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Modification of β-Cyclodextrin with Ferrocenyl Groups by Ring Opening of an Encapsulated [1]Ferrocenophane

Paula Ferreira, Isabel S. Gonçalves, Martyn Pillinger, João Rocha,
Pedro Santos, and José J. C. Teixeira-Dias*

Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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Summary: β-Cyclodextrin covalently grafted with ferrocenyl groups is obtained after formation of a 2:1 (host to guest) complex between β-CD and (1,1′-ferrocenediyl)dimethylsilane. Structural investigation in the solid state confirms −OH attack of the strained C−Si−C bridge to form an O−Si bond.

The functionalization of cyclodextrins (CDs) at their primary or secondary hydroxyl groups provides molecules that can be invaluable in investigations at the frontiers of chemistry ranging from enzyme-like catalytic activity to aesthetically pleasing molecules.[1] Native CDs have a natural tendency to react on their primary side, and this makes selective modification difficult. An attractive way to circumvent the relative nucleophilicities of the hydroxyl groups is to use the ability of the hydrophobic cavity of CDs to form a strong complex with the electrophilic reagent used (for further structural information see ref 2). In this case the predominant product formed will be dictated by the orientation of the reagent within the complex. Cyclodextrins form inclusion compounds with a wide variety of molecules including transition metal complexes and organometallic compounds.[3] Particularly suitable guests are those bearing hydrophobic ligands such as cyclopentadienyl (η^5-C_5H_5) and η^6-arene (η^6-C_6H_6) groups.[4] Ferrocene and its derivatives are some of the most favorable guest species for CDs due to their suitable size and molecular geometry. In this communication we report on the functionalization of β-cyclodextrin with ferrocenyl groups by ring-opening reaction of an encapsulated strained metallocenophane, $[Fe\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ (**1**).

Mixing of a warm saturated solution of β-CD in water with a solution of (1,1′-ferrocenediyl)dimethylsilane (**1**) in dichloromethane resulted in rapid formation of a pale orange precipitate, β-CD/$[Fe\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ (**2**).[8] Elemental analysis indicated that the β-CD:iron ratio in **2** was 2:1.

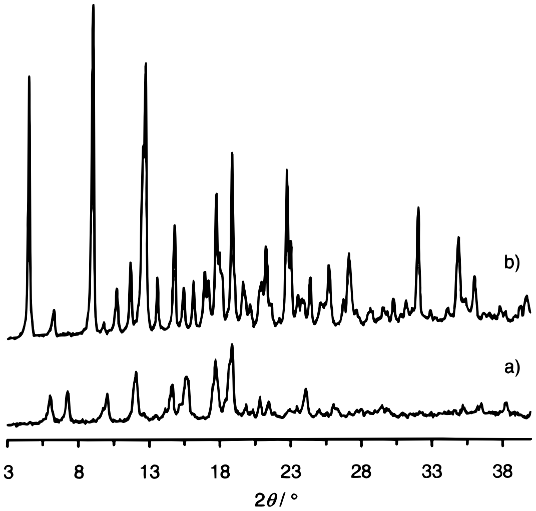

Figure 1. Powder XRD of (a) β-CD/$[Fe\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$, **2**, and (b) free β-CD hydrate ($\lambda = 1.5418$ Å).

Encapsulation of the organometallic guest in the solid state was confirmed by powder XRD. Compound **2** is crystalline, but its powder XRD pattern does not correspond to that of pristine β-CD hydrate (Figure 1). This can be taken as an initial indication for the occurrence of a true inclusion complex (Scheme 1).[3]

In the 950−400 cm^{-1} range, the KBr IR spectrum of compound **2** showed, in addition to several rather weak ring vibrations typical of β-CD, two absorption bands at 822 and 797 cm^{-1}, which do not appear in the spectrum of pristine β-CD and can therefore be ascribed to the guest molecule and/or its interaction with the host. Possible assignments include Si−Me, which usually appears in the range 860−760 cm^{-1}, Si−O−C stretch, which usually appears between 850 and 800 cm^{-1}, and/or C−H out-of-plane bending vibrations of the cyclopentadienyl ligand. Compound **2** displays bands at frequencies higher than 950 cm^{-1} that are very close to those reported for bulk KBr spectra of β-CD.[9] In the

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(1) Khan, A. R.; Forgo, P.; Stine, K. J.; D'Souza, V. T. *Chem. Rev.* **1998**, *98*, 1977−1996.

