

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

### New Bis- and Tris-Ferrocenoyl and Tris-Benzoyl Lower-rim Substituted Calix[5]arene Esters: Synthesis, Electrochemistry and X-ray Crystal Structures

Paul D. Beer<sup>a</sup>; Philip A. Gale<sup>ab</sup>; Zheng Chen<sup>ac</sup>; Michael G. B. Drew<sup>d</sup>

<sup>a</sup> Inorganic Chemistry Laboratory, University of Oxford, Oxford, UK <sup>b</sup> Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas, United States of America <sup>c</sup>

Department of Mining and Mineral Engineering, University of Leeds, Leeds, United Kingdom <sup>d</sup>

Department of Chemistry, University of Reading, Reading, UK

**To cite this Article** Beer, Paul D. , Gale, Philip A. , Chen, Zheng and Drew, Michael G. B.(1996) 'New Bis- and Tris-Ferrocenoyl and Tris-Benzoyl Lower-rim Substituted Calix[5]arene Esters: Synthesis, Electrochemistry and X-ray Crystal Structures', *Supramolecular Chemistry*, 7: 4, 241 – 255

**To link to this Article:** DOI: 10.1080/10610279608035195

**URL:** <http://dx.doi.org/10.1080/10610279608035195>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# New Bis- and Tris-Ferrocenoyl and Tris-Benzoyl Lower-rim Substituted Calix[5]arene Esters: Synthesis, Electrochemistry and X-ray Crystal Structures

PAUL D. BEER<sup>a,\*</sup>, PHILIP A. GALE<sup>a,†</sup>, ZHENG CHEN<sup>a,‡</sup> and MICHAEL G. B. DREW<sup>b</sup>

<sup>a</sup>Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK; <sup>b</sup>Department of Chemistry, University of Reading, Whiteknights, Reading RG2 6AD, UK.

(Received 14 December 1995)

New tris-benzoyl-, tris-ferrocenoyl- and bis-ferrocenoyl *p*-tert-butylcalix[5]arene esters have been synthesised (1-3 respectively) by reaction of the parent calixarene with the appropriate acid chloride. X-ray crystal structures of all three compounds have been determined with the structure of 2 revealing an ethanol guest molecule bound deep in the cavity of the calix[5]arene. The electrochemical properties of 2 have been extensively investigated using rotating disk electrode, cyclic and square wave voltammetric techniques. Electrochemical evidence is presented suggesting 2 has the capability of detecting neutral polar guest molecules, such as dimethylformamide, in dichloromethane solutions.

## INTRODUCTION

Calix[n]arenes are macrocyclic molecules composed of n phenol rings linked by methylene groups<sup>1</sup>. The chemistry of calix[4,6 and 8]arenes is well represented in the literature due to the ease with which these molecules can be synthe-

sised<sup>2-4</sup>. Calixarenes containing an odd number of phenolic groups have proved more difficult to produce in large yields<sup>5-8</sup> and therefore their chemistries are, as yet, relatively unexplored. *p*-tert-Butylcalix[5]arene possesses a larger phenolic cavity than *p*-tert-butylcalix[4]arene and so may allow small organic molecules to include more deeply within the calixarene cavity.<sup>9,10</sup> This has been confirmed by a number of X-ray crystal structures of calix[5]arenes containing neutral guests.<sup>11-13</sup> For example the crystal structure of *p*-tert-butylcalix[5]arene shows that the tert-butyl groups include in the cavity of an adjacent calix[5]arene forming chains of molecules in the solid state.<sup>11</sup>

The recognition and detection of guest species by receptors containing a redox- and/or photoactive signalling function is an area of intense current interest<sup>14,15</sup>. The incorporation of a responsive group allows the receptor to be used as

\*Corresponding author.

<sup>†</sup>Present Address: Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas, 78712-1167, United States of America.

<sup>‡</sup>Present Address: Department of Mining and Mineral Engineering, University of Leeds, Leeds, LS2 9JT, United Kingdom.

a sensor for a guest species as binding may perturb the signalling group's photo- or electrochemical properties. Electrochemical sensors for charged species have used a variety of redox-active signalling groups such as ferrocene,<sup>16–20</sup> cobaltocenium,<sup>21–25</sup> quinone,<sup>26–30</sup> anthraquinone<sup>31,32</sup> and nitroaromatic<sup>33</sup> species. For a number of years we have been pursuing a programme aimed at the solution binding and detection of neutral guest species by calixarene type receptors containing redox-active metallocene centres.<sup>34–40</sup> We describe here the synthesis and single crystal X-ray structures of new redox-active bis- and tris-ferrocenyl calix[5]arenes (**2** and **3**) and a new tris-benzoyl *p*-tert-butylcalix[5]arene (**1**) and report electrochemical evidence suggesting that receptor **2** detects polar neutral guest species.<sup>41</sup>

## EXPERIMENTAL SECTION

### Solvent and Reagent Pre-treatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Ethanol was distilled under nitrogen from sodium ethoxide. Triethylamine and dichloromethane was distilled from CaH<sub>2</sub>. Unless otherwise stated, commercial grade chemicals were used without further purification. The following compounds were prepared by published procedures: *p*-tert-butylcalix[5]arene<sup>6</sup> and chlorocarbonylferrocene.<sup>42</sup>

### Instrumentation

NMR Spectra were recorded on a Bruker AM 300 and AM250 spectrometers. Infrared spectra were recorded on a Mattson 10410E "Polaris" Fourier transform Spectrometer. Electrochemical measurements were conducted on a Princeton Applied Research Potentiostat/Galvanostat

Model 273. Fast atom bombardment mass spectra (FABMS) were carried out at EPSRC Mass Spectrometry Service, University of Wales, Swansea. All elemental analyses were carried out by the Inorganic Chemistry Laboratory Microanalysis Service.

## SYNTHESES

### *p*-tert-Butylcalix[5]arene Tris Benzoyl Ester **1**

*p*-tert-Butylcalix[5]arene<sup>6</sup> (0.76 g, 0.94 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (50 ml). Benzoyl chloride (1.22g, 8.6 mmol) and Et<sub>3</sub>N (0.88 g, 8.6 mmol) were added and the flask heated at reflux for 48 hours. The solution was then allowed to cool and washed with NaOH<sub>(aq)</sub> (100 ml, 1.0 M), H<sub>2</sub>SO<sub>4(aq)</sub> (100 ml, 1.0 M) and finally water (200 ml). The organic layer was then reduced in vacuo and the residue triturated with MeOH (25 ml). The mixture was then filtered and the product purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>/hexane (3:1 v/v). The fastest moving fraction was collected and reduced *in vacuo* affording the tris ester as a white powder (750 mg, 54%). <sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): 6.7–8.2 (br m, 25H, ArH), 5.31 (s, CH<sub>2</sub>Cl<sub>2</sub>), 4.13 (d, 2H, <sup>2</sup>J = 15.0 Hz, ArCH<sub>2</sub>Ar: H<sub>ax</sub>), 3.99 (d, 2H, <sup>2</sup>J = 13.9 Hz, ArCH<sub>2</sub>Ar: H<sub>ax</sub>), 3.88 (d, <sup>2</sup>J = 15.0 Hz, 1H, ArCH<sub>2</sub>Ar: H<sub>ax</sub>), 3.49 (d, <sup>2</sup>J = 14.8 Hz, 2H, ArCH<sub>2</sub>Ar: H<sub>eq</sub>), 3.41 (d, 3H, ArCH<sub>2</sub>Ar (coincident): H<sub>eq</sub>), 0.82–1.52 (m, 45H, (CH<sub>3</sub>)<sub>3</sub>C). <sup>13</sup>C-NMR (75.42 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 165.33 (C=O), 149.70 (Ar), 148.86 (Ar), 148.51 (Ar), 144.20 (Ar), 143.15 (Ar), 133.80 (ArH), 133.59 (ArH), 133.16 (Ar), 132.52 (Ar), 131.73 (Ar), 130.58 (ArH), 130.48 (ArH), 128.93 (ArH), 128.73 (ArH), 128.31 (Ar), 127.30 (Ar), 126.45 (ArH), 126.13 (ArH), 125.41 (ArH), 124.85 (ArH), 34.32 ((CH<sub>3</sub>)<sub>3</sub>C), 34.04 ((CH<sub>3</sub>)<sub>3</sub>C), 31.68 ((CH<sub>3</sub>)<sub>3</sub>C), 31.18 ((CH<sub>3</sub>)<sub>3</sub>C), 30.69 (ArCH<sub>2</sub>Ar). IR-KBr: 1602 cm<sup>-1</sup> (Carbonyl stretch). Anal. Cald. for C<sub>76</sub>H<sub>82</sub>O<sub>8</sub>·CH<sub>2</sub>Cl<sub>2</sub>; C, 76.53; H, 7.01. Found C,

77.68; H, 7.51. FAB MS (+ve ion) ( $m/z$ ) 1124 ( $MH^+$ ), 1256 ( $MCs^+$ ).

