\cdot$**2**. The pattern for $(\beta\text{-CD})_2\cdot$**2** indicates that the solid is microcrystalline and does not contain measurable amounts of either pure β-CD or compound **2**. The formation of a new phase is a good indication for the presence of a true inclusion compound.[18] Elemental analysis and thermogravimetry (TG, not shown) showed that the encapsulation of the trimetallic guest was accompanied by a slight decrease in the overall crystal water contents, from 14.4% for β-CD (10–11 water molecules per β-CD molecule) to 8.5% for $(\beta\text{-CD})_2\cdot$**2** (about 8 water molecules per β-CD molecule). This is usual for CD inclusion complexes, as a certain fraction of the water molecules initially present in the cyclodextrin cavity must be expelled upon encapsulation of the guest molecule. TG of $(\beta\text{-CD})_2\cdot$**2** showed a second mass loss of about 60% between 250 and 315 °C, because of simultaneous decomposition of the guest and the host. The fact that the two components decompose in the same range is another indication for the formation of an inclusion complex.

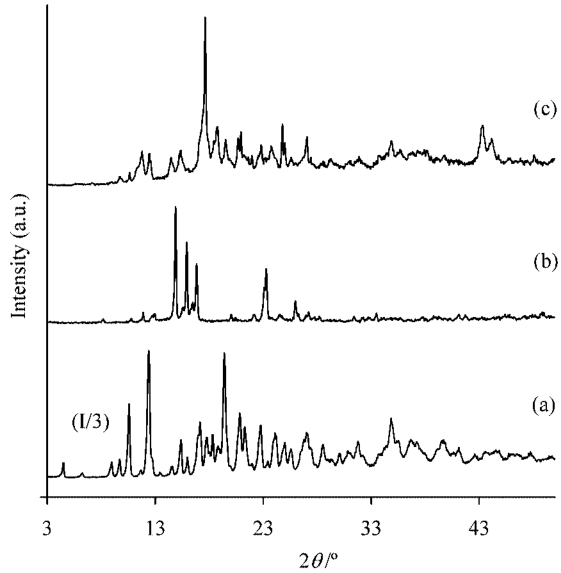

Figure 1. Powder XRD patterns of β-CD hydrate (a), the trimer **2** (b) and the inclusion compound $(\beta\text{-CD})_2\cdot$**2** (c).

Figure 2 shows the solid-state ^{13}C CP MAS NMR spectra of β-CD hydrate, the trimer **2** and the inclusion compound $(\beta\text{-CD})_2\cdot$**2**. The spectrum of β-CD hydrate is similar to that reported previously and exhibits multiple resonances for each type of carbon atom.[19,20] This has been mainly correlated with different torsion angles about the (1→4) linkages for C-1 and C-4,[19] and with torsion angles describing the orientation of the hydroxy groups.[20] The different carbon resonances are assigned to C-1 (101–104 ppm), C-4 (78–84 ppm), C-2,3,5 (71–76 ppm) and C-6 (57–65 ppm). The spectrum of the trimer **2** shows single sharp peaks for the Cp ($\eta^5\text{-}C_5H_5$) and methyl groups at 68.5 and 0 ppm, respectively. Several overlapping signals in the range 71–73 ppm are assigned to the carbon atoms of substituted cyclopentadienyl rings. In the spectrum of $(\beta\text{-CD})_2\cdot$**2**, a single sharp peak is observed at $\delta = 68.6$ ppm for the guest Cp group, and the methyl groups give rise to one main peak at 0.5 ppm. The multiplicities in the resonances for the β-CD carbon atoms are reduced in the spectrum of the inclusion compound, giving broad signals with very little structure. This is a common result for CD inclusion compounds containing either organic or organometallic guests, and can be attributed to an increase in the symmetry of the