(2) β-Cyclodextrin (β-CD) is a macrocyclic oligosaccharide consisting of seven α(1→4)-linked glucopyranose units which define a slightly V-shaped toroidal cavity, the diameter of which is in the range 6.0−6.5 Å. The β-CD molecule carries 21 O−H groups, 14 secondary groups located at the 2- and 3-positions on the wider opening and 7 primary groups located at the 6-position on the narrower opening.

(3) Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344−362.

(4) Several reports have discussed the noncovalent complexation between cyclodextrin and cyclopentadienyl or η^6-arene transition metal complexes. Examples include ferrocene and its derivatives (ref 5), mixed sandwich complexes such as $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]PF_6$ (ref 6), and half-sandwich complexes such as $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (ref 7).

(5) (a) Odagaki, Y.; Hirotsu, K.; Higuchi, T.; Harada, A.; Takahashi, S. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1230−1231, and literature cited therein. (b) Bakhtiar, R.; Kaifer, A. E. *Rapid Commun. Mass Spectrom.* **1998**, *12*, 111−114, and literature cited therein.

(6) (a) Klingert, B.; Rihs, G. *Organometallics* **1990**, *9*, 1335. (b) Klingert, B.; Rihs, G. *J. Inclusion Phenom.* **1991**, *10*, 255−265. (c) Klingert, B.; Rihs, G. *J. Chem. Soc., Dalton Trans.* **1991**, 2749−2760.

(7) (a) Aime, S.; Canuto, H. C.; Gobetto, R.; Napolitano, F. *Chem. Commun.* **1999**, 281−282. (b) Patel, P. P.; Welker, M. E. *J. Organomet. Chem.* **1997**, *547*, 103.

(8) A saturated aqueous solution of β-CD (Wacker Chemie, München, 0.50 g, 0.44 mmol) was treated with a solution of $[Fe\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ (0.05 g, 0.22 mmol) in CH_2Cl_2. After reaction at room temperature for 30 min, the suspension was centrifuged and the supernatant decanted. The pale orange powder was washed several times with CH_2Cl_2 and water and vacuum-dried. Yield: 0.6 g (66%) Anal. Calcd for $(C_{12}H_{14}FeSi)\cdot 2(C_{42}H_{70}O_{35})\cdot 14H_2O$ (**2**): C, 41.71; H, 6.64; Fe, 2.02; Si, 1.02. Found: C, 41.50; H, 6.38; Fe, 2.20; Si, 1.10.

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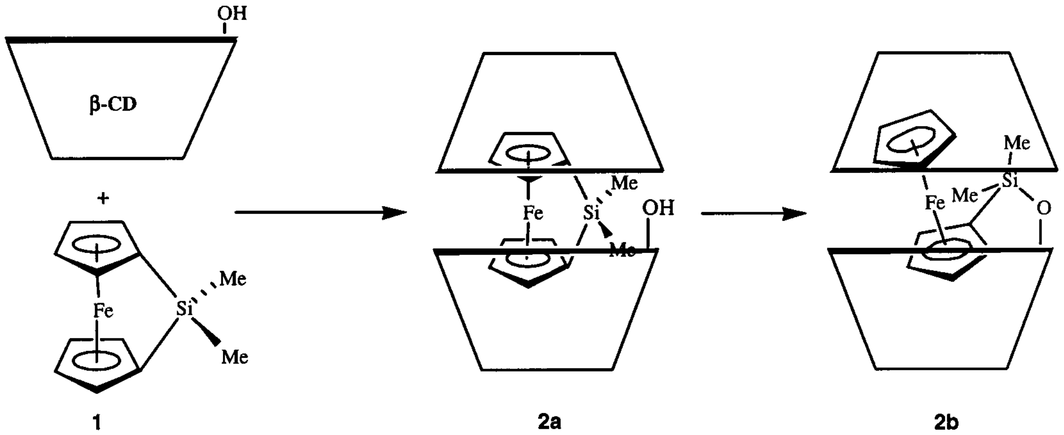
Scheme 1