### *p*-tert-Butylcalix[5]arene Tris Ferrocenoyl Ester 2

*p*-tert-Butylcalix[5]arene<sup>6</sup> (0.38g, 0.47 mmol) was dissolved in dry  $CH_2Cl_2$  (25 ml). Triethylamine (distilled) (0.40 g, 3.96 mmol) was added. Chlorocarbonylferrocene<sup>42</sup> (0.82 g, 3.3 mmol = 7 equivalents) was dissolved in  $CH_2Cl_2$  (25 ml) and added dropwise to the stirred solution. The solution was refluxed overnight and then the flask was then allowed to cool. The organic phase was then washed with HCl (100 ml, 1M) (quickly) and water (3 × 100 ml) and then dried over  $MgSO_4$  and reduced *in vacuo*. The mixture was initially purified by column chromatography on silica, eluting with  $CH_2Cl_2$ , which produced a fast moving fraction containing the product. TLC of this fraction in 4 ml petroleum ether 40–60: 4 ml  $CH_2Cl_2$ : 0.2 ml acetone showed a main orange spot and some weaker UV active spots which may also have been coloured but which were too weak to see without the UV lamp. This fraction was then purified by column chromatography on silica using 18.7 petroleum ether 40–60: 18.7  $CH_2Cl_2$ : 1 acetone (v/v) affording an orange powder (0.11g, 16%). <sup>1</sup>H-NMR (300MHz,  $CDCl_3$ ): 7.44–6.98 (v br. m, 10H, ArH), 6.06 (br, 2H, FcH), 5.24 (br, 2H, FcH), 4.99 (br, 2H, FcH), 4.80 (br, 2H, FcH), 4.67 (br, 2H, FcH), 4.43 (br s, 5H, free cyclopentadienyl FcH), 4.30 (approx.) (coincident 2H, FcH and 5H  $ArCH_2Ar$ ), 4.21 (br s, 10H, free cyclopentadienyl FcH), 3.90 (br, m, 1H,  $CH_2$ ), 3.41–3.54 (br, m, 4H,  $CH_2$ ), 1.37 (s, 18H,  $(CH_3)_3C$ ), 1.04 (br, 27H,  $(CH_3)_3C$ ). <sup>13</sup>C-NMR (75.42MHz,  $CD_2Cl_2$ ): 171.53 (C=O), [126.75, 127.25, 131.63, 132.06, 132.75, 143.00, 143.94, 158.37, 158.68, 150.13, (Ar)], 126.00 (ArH), 125.50 (ArH), 125.00 (ArH), [70.19, 70.45, 71.36, 71.67, 72.03, 72.42, (FcH)], 34.31( $CH_3C$ ), 34.06( $CH_3C$ ), 31.51( $CH_3C$ ), 31.18( $CH_3C$ ), 30.92( $CH_3C$ ), 30.66( $CH_2$ ),

30.21( $CH_2$ ). IR KBr 1731  $cm^{-1}$  (carbonyl stretch). Anal. Calcd. for  $C_{88}H_{94}Fe_3O_8 \cdot CH_3CH_2OH$ : C, 72.39; H, 6.75; Fe, 11.22. Found C, 72.32; H, 6.54; Fe, 11.53. FAB MS (+ve ion) ( $m/z$ ) 1446 ( $M^+$ )

### *p*-tert-Butylcalix[5]arene Bis Ferrocenoyl Ester 3

The reaction was repeated as above. On one occasion a faster moving fraction than the tris ester was observed by chromatography on silica eluting with dichloromethane. This fraction was isolated and further purified by column chromatography on silica using 18.7 petroleum ether: 18.7  $CH_2Cl_2$ : 1 acetone (v/v) and was found to be *p*-tert-butylcalix[5]arene bisferrocenoyl ester, an orange powder produced in 7% yield (50 mg).

<sup>1</sup>H-NMR (300MHz,  $CD_2Cl_2$ ) 7.22 (br m, 10H, ArH), 5.21 (m, 4H, FcH), 4.70 (m, 4H, FcH), 4.44 (s, 10H, FcH), 4.22 (br m, 5H,  $CH_2$ ), 3.58 (br m, 5H,  $CH_2$ ), 1.38–1.34 (br m, 45H,  $(CH_3)_3C$ ). <sup>13</sup>C-NMR (75.42MHz,  $CD_2Cl_2$ ) [126.09, 126.90, 130.58, 142.52, 142.60, 145.63, 149.37, 151.04 (Ar)], [70.09, 70.34, 71.06, 72.39 (Fc)], 33.99 ( $(CH_3)_3C$ ) 31.62 ( $(CH_3)_3C$ ), 31.49 ( $(CH_3)_3C$ ), 31.07( $CH_2$ ). IR KBr 1733 $cm^{-1}$  (carbonyl stretch). A satisfactory microanalysis for this material could not be obtained. FAB MS (+ve ion) ( $m/z$ ) 1235 ( $M^+$ ).

### Crystal Structure Determinations

Crystal Data are given in Table I, together with refinement details. Data for all three crystals were collected with  $MoK\alpha$  radiation using the MARresearch Image Plate System. The crystals were positioned at 75 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 mins. Data analyses were carried out with the XDS program<sup>43</sup>. The structures were then solved using direct methods with the Shelx86 program<sup>44</sup>. In 1 there was a solvent eth-

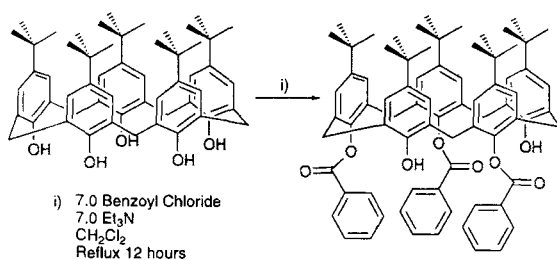
TABLE I Crystal data and structure refinement for 1, 2 and 3

Compound		(1)	(2)	(3)
Empirical formula		C79 H87 Cl2 O8.5	C92 H112 Fe3 O14	C77 H83 Fe2 O7
Formula weight		1243.38	1609.36	1232.13
Temperature (K)		295 (2)	293 (2)	293 (2)
Wavelength (Å)		0.71070	0.7107	0.7107
Crystal system		triclinic	triclinic	monoclinic
Space group		PT	PT	P2 <sub>1</sub> /n
Unit cell dimensions (Å, °)	a	14.039 (7)	14.004(6)	15.600 (7)
	b	15.232 (8)	14.482(6)	14.006 (7)
	c	18.511(11)	22.511(6)	30.899(14)
	α	109.43 (1)	79.61 (1)	(90)
	β	99.29 (1)	82.09 (1)	94.82 (1)
	γ	99.81 (1)	79.06 (1)	(90)
Volume Å <sup>3</sup>		3575.7	4384.0	6727.1
Density (calculated) Mg/m <sup>3</sup>		1.155	1.219	1.217
Absorption coefficient mm <sup>-1</sup>		0.15	0.548	0.48
F(000)		1284	1708	2612
Crystal size mm		0.35 * 0.25 * 0.10	0.25 * 0.25 * 0.15	0.30 * 0.10 * 0.25
Theta range for data collection (°)		1.70 to 24.84	1.84 to 24.96	3.03 to 25.98
Index ranges		0 < h <= 16, -17 < k <= 17, -21 < l <= 21	0 < h <= 16 -16 < k <= 17 -23 < l <= 23	-9 < h <= 8 0 <= k <= 15 -30 <= l <= 29
Reflections collected		11273	13407	10192
Independent reflections		11273	13407	6997 (R <sub>int</sub> = 0.0304)
Data/restraints/parameters		11273/0/785	13407/0/977	4263/18/743
Goodness-of-fit on F <sup>2</sup>		1.034	1.082	0.642
Weighting Scheme* (a,b)		0.209 2.98	0.265 15.12	0.39 43.83
Final R indicates [I > 2σ(I)]		R1 = 0.082 wR2 = 0.196	0.094 0.174	0.065 0.176
R indicates (all data)		R1 = 0.112 wR2 = 0.296	0.133 0.260	0.142 0.236
Largest diff. peak and hole (eÅ <sup>-3</sup> )		0.557, -0.661	1.43, -1.03	0.464, -0.541