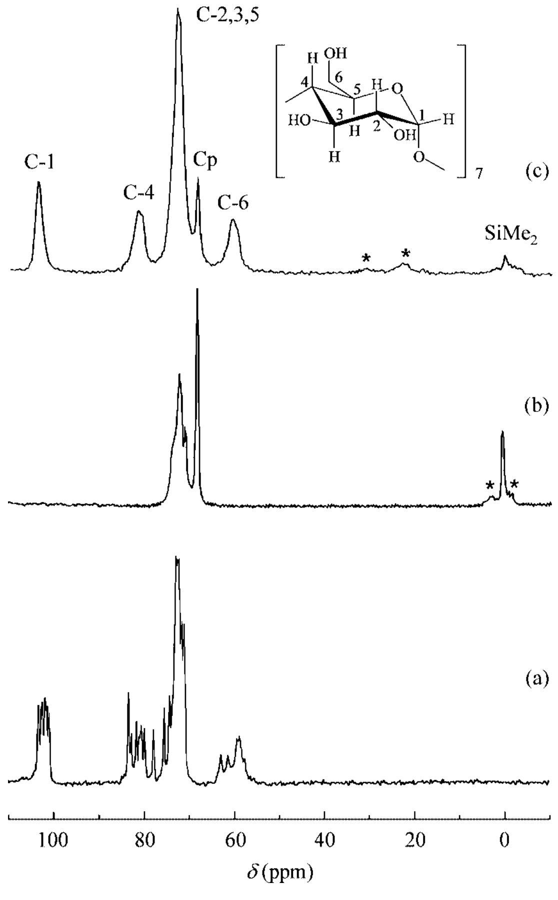

Figure 2. Solid-state ^{13}C CP MAS NMR spectra of β-CD hydrate (a), the trimer **2** (b) and the inclusion compound $(\beta\text{-CD})_2\cdot$**2** (c). Spinning sidebands are denoted by asterisks.

β-CD macrocycle upon inclusion complexation.[21] In other words, encapsulation of the guest molecule induces the ring to adopt a more symmetrical conformation, with each glucose unit in a similar environment. ^{29}Si CP MAS NMR spectra were also recorded for the trimer **2** and (β-CD)$_2$·**2** (Figure 3). Crystalline **2** exhibits one fairly broad peak for the bridging dimethylsilyl group at δ = –8.0 ppm. After inclusion in β-CD, four resolved signals are found at –6.7, –6.9, –7.6 and –8.0 ppm. At the time of writing, attempts to prepare single crystals of the inclusion compound suitable for X-ray diffraction have been unsuccessful. Therefore, we cannot be certain about the reasons for having nonequivalent silicon nuclei in the complex. It may simply be due to crystal packing effects, subtle conformational changes of the guest molecule, variations in the host–guest interaction (even within a single β-CD/trimer complex) and/or the effect of inclusion complexation, which results in "isolation" of the trimetallic guest. It is interesting to note that the ^{29}Si NMR resonances for solutions of oligo(ferrocenyldimethylsilanes), FcSiMe$_2$[(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_4$SiMe$_2$)]$_n$Fc (n = 0–7), are all found at –6.6 ± 0.1 ppm.[10a,10b]

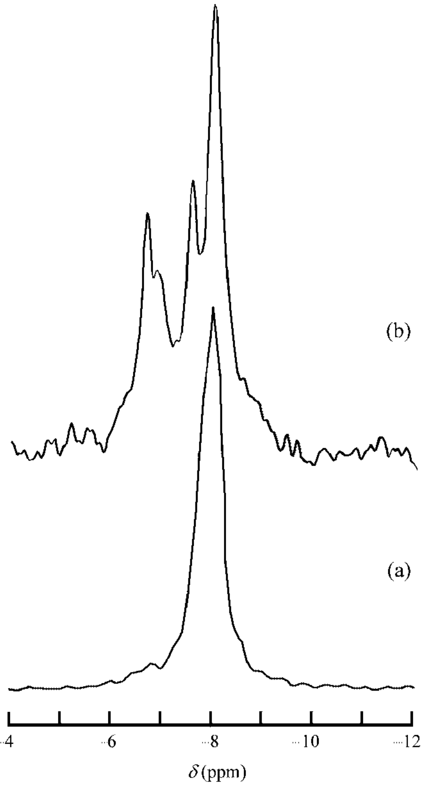

Figure 3. Solid-state ^{29}Si CP MAS NMR spectra of the trimer **2** (a) and the inclusion compound (β-CD)$_2$·**2** (b).