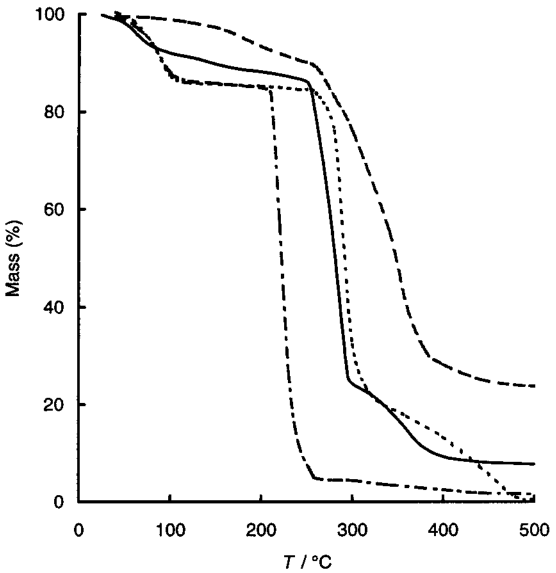


Figure 2. Thermogravimetric analysis of β-CD/[Fe{(η^5-C_5H_4)$_2$SiMe$_2$}], **2** (—), free [Fe{(η^5-C_5H_4)$_2$SiMe$_2$}], **1** (— — —), free β-CD hydrate (- - -), and a physical mixture of β-CD and **1** in a 2:1 molar ratio (— - — -). Heating rate 5 K min^{-1} (air).

Raman spectrum of **2**, bands at 1158, 1101, and 318 cm^{-1} of the substituted ferrocenylsilane unit appear on top of the characteristic vibrations of the host. Corresponding bands for **1** appear at 1148, 1095, and 318 cm^{-1}.

β-CD/[Fe{(η^5-C_5H_4)$_2$SiMe$_2$}] (**2**) remains stable for months in the solid state at ambient conditions. Figure 2 shows the results of thermogravimetric analysis of **2**, the organometallic [Fe{(η^5-C_5H_4)$_2$SiMe$_2$}] (**1**), pristine β-CD hydrate, and a physical mixture of β-CD and **1** in a 2:1 molar ratio. TGA mass loss of β-CD showed 14.4% water loss (10−11 water molecules per β-CD molecule) up to 130 °C, with a peak temperature at 90 °C. There is no further mass loss until 260 °C, when the compound starts to melt and decompose, characterized by a strong, sharp peak in the differential thermogravimetric (DTG) profile at 287 °C. At 500 °C, 100% mass loss is complete. The thermal behavior of compound **2** is similar except that loss of water (12.3%, 9−10 water molecules per β-CD molecule) occurs over a wider range, between 30 and 230 °C, at which point the compound begins to decompose. It loses 62.3% mass between 230 and 290 °C, the midpoint being at 276 °C, only slightly lower than that observed for free β-CD. A total mass loss of 92% is complete at about 400 °C.

The thermal behavior of [Fe{(η^5-C_5H_4)$_2$SiMe$_2$}] (**1**) is well documented.[10] It melts at 78 °C and then undergoes spontaneous, exothermic, and quantitative ring-opening polymerization (ROP) at 120−170 °C to yield a poly(ferrocenylsilane). A surprising result was obtained in the TGA of a mixture of **1** and free β-CD in a 1:2 molar ratio. The cyclodextrin decomposes at around 220 °C, 60−70 °C lower than either compound **2** or pristine β-CD. Exothermic ROP of **1** probably induces decomposition of the cyclodextrin at a lower temperature. These results suggest that the ferrocenyl groups in **2** are isolated from each other by encapsulation in the β-CD cavities. Compound **2** did not liberate the guest when heated at 120 °C under vacuum, while **1** sublimes under the same conditions. This is further evidence that the guest complex is stabilized by inclusion and, probably, covalent grafting into β-CD.