\*Weighting Scheme  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ,  $P = [\text{Max}(F_o^2, 0) + 2F_o^2]/3$

anol molecule with 50% occupancy and a disordered solvent dichloromethane molecule. Two positions with relative occupancies  $x$  and  $1-x$  were refined for each chlorine atom. Thermal parameters for the chlorine atoms were constrained to be equivalent. There were two hydrogen atoms bonded to oxygens at the lower rim of the calixarene which were located in a difference Fourier map and their parameters were allowed to refine independently. In **2**, two of the *tert*-butyl groups were disordered and both were refined in two different orientations so that the sum of the occupancies was 1.0. In addition

there were several molecules of solvent. Two ethanol molecules were located and in addition there were nine water molecules which were given occupancies of either 0.33 or 0.50. In **3**, one of the *tert*-butyl was disordered and this was refined as above. In addition one of the cyclopentadienyl rings was disordered and two orientations of the ring were refined with occupancies of  $x$  and  $1-x$ . In neither **2** nor **3** could the hydrogen atoms bonded to oxygen atoms at the lower rim be located. In all three structures all non-hydrogen atoms in the calix[5]arenes were refined anisotropically apart from those disor-



SCHEME 1

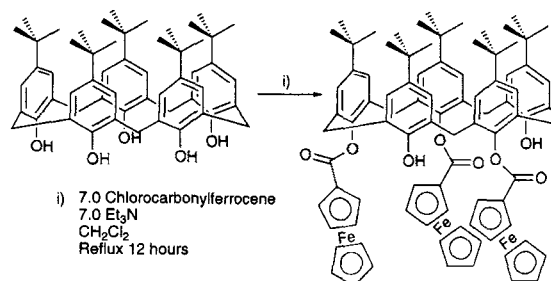
dered atoms which were given isotropic thermal parameters. Solvent molecules were also refined with isotropic thermal parameters. Hydrogen atoms were included in calculated positions with thermal parameters equivalent to 1.2 times the atom to which they were bonded. All three structures were then refined on F<sup>2</sup> using Shelxl<sup>45</sup>. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Positional coordinates, molecular dimensions, thermal parameters and hydrogen atom positions are provided in the supporting information.

## RESULTS AND DISCUSSION

The reaction of an excess amount of benzoyl chloride with *p-tert*-butylcalix[5]arene in CH<sub>2</sub>Cl<sub>2</sub> and subsequent purification by column chromatography gave the new tris-benzoyl *p-tert*-butylcalix[5]arene **1** in 54% yield (Scheme 1).

The reaction was repeated substituting chlorocarbonylferrocene for benzoyl chloride and the trisferrocenoyl *p-tert*-butylcalix[5]arene **2** was isolated as an orange powder in 16% yield (Scheme 2). Bis-ferrocenoyl-*p-tert*-butylcalix[5]arene **3** was obtained in variable, but always low, yields using the same chromatographic separation techniques.

The 1, 3, 4-pattern of substitution is expected on steric grounds, as analogous reactions carried out on several calix[4]arenes have produced 1,3-substituted products<sup>37</sup>. The low yield of this reaction can be attributed to the production of



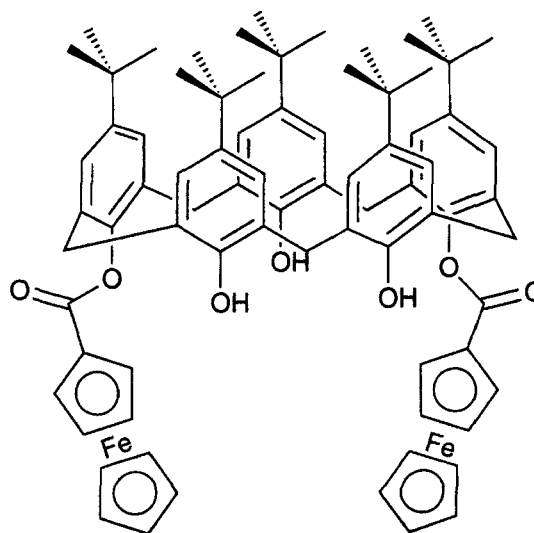
SCHEME 2

other substituted calix[5]arenes. The possibility also exists for the formation of substituted calix[5]arenes in conformations other than the cone. The majority of the reaction mixture forms a fraction which has to date proved to be inseparable using various column chromatographic techniques.

Both **2** and **3** display broad <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> at room temperature presumably due to fluxional processes occurring in the molecules in solution. The dynamic properties of **2** were studied by variable temperature <sup>1</sup>H NMR.

### <sup>1</sup>H NMR Variable Temperature Studies

At 292K the majority of the resonances in the <sup>1</sup>H NMR spectrum of **2**, in CD<sub>2</sub>Cl<sub>2</sub> are broad (Figure



Compound 3.

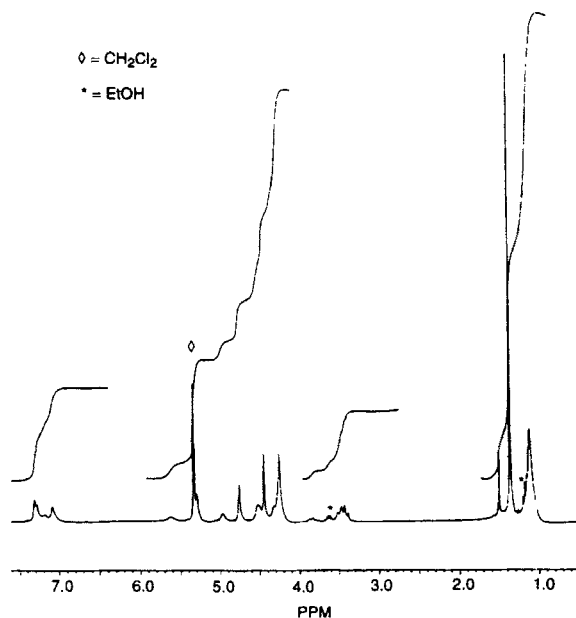


FIGURE 1  $^1\text{H}$  NMR of 2 in  $\text{CD}_2\text{Cl}_2$  at room temperature.

1). Variable temperature NMR studies of this molecule were carried out in  $d_8$ -toluene (hot) and  $d_2$ -dichloromethane (cold) solutions.