Ab Initio Calculations

Ab initio calculations were used in order to obtain information concerning the possible inclusion geometries, with particular attention being given to the plausibility of the host–guest fit. Figure 4 presents three conformers found for 1,1′-bis(ferrocenyldimethylsilyl)ferrocene (**2**). These conformers were obtained from a set of different starting geometries (generated by the combination of *trans* and *gauche* Fe–C$_{(ring)}$–Si–C$_{(ring)}$ dihedral angles) and are thought to be representative of the minimum energy configurations for the trimer. The most stable form, **2a**, has a helical-type structure, with Fe–C$_{(ring)}$–Si–C$_{(ring)}$ dihedral angles of about 103°, 156° and 66°, 69°. Conformers **2b** and **2c** lie above **2a** by about 4.7 and 5.9 kJ·mol^{-1}, respectively. Conformer **2b** mimics the extended structure found in the crystal and conformer **2c** has a ladder-type structure. The relative orientations of the cyclopentadienyl rings in the ferrocene units of **2b** are staggered for the central ferrocene and eclipsed for the terminal ones, as found in the crystal.[10d] The preference for the staggered configuration in the central ferrocene fragment in **2b** is probably due to repulsion between the substituent groups. In fact, for ferrocene itself, calculations at the same level predict the eclipsed D_{5h} form to be about 3.1 kJ·mol^{-1} more stable than the staggered D_{5d} form.

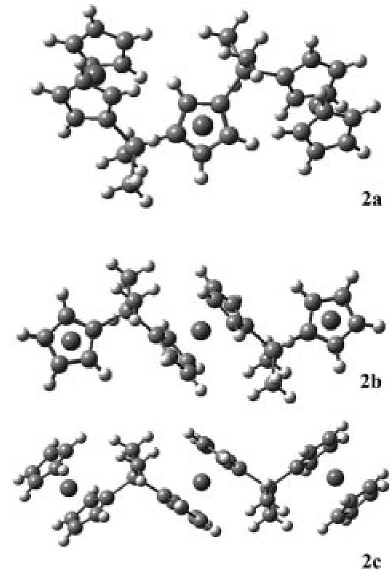

Figure 4. The three conformers found for the trimer **2**.

Figure 5 shows the definition of the coordinates used in the geometry scanning procedure to locate the best inclusion geometry of ferrocene units in β-CD. In a first step, the inclusion geometry of the complex containing ferrocene itself was determined in order to assess the reliability of the method used and to provide a starting point for the search of optimum β-CD·**2** inclusion geometries. Three different structures were found for the β-CD·ferrocene adduct (Figure 6). The lowest energy structure is achieved with axial orientation of the ferrocene guest, with ΔE = –102 kJ·mol^{-1} and z_{Fe} = –380 pm (Figure 6, b). This is a less-common structure, with the ferrocene guest protruding from the lower rim of the β-CD. The equatorial orientation shown in Figure 6 (a) has an inclusion energy of –28 kJ·mol^{-1} and z_{Fe} = –30 pm. The possible occurrence of a tilted inclusion geometry, as found for the (α-CD)$_2$·ferrocene complex,[16] was tested. A stable geometry was found at (r_{Fe}, z_{Fe}) = (100, –40) pm and φ = 18°, with an inclusion energy of –70 kJ·mol^{-1}. As expected, α and θ values present sevenfold and fivefold periodicity, with barriers between minima of about 8 and 23 kJ·mol^{-1}, respectively. This structure, represented in part c of Figure 6, was considered to be the most reasonable starting point for the calculations of the β-CD·**2** inclusion geometry.

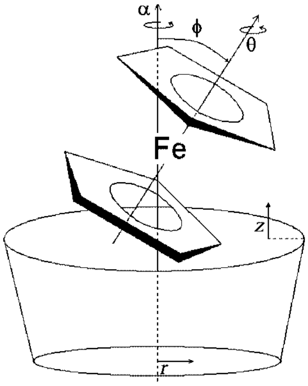

Figure 5. Definition of the variables used in the single-point scanning calculations.