The solid-state ^{29}Si MAS NMR spectrum of β-CD/[Fe{(η^5-C_5H_4)$_2$SiMe$_2$}] (**2**) exhibited two defined resonances (Figure 3). The signal at 7.6 ppm is assigned to a C−O−SiMe$_2$Fc moiety (Fc = ferrocenyl group) (**2b**), by comparison with the ^{29}Si chemical shift of 10.5 ppm observed for the monosubstituted ferrocene derivative [Fe(η^5-C_5H_5)(η^5-C_5H_4Si(OMe)Me$_2$)], prepared as described previously by the reaction of **1** with methanol.[11] The cyclopentadienyl rings in the *ansa*-bridged ferrocene **1** are tilted with respect to one another by an angle of 20.8°, and the compound is appreciably strained.[10] Consequently, the C−Si−C bridge is susceptible to nucleophilic attack by ROH.[11] This ring-opening reaction of **1** has been exploited to attach ferrocenyl groups to a variety of inorganic materials that have reactive surface hydroxyl functionalities.[12]

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(9) Sabapathy, R. C.; Bhattacharyya, S.; Cleland, W. E., Jr.; Hussey, C. L. *Langmuir* **1998**, *14*, 3797−3807, and literature cited therein.

(10) (a) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131−168. (b) Finckh, W.; Tang, B.-Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823−829.

(11) Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501−6506.

(12) For examples where compound **1** undergoes encapsulation and subsequent ring-opening reaction within ordered mesoporous silica hosts, see: (a) O'Brien, S.; Keates, J. M.; Barlow, S.; Drewit, M. J.; Payne, B. R.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 4088−4099. (b) Ferreira, P.; Gonçalves, I. S.; Mosselmans, F.; Pillinger, M.; Rocha, J.; Thursfield, A. *Eur. J. Inorg. Chem.* **2000**, 97−102.

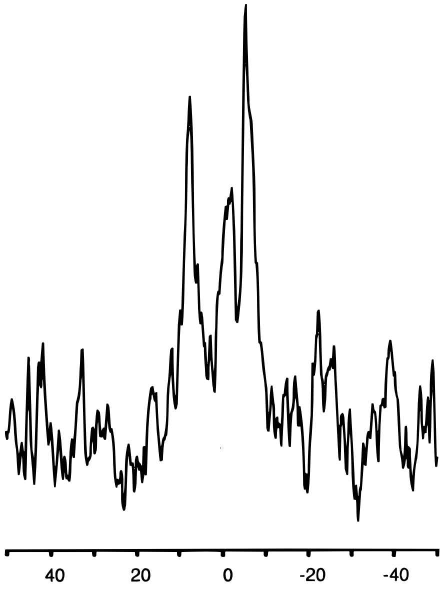

Figure 3. Room-temperature 79.49 MHz solid-state ^{29}Si MAS NMR spectrum of β-CD/[Fe{(η^5-C_5H_4)$_2$SiMe$_2$}], **2** (spinning rate 5 kHz, 40° pulse, 60 s recycle delay, 3959 transients). Recorded on a Bruker MSL400P.

The ^{29}Si signal at −5.3 ppm is assigned to encapsulated **1** (**2a**), by comparison with the ^{29}Si chemical shift of −5.2 ppm observed for the free organometallic.[13] Deconvolution/integration of the spectrum indicated that the ratio of **2a** to **2b** was 1.1:1.0. Under the conditions used, clean conversion of **2a** to **2b** was never observed. A third weak broad peak is also seen around 0 ppm. This may be attributed to the presence of a small amount of H−O−SiMe$_2$Fc, formed by reaction of water with **1**. Wrighton and co-workers studied the reaction of **1** with water and found that it was slow enough to be followed by ^{1}H NMR.[11] We also studied this reaction, by allowing a solution of **1** in dichloromethane to react with excess water for several hours. ^{29}Si MAS NMR of the product indicated that the reaction was slow, but a new peak appeared at about 0 ppm.