The *tert*-butyl region of the spectrum shows two resonances; a sharp singlet at 1.35 ppm (18H) and a broad resonance at 1.11 ppm (27H) which splits, as the temperature is lowered, into two resonances that integrate in the ratio of 2:1 (Figure 2). The resonances corresponding to the ferrocene protons also sharpen as the temperature is lowered. This behaviour is due to the dynamic process of the ferrocene substituted phenol groups rocking in and out of the cavity of the calixarene. As they carry bulky substituents on the lower rim they are too large to rotate all the way through the cavity of the calixarene. The broad resonance corresponds to the *tert*-butyl groups of these substituted phenol rings. As the temperature is lowered this rocking motion is frozen out. The sharp singlet at 1.35 ppm corresponds to the *tert*-butyl groups on the free phenol rings. The free phenol groups are not part of a hydrogen bonded array and therefore the OH group is free to rotate through the cavity. This

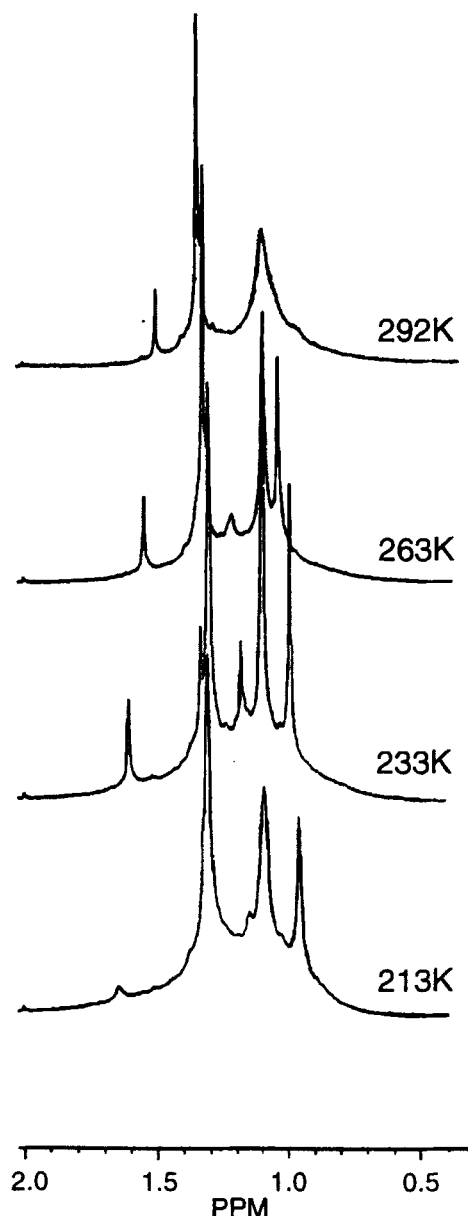


FIGURE 2 Partial NMR spectra of 2 in  $d_2$ -dichloromethane showing changes in the *tert*-butyl resonances as the temperature is lowered.

process is fast on the NMR timescale and therefore the *tert*-butyl groups appear as a sharp singlet.

At high temperatures in  $d_8$ -toluene this rocking process also becomes fast on the NMR timescale and the broad resonance is resolved again

into two peaks corresponding to the two chemically distinct *tert*-butyl groups. The ferrocene and ArCH<sub>2</sub>Ar proton resonances also sharpen at high temperature allowing assignments to be made. The presence of two chemically distinct types of ferrocene in the molecule and three types of methylene ArCH<sub>2</sub>Ar group makes this region of the spectrum rather complicated. A proposed assignment is shown schematically in Figure 3. The two types of ferrocene present in the molecule have been designated **A** and **B**. The free Cp ring of **A** appears as a singlet at 4.20 ppm and the two **B** rings also as a singlet at 4.16 ppm. The substituted ferrocene rings are in different environments and so will display different splitting patterns. The **A** ring lies on a mirror plane and hence H<sub>a</sub> and H<sub>b</sub> give a simple AA'BB' pattern of observed triplets in the ratio 2:2. The **B** rings however lie off this plane and so all four protons are inequivalent resulting in a more complex pattern. H<sub>c</sub> and H<sub>f</sub> both resonate at different frequencies, however H<sub>d</sub> and H<sub>e</sub> are both in very similar environments and hence they resonate coincidentally at 4.32 ppm.

### X-ray Structural Investigations

Crystals of **1** suitable for X-ray crystal structure determination were grown by slow evaporation from a mixture of dichloromethane/hexane and ethanol. Crystals of **2** and **3** were obtained in a similar manner from dichloromethane/ethanol and dichloromethane/hexane solutions respectively. The structures of **1**, **2** and **3** are shown in Figures 4, 5 and 6 respectively and the conformations are described by torsion angle, least squares planes and distances in Table II. As is apparent from the Figures, **2** and **3** have the cone conformation which has been found in all the calix[5] structures that have so far been structurally determined but **1** does not, and has a conformation that can be described as a partial cone in that one of the five rings (identified as ring 5 in Figure 4) is rotated through 180° so that the

oxygen atom is pointing upwards (in the same direction as the *tert*-butyl groups of the other four rings) and the *tert*-butyl group is pointing downwards. This is analogous to the well known partial cone conformation of the calix[4]arene but has never before been observed in calix[5]arenes.

It is significant that this unique ring is of the only two non-substituted rings. This feature is also often found in the substituted calix[4]arenes with the partial cone conformation and is presumably due to the fact that this rotation is only possible when the lower rim oxygen atom is unsubstituted as bulky groups would prohibit rotation because of steric repulsions. The three benzoyl groups on rings 1, 3 and 4 are therefore on the lower rim of the calix[5]arene (Figure 4). The solvent molecules are present in the lattice and are not close to the calix[5]arenes.

The conformations of **2** and **3** are distorted cones as detailed by the dimensions in Table II; thus the five methylene groups are approximately co-planar, as indeed are the five oxygen atoms at the lower rim of the cone. Because of the substituents at the lower rim, the conformations are somewhat distorted from the regular cone shape although the signs of the torsion angles around the C(Ar)-C(CH<sub>2</sub>) bonds are alternatively + and -, a feature which is characteristic of the cone conformation. However the range of the absolute angles is far greater (81.9 to 128.6° in **2** and 63.7 to 146.6° in **3**) compared to that found in calix[5]arene<sup>46</sup> (87.4 to 101.9°). In the latter regular structure the distances between the oxygen atoms at the bottom of the cone ranged from 2.83 to 2.85 Å indicative of intramolecular hydrogen bonding.

Not surprisingly the bulky substituents at the lower rim of **2** and **3** have broken up the regular pattern (Table II). In **2**, there are three ferrocenoyl groups located in positions 1, 2 and 4, and as a result the distances between oxygen atoms at the lower rim are all increased to the range 3.29 to 3.50 Å. There is an ethanol molecule within the cone cavity as shown in Figure 5. The oxygen