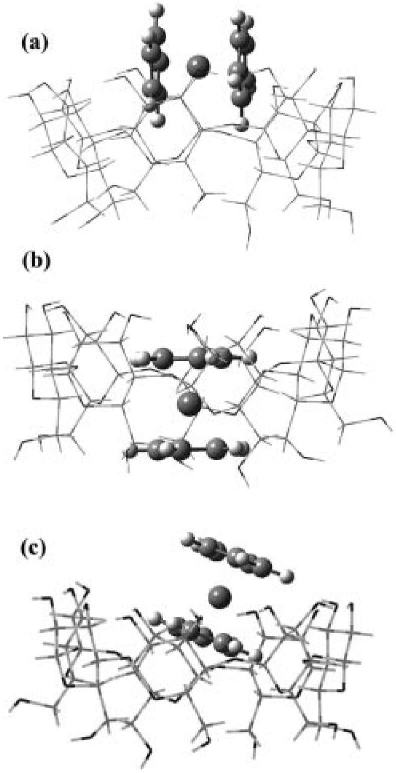

Figure 6. Inclusion geometries found for the β-CD·ferrocene adduct: (a) equatorial, (b) axial and (c) tilted.

Figure 7 shows the minimum energy structure found for the complex β-CD·**2b**. Structure **2b** was selected for the guest because it provides a better host–guest fit than either **2a** or **2c**. The corresponding optimised values are (r_{Fe}, z_{Fe}) = (110, –140) pm and φ = 29°. This structure presents some short contact interactions between the oxygen atoms of β-CD and the cyclopentadienyl hydrogen atoms of terminal and central ferrocenes. These C–H···O interactions, which lie within the 208–244 pm range, are likely to contribute to the stability of the complex.[22]

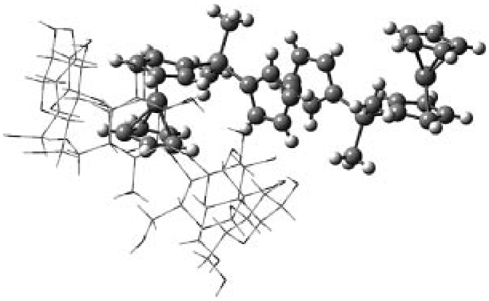

Figure 7. Best geometry obtained for a 1:1 inclusion compound comprising β-CD and **2b**.

The reliability of the inclusion geometries obtained at different computational levels has recently been assessed by Casadesús et al.,[23] based on the occurrence of unrealistic H···H host–guest contacts. In the present structure, there are only three H···H contacts which fall below the 220-pm limit (at 184, 209 and 212 pm). As noted in ref.[23], a small number of short contacts is acceptable and even values below 200 pm are not necessarily unphysical. Thus we may assume that the calculated structure is plausible, despite the well-known limitations of the present approach.

The 2:1 inclusion complex (β-CD)$_2$·**2b** was built from the previous 1:1 structure using the symmetry properties of the inversion centre located at the central iron atom of the guest molecule (Figure 8). This operation assumes that the two CD host molecules do not interact with one another, which is a reasonable approximation for the structure shown, because the distance between the two CDs is about 7 Å. The inclusion energy found for the 2:1 adduct (–302 kJ·mol^{-1}) is roughly double that for the 1:1 adduct (–157 kJ·mol^{-1}), as would be expected. Both values are quite large compared with the corresponding value of –70 kJ·mol^{-1} for the β-CD·ferrocene complex. This increase can be explained by the additional interaction provided by the central ferrocenyl moiety with the CD hosts. Nevertheless, a word of caution is required concerning the magnitude of these values, as they are not corrected for basis set superposition error (BSSE), expected to be important when small basis sets are used, or for zero point vibrational energy (the BSSE correc-

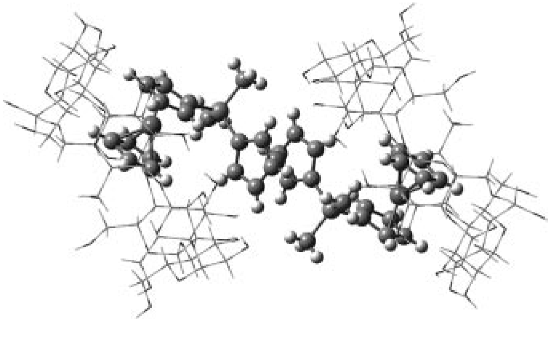

Figure 8. Possible geometry for a 2:1 inclusion compound comprising β-CD and **2b**.

tion is not available for ONIOM calculations and frequency calculations only apply to fully-optimised structures).