The solid-state ^{13}C cross-polarization (CP) MAS NMR spectrum of β-CD/[Fe{(η^5-C_5H_4)$_2$SiMe$_2$}] (**2**) is shown in Figure 4. The different carbon resonances of β-CD are assigned to C-1 (104 ppm), C-4 (81 ppm), C-2,3,5 (73 ppm), and C-6 (61 ppm). These peaks are all rather broad, comparable to the ^{13}C CP MAS NMR spectrum of a β-cyclodextrin−ferrocene (1:1) inclusion compound.[14] In addition, one peak is observed at 68.9 ppm and a weaker one at −1.2 ppm, both ascribed to a monosubstituted ferrocene derivative. The resonance at 68.9 ppm is assigned to the unsubstituted C_5 ring (η^5-C_5H_5) by comparison with the chemical shift observed for the cyclopentadienyl ring formed from the ring-opening reaction of (1,1′-ferrocenediyl)dimethylsilane (**1**) with CD_3OD.[15] The ^{13}C resonance of ferrocene enclathrated in β-CD also appeared at 69 ppm.[14] The peak at −1.2 ppm is assigned to SiMe groups. A very weak peak can also be seen at about 30 ppm, which may be assigned to the cyclopentadienyl carbon attached to silicon in **1**,[13] indicating that not all of encapsulated **1** had reacted. The unusual, high-field resonance at 33.8 ppm for the *ipso* carbon in **1** shifts to more conventional values of 68−75 ppm when **1** undergoes ring-opening reactions.[9]

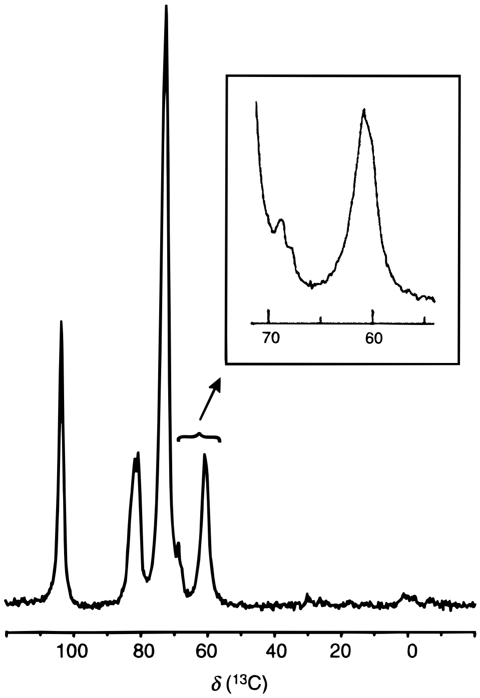

Figure 4. Room-temperature 100.62 MHz solid-state ^{13}C CP MAS NMR spectrum of β-CD/[Fe{(η^5-C_5H_4)$_2$SiMe$_2$}], **2** (spinning rate 8 kHz, 4.5 μs pulse, 4 s recycle delay, 18496 transients).

In conclusion, treatment of a solution of β-cyclodextrin in water with a solution of [Fe{(η^5-C_5H_4)$_2$SiMe$_2$}] in dichloromethane results in rapid formation of a pale orange microcrystalline powder. It is proposed that the initial step is rapid inclusion of [Fe{(η^5-C_5H_4)$_2$SiMe$_2$}] in the β-cyclodextrin cavity, forming a 2:1 (host to guest) stoichiometric inclusion compound. The strained C−Si−C bridge is then placed in close proximity to the secondary hydroxyl groups of the host, located on the wide rim of the torus-like macroring. Nucleophilic attack by one of these hydroxyl groups results in cleavage of a Si−C bond and formation of a modified cyclodextrin with covalently bound “pendant” ferrocenyl groups with self-inclusion properties. This work demonstrates an important concept, that cyclodextrins modified with organometallic functional groups may be prepared by ring-opening reaction of encapsulated strained molecules such as **1**. The resulting systems may be promising for analytical or catalytic applications.

Acknowledgment. We are grateful to PRAXIS XXI for partial funding and to Gilberto Vasco for assistance with the TGA experiments.

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[13] Selected spectroscopic data for **1**: ^{13}C CP MAS NMR (100.62 MHz, 25 °C, TMS): δ = 78.9−77.0 (C_5H_4), 33.8 (*ipso*-C_5H_4), −2.9 (SiMe); ^{29}Si MAS NMR (79.49 MHz, 25 °C, TMS): δ = −5.2 [SiMe$_2$-(η^5-C_5H_4)$_2$].

[14] Imashiro, F.; Kuwahara, D.; Kitazaki, N.; Terao, T. *Magn. Reson. Chem.* **1992**, *30*, 796−797.

[15] O'Brien, S.; Tudor, J.; Barlow, S.; Drewitt, M. J.; Heyes, S. J.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1997**, 641−642.