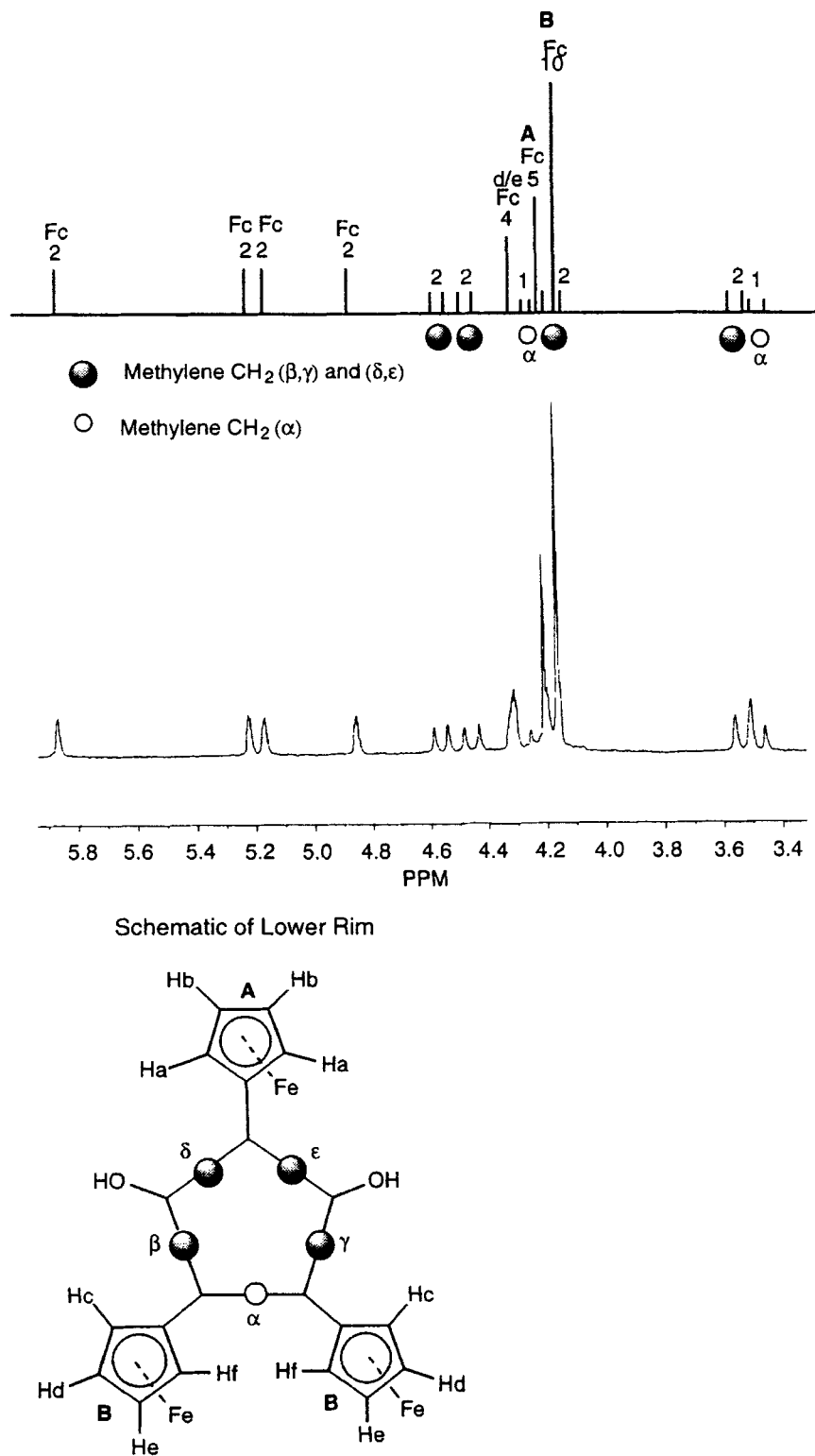


FIGURE 3 Partial NMR spectrum of **2** in  $d_8$ -toluene at 353K and schematic showing proposed assignment and relative integration of peaks.

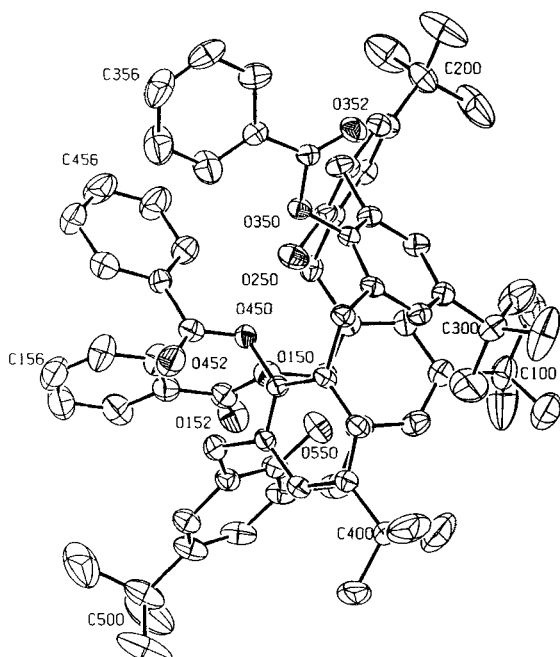


FIGURE 4 The structure of (1). Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted for clarity. The solvent molecules are not included.

atom O(800) of this solvent molecule is lying within hydrogen bonding distance of both unsubstituted oxygen atoms at the bottom of the cone [e.g. O(350) 2.81, O(550) 2.82Å]. This contrasts with the usual position of solvent in the calix[4]arene cone which is found to be in the body of the cone, well above the lower rim. By contrast in **3** there are only two substituted ferrocenoyl groups at positions 2 and 5 and there are only two close O...O contacts (O(150)... O(250) 2.81 and O(350)...O(450) 2.74Å) that are indicative of intramolecular hydrogen bonding. There are no solvent molecules in **3**. There is however an intramolecular hydrogen bond of 2.73Å between the carbonyl oxygen atom O(552) and O(450).

The contrast between the partial cone conformation of **1** and the cone conformations in **2** and **3** is clearly indicated by the torsion angles and the least squares planes in Table II. Thus in **2** and **3** the five methylene carbon atoms are approximately planar but in **1**, C(47) is  $-2.92\text{Å}$  from the

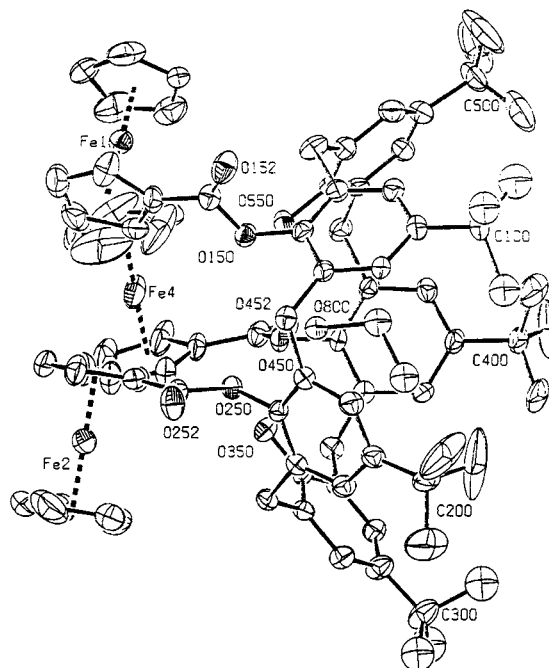


FIGURE 5 The structure of (2). Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted for clarity. Only one of the alternative positions for two of the t-butyl groups is shown. The position of the included ethanol molecule is shown but the other lattice solvent molecules are not shown.

plane of the other four methylene carbon atoms. The C-C(Ar)-C(CH<sub>2</sub>)-C torsion angles in **1** do not follow the alternate sign characteristics found in the cone and their values are more disparate. However the five oxygen atoms still maintain an approximate plane with deviations of  $<0.80\text{Å}$ . In **2** and **3**, the ferrocenoyl groups have the expected geometry with Fe-C distances ranging from 1.97 to 2.07Å.

### Electrochemistry

The electrochemical properties of **2** were studied by both voltammetric and coulometric methods using stationary, rotating disk and thin layer electrodes. Unfortunately compound **3** could not be produced in high enough quantities to carry out electrochemical investigations.

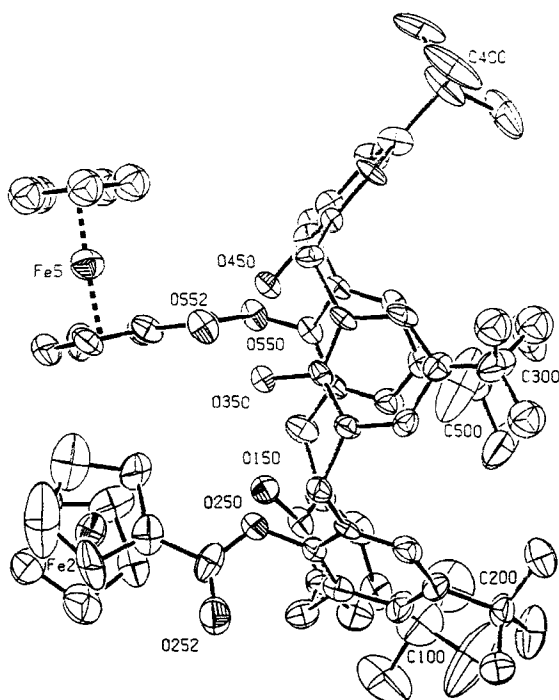


FIGURE 6 The structure of (3). Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted for clarity. Only one of the alternative positions for one of the *t*-butyl groups and one of the cp rings is shown.

Cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$  (Figure 7) shows two oxidation processes—a shoulder at  $E_{\text{pal}} \approx 350\text{mV}$  and a peak at  $E_{\text{pa2}} = 470\text{mV}$ . The presence of two waves may mean one of two things. Firstly, that there are two chemically distinct types of ferrocene in the molecule which are being oxidised at differing potentials due to their different environments or secondly, that the oxidation of the initial ferrocene moiety perturbs the other two in the molecule which then oxidise at a different potential. The second explanation is supported by the fact that the ferrocene groups in 2 are all linked to the calixarene framework by identical ester groups. Thus this perturbation should be in accordance with the electrostatic interaction between the ferrocenium groups.