Conclusions

The encapsulation of a trimetallic oligo(ferrocenyldimethylsilane) by β-cyclodextrin has been achieved and supported by a combination of experimental and theoretical methods. This compound and the corresponding adduct containing diferrocenyldimethylsilane are a potentially interesting family of organic–organometallic inclusion compounds. Future work in our laboratories will be directed towards investigating the effect of CD inclusion on certain properties of the guest molecules, for example, their electrochemical behaviour. We are also studying the interaction of the oligo(ferrocenes) with other CDs, such as α- and γ-CD.

Experimental Section

General Methods and Procedures: All air-sensitive reactions and manipulations were performed using standard Schlenk techniques under oxygen-free and water-free argon. Solvents were dried by standard procedures (*n*-hexane, THF and Et_2O over Na/benzophenone ketyl; CH_2Cl_2 and NCMe over CaH_2), distilled under argon and kept over 4-Å molecular sieves. β-CD (Fluka) and ferrocene (Aldrich) were obtained from commercial sources and used as received. Monolithioferrocene[24] and (1,1′-ferrocenediyl)dimethylsilane (**1**)[13] were prepared using published procedures.

Microanalyses for CHN were performed at the ITQB, Oeiras, Portugal (by C. Almeida), and Fe was determined by ICP-AES at the Central Laboratory for Analysis, University of Aveiro (by E. Soares). Powder XRD data were collected with a Philips X′pert diffractometer using Cu-K_α radiation filtered by Ni (λ = 1.5418 Å). TGA studies were performed using a Mettler TA3000 system at a heating rate of 5 $K\cdot min^{-1}$ under static air. Infrared spectra were recorded with a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets. Solid state ^{13}C and ^{29}Si CP MAS NMR spectra were recorded at 100.62 and 79.49 MHz respectively, on a (9.4-T) Bruker Avance MSL 400P spectrometer. ^{13}C CP MAS NMR spectra were recorded with 4.5 μs ^1H 90° pulses, 1.0 ms contact time, a spinning rate of 5.0 kHz and 4-s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 5 μs ^1H 40° pulses, 5.0 ms contact time, a spinning rate of 5.0 kHz and 5-s recycle delays. Chemical shifts are quoted in parts per million from TMS.

1,1′-Bis(ferrocenyldimethylsilyl)ferrocene (2): Following the literature method,[10a,10b] a mixture of ferrocenylsilane oligomers was obtained from the reaction of (1,1′-ferrocenediyl)dimethylsilane (**1**) (15.4 g, 64 mmol) with monolithioferrocene (29.6 mg, 108 mmol). The mixture was fractionated using an alumina chromatographic column (90 active, acidic [Activity I] Merck 0.063–0.200 mm, 70–230 mesh ASTM) and a 9:1 hexane/dichloromethane mixture as the mobile phase. Fractions of 250 mL were collected, of which the first six contained pure ferrocene. Fractions 7–39, containing a mixture of ferrocene, diferrocenyldimethylsilane and 1,1′-bis(ferrocenyldimethylsilyl)ferrocene (**2**), were submitted to a second chromatography using neutral alumina (Typ. 507C Brockmann I, STD grade, Approx. 150 Mesh, 58 Å) and the same mobile phase to yield 0.9 g of pure **2**. Fractions 40–65, containing a mixture of **2**, traces of diferrocenyldimethylsilane and larger oligomers, were also submitted to another chromatography using neutral alumina and 0.15 g of **2** was isolated. The total amount of compound **2** obtained was therefore 1.05 g. ^1H and ^{13}C solution NMR spectroscopic data for **2** were in agreement with those reported.[10a,10b] IR (KBr): $\tilde{\nu}$ = 3096 (m), 3089 (m), 3072 (m), 2958 (m), 2924 (m), 2904 (m), 1419 (m), 1409 (m), 1383 (m), 1367 (m), 1245 (vs), 1164 (vs), 1104 (s), 1036 (vs), 1027 (s), 1000 (m), 895 (m), 886 (m), 863 (m), 820 (vs), 798 (vs), 775 (vs), 666 (m), 486 (s), 434 (s) cm^{-1}. ^{13}C CP MAS NMR: δ = 72.5, 72.1, 71.2 (η^5-C_5H_4), 68.5 (η^5-C_5H_5), 0.0 ($SiMe_2$). ^{29}Si CP MAS NMR: δ = –8.0 ppm ($SiMe_2$).