It was found by coulometry that at potentials higher than the marked position (Figure 7) three electrons were transferred to each molecule of 2.

Compound 2 was also studied by rotating disk electrode (RDE) voltammetry. The voltammograms were recorded at different rotation rates and are shown in Figure 8. Plotting the limiting current against the square root of the rotation rate resulted in a straight line, indicating the overall process is diffusion controlled.

Using the known relation between the RDE's potential and current and taking into account the two separate redox processes, the following equation can be derived, in which,  $i$  is the instantaneous current,  $i_L$  is the limiting current, and others have their usual physical meanings.

$$i = \frac{i'_L}{\exp\left[(E'^{\circ} - E)\frac{nF}{RT}\right] + 1} + \frac{i''_L}{\exp\left[(E''^{\circ} - E)\frac{nF}{RT}\right] + 1}$$

The results from a non-linear fitting of the voltammogram recorded at 121rpm is shown in Figure 9. It can be seen that the limiting current of the first process ( $i'_L$ ) is about half that of the second ( $i''_L$ ). This corresponds to one ferrocene being oxidised followed by the other two. The fitting program also generates values for the half-wave potentials of each process. In this case they are at  $E'^{\circ} = 351.5\text{mV}$  and  $E''^{\circ} = 441.8\text{mV}$ . This is in good agreement with the values obtained by cyclic voltammetry (Figure 7).

#### *Electrochemistry in the Presence of Neutral Guest Species*

A fundamental difference between the electrochemical recognition of a charged and a neutral guest species lies in the pathways for coupling the redox responsive process and the complexation reaction. In the majority of cases with charged guests the electrochemical sensing is aided largely by electrostatic interactions be-

TABLE II Conformational descriptions of (1), (2), and (3)<sup>a</sup>

(a) Torsion Angles (°)			
	(1)	(2)	(3)
C(16) - C(15) - C(17) - C(21)	119.6	116.4	-74.9
C(15) - C(17) - C(21) - C(26)	-77.0	-100.5	107.6
C(26) - C(25) - C(27) - C(31)	63.3	117.1	-121.2
C(25) - C(27) - C(31) - C(36)	-153.2	-92.1	107.4
C(36) - C(35) - C(37) - C(41)	117.1	81.9	-102.2
C(35) - C(37) - C(41) - C(46)	-72.6	-125.5	83.7
C(46) - C(45) - C(47) - C(51)	131.7	128.6	-63.7
C(45) - C(47) - C(51) - C(56)	-48.8	-84.5	146.6
C(56) - C(55) - C(57) - C(11)	-59.3	86.9	-157.9
C(55) - C(57) - C(11) - C(16)	-21.5	-126.8	67.7
(b) Deviations (Å) from Least Squares Planes			
Plane 1			
C(17)	-0.19	0.23	-0.07
C(27)	0.20	-0.30	0.13
C(37)	-0.13	0.25	-0.13
C(47)	-2.92*	-0.11	0.08
C(57)	0.12	-0.08	-0.01
Plane 2			
O(150)	-0.47	-0.06	0.15
O(250)	0.09	-0.08	-0.10
O(350)	0.36	0.17	-0.23
O(450)	-0.78	-0.18	0.09
O(550)	0.80	0.15	-0.11
Angle of intersection (°) of phenyl rings with plane 1			
ring 1	76.3	83.0	37.9
ring 2	35.4	66.1	72.7
ring 3	52.2	45.9	61.8
ring 4	47.9	89.3	40.6
ring 5	62.9	42.5	60.0
(c) Distances (Å) between oxygen atoms at the bottom rim of the cone			
O(150) ... O(250)	3.19	3.50	2.81
O(250) ... O(350)	4.28	3.29	3.58
O(350) ... O(450)	3.16	3.39	2.74
O(450) ... O(550)	3.87	3.58	4.21
O(550) ... O(150)	3.01	3.50	4.16

<sup>a</sup>Numbering scheme (nm) is such that the first digit n refers to the ring number (1-5). The second digit(s) m defines the atom position; 1-6 refer to the phenyl ring, (such that 3 is attached to the t-butyl group and 6 to the oxygen atom), 7 to a methylene group, and 50 to the oxygen atom at the bottom of the cone.

tween the charged guest and redox centre. These interactions are obviously not so apparent for the detection of a neutral guest. Compound 2 contains three electrostatically interactive ferrocenyl redox centres located in close proximity to the lower rim of the calix[5]arene. Prompted by the structure of 2 revealing a totally included

ethanol molecule (Figure 5) located relatively near to the redox centres an electrochemical recognition study with a variety of neutral guests of differing polarities was undertaken.

Voltammetric measurements were carried out in dichloromethane as this solvent medium has a low dielectric constant ( $\epsilon = 8.9$ ) in which, as

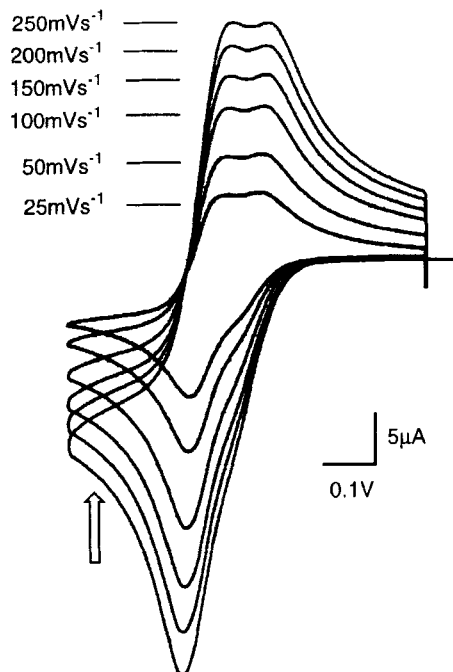


FIGURE 7 CVs of compound **2** ( $5 \times 10^{-4}$ M) in  $\text{CH}_2\text{Cl}_2$  in the presence of  $0.1 \text{ M}^n\text{Bu}_4\text{NBF}_4$  as supporting electrolyte. Recorded at various scan rates.

shown in the previous section, **2** displays the mutual electrostatic interactions between the three ferrocenyl redox centres.

The addition of less polar guests (relative to  $\text{CH}_2\text{Cl}_2$ ) such as toluene ( $\epsilon = 2.4$ ) led to negligible changes in the CVs (Figure 11c). In contrast, the addition of more polar species such as  $\text{CH}_3\text{CN}$  ( $\epsilon = 37.5$ ) (Figure 10), DMF ( $\epsilon = 36.7$ )

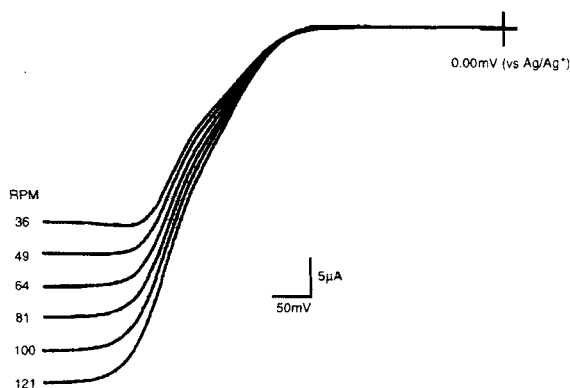


FIGURE 8 Rotating Disk Electrode Electrochemistry of  $8 \times 10^{-4}$ M solution **2** in  $\text{CH}_2\text{Cl}_2$   $0.1 \text{ M}^n\text{Bu}_4\text{NBF}_4$  supporting electrolyte. Scan rate =  $50 \text{ mVs}^{-1}$ .

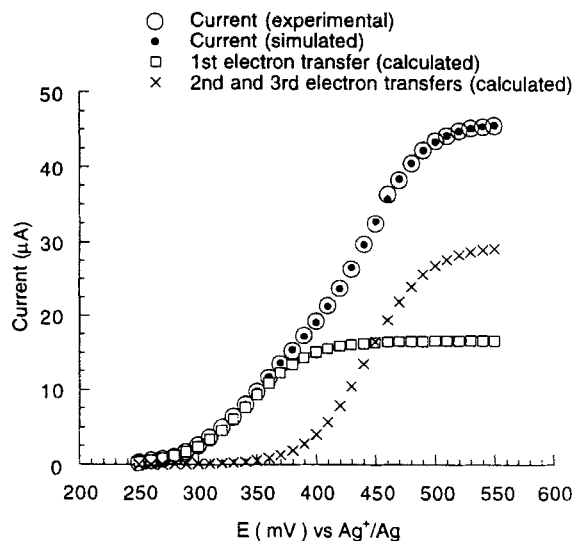


FIGURE 9 A breakdown of the oxidation processes occurring in **2** at 121 rpm.

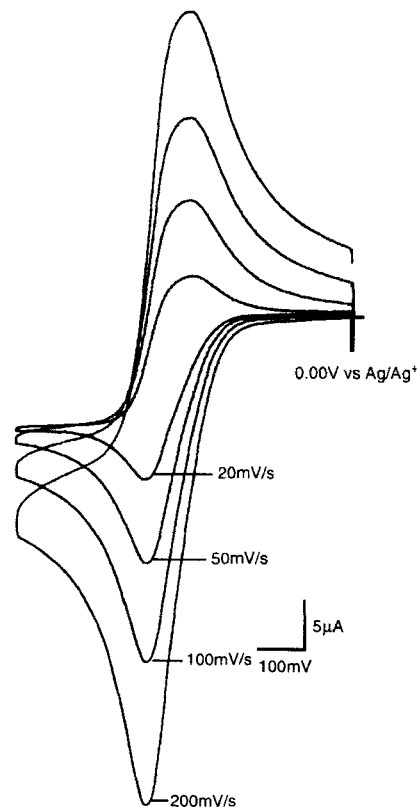


FIGURE 10 The cyclic voltammogram of **2** ( $8 \times 10^{-4}$ M) in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (2:3 v/v). Glassy carbon working electrode,  $\text{Ag}/\text{Ag}^+$  Ref., recorded at various scan rates.

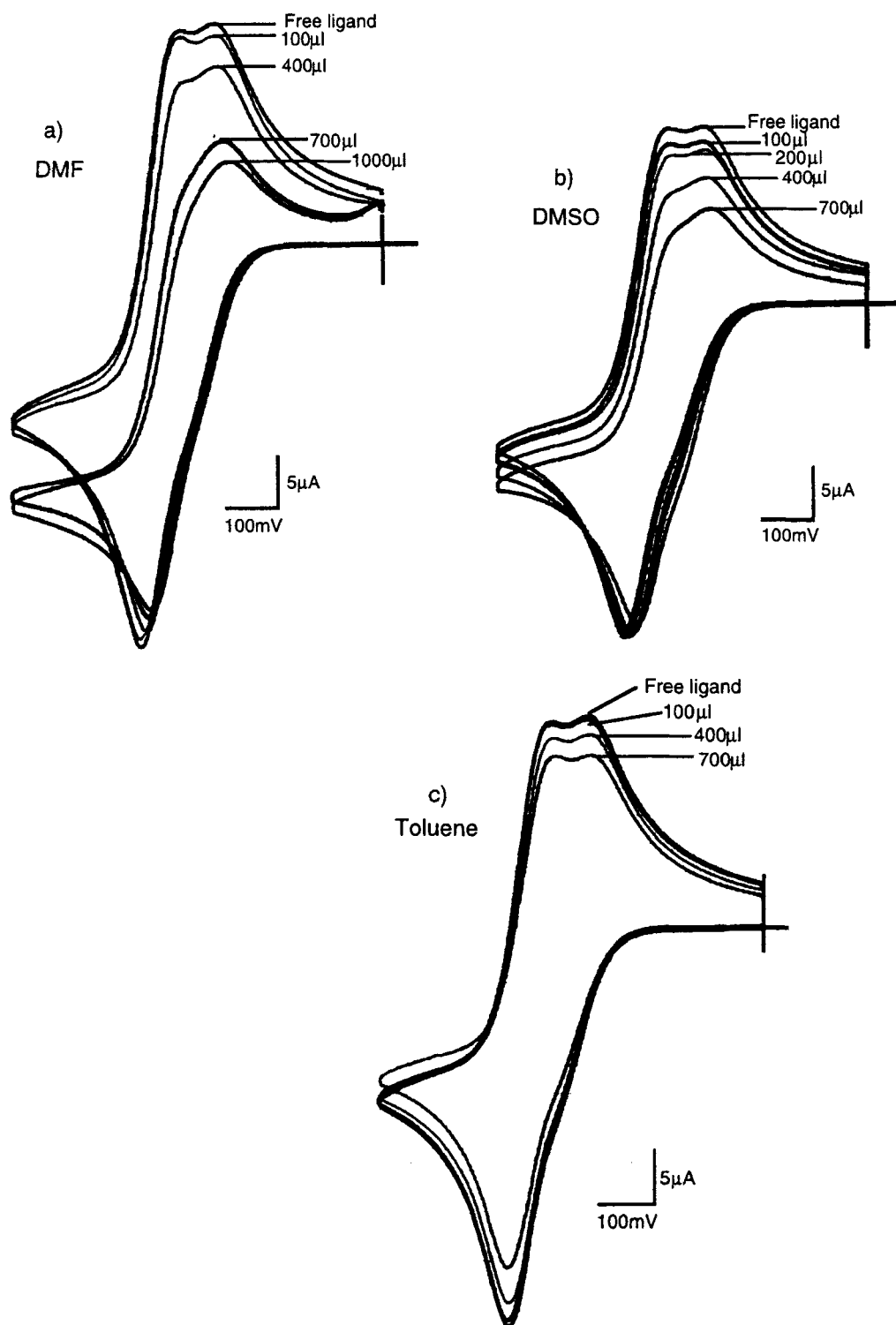


FIGURE 11 Cyclic Voltammograms of **2** ( $5 \times 10^{-4} \text{ M}$ ) in  $\text{CH}_2\text{Cl}_2$  (5 ml) in the presence of  $0.1 \text{ M}$   $\text{Bu}_4\text{NBF}_4$  as supporting electrolyte upon addition of neutral species. Scan rate  $100 \text{ mV s}^{-1}$ , glassy carbon working electrode,  $\text{Ag}/\text{Ag}^+$  reference.

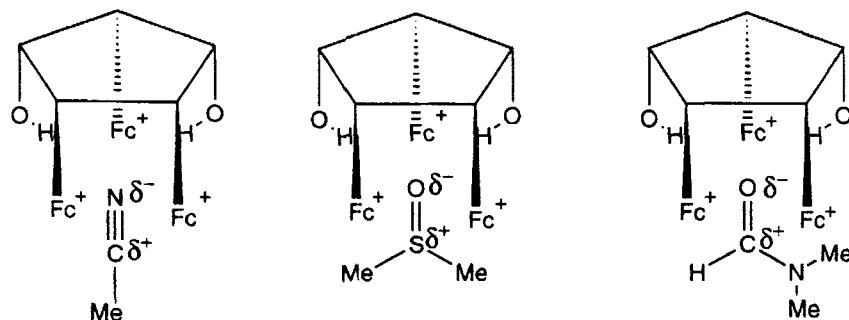


FIGURE 12 Proposed insertion of solvent into the lower rim of **2**.

(Figure 11a) and DMSO ( $\epsilon = 46.7$ ) (Figure 11b) caused the two redox waves of **2** to noticeably merge and shift slightly to more negative potentials. Addition of ethanol ( $\epsilon = 24.3$ ) to electrochemical solutions of (**2**) in  $\text{CH}_2\text{Cl}_2$  caused similar but smaller changes in the CV than either DMSO or DMF as expected due to its relatively smaller  $\epsilon$  value. Square wave voltammetry was used to examine the changes occurring in greater detail. It was found that the second and third electron transfers shift slightly to more negative potential thus becoming equivalent to the first oxidation process.