Reaction of β-CD with 1,1′-Bis(ferrocenyldimethylsilyl)ferrocene [(β-CD)$_2$·2]: β-CD (157 mg, 0.12 mmol) was dissolved in water (10 mL) at 50 °C. This solution was treated with **2** (40 mg, 0.06 mmol) dissolved in CH_2Cl_2 (8 mL). The mixture was stirred for 4 days at room temperature, during which time a homogeneous solid product formed at the water–dichloromethane interface. The mixture was left to settle and the product isolated by centrifugation, washed twice with 2 mL-aliquots of water, and dried under air in a desiccator. Yield: 70 mg (36%). $(C_{42}H_{70}O_{35})_2\cdot(C_{34}H_{38}Fe_3Si_2)\cdot15H_2O$ (3210.6): calcd. C 44.14, H 6.53, Fe 5.22; found C 43.77, H 6.06, Fe 5.28. IR (KBr): $\tilde{\nu}$ = 3373 (vs), 2925 (m), 1638 (m), 1419 (m), 1383 (m), 1368 (m), 1333 (m), 1299 (m), 1245 (m), 1158 (s), 1105 (s), 1081 (s), 1053 (sh), 1029 (vs), 1002 (s), 938 (m), 861 (m), 819 (m), 797 (m), 775 (m), 756 (m), 703 (m), 665 (m), 606 (m), 576 (m), 530 (m), 502 (m), 482 (m), 444 (m) cm^{-1}. ^{13}C CP MAS NMR: δ = 103.9 (β-CD, C-1), 81.8 (β-CD, C-4), 73.1 (β-CD, C-2,3,5), 68.6 (guest, Cp), 60.8 (β-CD, C-6), 0.5 (guest, $SiMe_2$). ^{29}Si CP MAS NMR: δ = –6.7, –6.9, –7.6, –8.0 ppm (guest, $SiMe_2$).

Computational Details: Ab initio calculations were carried out using the Gaussian 03W programme package, running on a personal computer.[25] Compound **2** and ferrocene were fully optimised at the B3LYP/LanL2DZ level. The internal rotation of Cp rings about the C_5 axis in ferrocene allows the existence of eclipsed (D_{5h}) and staggered (D_{5d}) conformations. For compound **2**, the additional degrees of freedom due to the rotation about the $C_{(ring)}$–Si bonds lead to the existence of several conformers. Some attempts to characterise these conformers using computational methods have been reported in the literature.[10d,11,26] In ferrocene, the eclipsed form was found to be more stable than the staggered form by 2.78 $kJ\cdot mol^{-1}$.[26] Molecular mechanics studies of **2** yield somewhat conflicting results. While Pannell et al. point to large energy differences between conformers,[10d] Barlow et al. found at least 10 noncentrosymmetrical conformers within an interval of 8.8 $kJ\cdot mol^{-1}$, with the centrosymmetrical conformers lying 12 $kJ\cdot mol^{-1}$ above the absolute minimum.[11]

The models of the inclusion compound were performed by single-point calculations scanning, using the two-layer approximation of Morokuma et al.,[27] with the organometallic guests treated at high layer (B3LYP/LanL2DZ), and cyclodextrins set as low layer (HF/CEP-4G). The crystal structures of β-cyclodextrin hydrate[28] and the trimer **2**[10c,10d] were used to generate the model for the host and the initial model (structure **2b**) for the guest. The optimisation through single-point calculations was used because of the failure of the built-in optimisation procedures to converge to a stable geometry under the ONIOM conditions. The scanning was performed on a 20 pm/4° grid for the r, z, φ, θ and α coordinates (see Figure 5 for the definition of these coordinates). The minimum energy structure was determined from quadratic interpolation, using the lowest energy points in the grid.

Acknowledgments

This work was partly funded by the FCT, POCTI and FEDER (Project POCTI/CTM/46780/2002). S. S. B. and J. A. F. thank the

FCT for grants. S. L. acknowledges grants from the University of Aveiro. We also wish to thank Prof. João Rocha for access to research facilities, and Paula Esculcas and Paula Brandão for assistance in the NMR experiments.

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Received: June 23, 2005