Compound **2** contains three ferrocene moieties which electrochemically interact with each other. A possible explanation for the peak merging effects and its dependence on the polarity of the added neutral guest species centres on the neutral guest disrupting or interfering with the interaction between the oxidised ferrocenium moieties. The decrease in this interaction upon the addition of the polar, high dielectric constant, guest implies that the polar species is interposing itself between the ferrocenium moieties (Figure 12). The higher the dielectric constant of the interposed guest molecule the greater the shielding perturbation between the ferrocenium centres and consequently the more electrochemically detectable the effect.

## CONCLUSIONS

The preparation and single-crystal X-ray structures of new partially substituted tris-benzoyl-, tris-ferrocenyl- and bis-ferrocenyl *p*-tert-butyl-calix[5]arene esters have been achieved. The structure of the tris-ferrocenyl *p*-tert-butyl-calix[5]arene **2** reveals an ethanol molecule totally included within the cavity of the calixarene. The electrochemical properties of **2** in dichloromethane display a one electron oxidation followed by a separate two electron oxidation corresponding to the redox chemistry of the three ferrocenyl moieties. The addition of neutral polar guest molecules such as DMF and DMSO to dichloromethane electrochemical solutions of **2** causes the two redox waves to significantly merge suggesting **2** is capable of detecting these types of neutral polar organic guest species in relatively non-polar organic media.

## Acknowledgement

We thank the EPSRC for a studentship to P.A.G. and for use of the mass spectrometry service at University College, Swansea, U.K. The University of Reading and the EPSRC are gratefully ac-

knowledge for funding toward the crystallographic Image Plate System.

### Supporting Information Available

Tables of atom coordinates, bond distances and angles, and anisotropic thermal parameters for 1, 2 and 3. Ordering information is given on any current masthead page.

### References

- [1] Böhmer, V. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713.
- [2] Gutsche, C. D.; Iqbal, M. *Org. Synth.* **1990**, *68*, 234.
- [3] Gutsche, C. D.; Dhawan, B.; Leonis, M.; Stewart, D. *Org. Synth.* **1990**, *68*, 238.
- [4] Munch, J. H.; Gutsche, C. D. *Org. Synth.* **1990**, *68*, 243.
- [5] Ninagawa, A.; Matsuda, H. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 65.
- [6] Gutsche, C. D.; Stewart, D. R. *Org. Prep. Proc. Intl.* **1993**, *25*, 137.
- [7] Iwamoto, K.; Araki, K.; Shinkai, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1499.
- [8] Vocanson, F.; Lamartine, R.; Lanteri, P.; Longaray, R.; Gauvrit, J. Y. *New J. Chem.* **1995**, *19*, 825.
- [9] Gutsche, C. D.; Alam, I. *Tetrahedron* **1988**, *44*, 4689.
- [10] Stewart, D. R.; Krawiec, M.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *J. Am. Chem. Soc.* **1995**, *117*, 586.
- [11] Gallagher, J. F.; Ferguson, G. *Acta Crystallogr.* **1994**, *C50*, 73.
- [12] Juneja, R. K.; Robinson, K. D.; Orr, G. W.; Dubois, R. H.; Belmore, K. A.; Atwood, J. L.; Ripmeester, J. A.; Ratcliffe, C. I. *J. Inc. Phenom. Mol. Recognit. Chem.* **1992**, *13*, 93.
- [13] Perrin, M.; Lecocq, S. J. *Inc. Phenom. Mol. Recognit. Chem.* **1991**, *11*, 171.
- [14] Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79.
- [15] Beer, P. D.; Gale, P. A.; Chen, Z. *Adv. Phys. Org. Chem.* **1996**, In the press.
- [16] Saji, T. *Chem. Lett.* **1986**, 275.
- [17] Beer, P. D.; Blackburn, C.; McAleer, J. F.; Sikanyika, H. *Inorg. Chem.* **1990**, *29*, 378.
- [18] Beer, P. D.; Chen, Z.; Goulden, A. J.; Graydon, A.; Stokes, S. E.; Wear, T. J. *Chem. Soc. Chem. Commun.* **1993**, 1834.
- [19] Beer, P. D.; Crane, C. G.; Danks, J. P.; Gale, P. A.; McAleer, J. F. *J. Organometallic Chem.* **1995**, *490*, 143.
- [20] Beer, P. D.; Drew, M. G. B.; Heseck, D.; Jagessar, R. J. *Chem. Soc. Chem. Commun.* **1995**, 1187.
- [21] Beer, P. D.; Keefe, A. D. *J. Organometal. Chem.* **1989**, *375*, C40.
- [22] Beer, P. D.; Heseck, D.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc. Chem. Commun.* **1992**, 270.
- [23] Beer, P. D.; Drew, M. G. B.; Hazlewood, C.; Heseck, D.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc. Chem. Commun.* **1993**, 229.
- [24] Beer, P. D.; Hazlewood, C.; Heseck, D.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc. Dalton Trans.* **1993**, 1327.
- [25] Beer, P. D.; Drew, M. G. B.; Graydon, A. R.; Smith, D. K.; Stokes, S. E. *J. Chem. Soc. Dalton Trans.* **1995**, 403.
- [26] Delgado, M.; Wolf Jr., R. E.; Hartman, J. R.; McCafferty, G.; Yagbasan, R.; Rawle, S. C.; Watkin, D. J.; Cooper, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8983. 931.
- [27] Beer, P. D.; Chen, Z.; Gale, P. A. *Tetrahedron* **1994**, *50*, 2207.
- [28] Beer, P. D.; Chen, Z.; Drew, M. G. B.; Gale, P. A. *J. Chem. Soc. Chem. Commun.* **1994**, 2207.
- [29] Beer, P. D.; Chen, Z.; Drew, M. G. B.; Gale, P. A.; Heath, J. A.; Knubley, R. J.; Ogden, M. I. *J. Inc. Phenom. Mol. Recognit. Chem.* **1994**, *19*, 343.
- [30] Chen, Z.; Gale, P. A.; Heath, J. A.; Beer, P. D. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2931.
- [31] Delgado, M.; Gustowski, D. A.; Yoo, H.; Gokel, G. W.; Echevoyen, L. *J. Am. Chem. Soc.* **1988**, *110*, 119.
- [32] Bethell, D.; Dougherty, G.; Cupertino, D. C. *J. Chem. Soc. Chem. Commun.* **1995**, 675.
- [33] Kaifer, A.; Custowski, D. A.; Echevoyen, L.; Gatto, V. J.; Schultz, R. A.; Cleary, T. P.; Morgan, C. R.; Goli, D. M.; Rios, A. M.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 1958.
- [34] Beer, P. D.; Keefe, A. D. *J. Inc. Phenom.* **1987**, *5*, 499.
- [35] Beer, P. D.; Keefe, A. D.; Drew, M. G. B. *J. Organometal. Chem.* **1988**, *353*, C10.
- [36] Beer, P. D.; Drew, M. G. B.; Ibbotson, A.; Tite, E. L. *J. Chem. Soc. Chem. Commun.* **1988**, 1498.
- [37] Beer, P. D.; Keefe, A. D.; Drew, M. G. B. *J. Organometal. Chem.* **1989**, *378*, 437.
- [38] Beer, P. D.; Tite, E. L.; Drew, M. G. B.; Ibbotson, A. *J. Chem. Soc. Dalton Trans.* **1990**, 2543.
- [39] Beer, P. D.; Keefe, A. D.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc. Dalton Trans.* **1990**, 3675.
- [40] Beer, P. D.; Tite, E. L.; Ibbotson, A. *J. Chem. Soc. Dalton Trans.* **1991**, 1691.
- [41] Beer, P. D.; Chen, Z.; Drew, M. G. B.; Gale, P. A. *J. Chem. Soc. Chem. Commun.* **1995**, 1851.
- [42] Lau, H. H.; Hart, H. J. *Org. Chem.* **1959**, *24*, 280.
- [43] Kabsch, W. *J. Appl. Cryst.* **1988**, *21*, 916.
- [44] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.
- [45] Sheldrick, G. M. *Personal communication* **1993**.
- [46] Coruzzi, M.; Andreetti, G. D.; Bocchi, V.; Pochini, A.; Ungaro, R. *J. Chem. Soc. Perkin Trans. 2* **1982**, 1133.