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## **Mono- and bis-metallocene calix[4]arene hydrophobic receptor molecules; their synthesis, structure and electrochemical properties**

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### **Abstract**

The condensation of ferrocene carbonylchloride (**1**) with *p*-*t*-butylcalix[4]arene (**2**) and calix[4]arene (**3**), and that of cobalticinium carbonylchloride chloride (**6**) with **2**, leads to the corresponding new redox-active bis-ferrocene calix[4]arenes (**4** and **5**) and the mono-substituted cobalticinium analogue **7**. An X-ray diffraction study of **5** shows the calix[4]arene is in a cone conformation. Cyclic voltammetric and coulometric studies in acetonitrile reveal that **4** and **5** undergo reversible two electron oxidations at +0.90 V (versus SCE), suggesting that the two respective ferrocene moieties are oxidised in one step; **7** exhibits a reversible one electron reduction at -0.45 V. Variable temperature <sup>1</sup>H NMR studies show **4**, **5** and **7** to exist in rigid cone conformations in solution. <sup>1</sup>H NMR complexation studies (CD<sub>3</sub>CN) showed that none of the metallocene calix[4]arene receptors form solution host-guest complexes with *t*-butylamine and benzylamine.

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The calixarenes are phenol-formaldehyde cyclic oligomers which possess hydrophobic cavities capable of forming inclusion complexes with a variety of neutral organic molecules and guest metal cations in the solid state [1,2,3]. Some of the water soluble analogues containing dialkylamino [4], sulphonate [5], carboxyl [6], and phosphonic acid [7] groups have recently been shown to form solution host-guest complexes with a variety of aromatic hydrocarbon guest species [4]. Moreover, calixarenes can function as ion carrier molecules in proton-coupled ion transport across organic liquid membranes [8] as well as act as enzyme mimics [5].

Calix[4]arenes in solution are conformationally mobile and can exist in principle in four discrete forms, the 'cone', 'partial cone', '1,2-alternate' and '1,3-alternate'

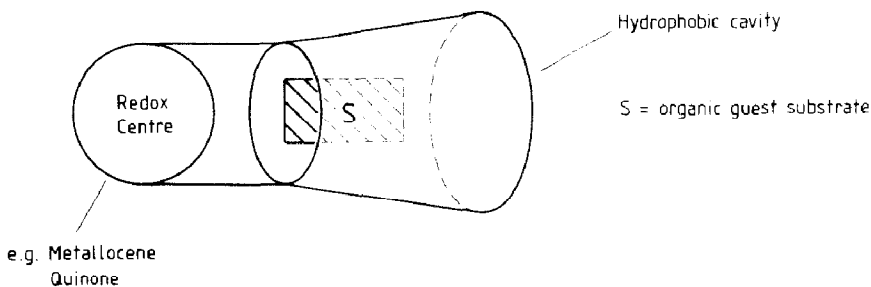


Fig. 1. Depicting the simple concept of electrochemical recognition, the binding of an organic guest in close proximity to redox-active centres.

conformations [1,2]. Above room temperature these conformations are rapidly undergoing interconversion, as shown by dynamic  $^1\text{H}$  NMR investigations [9]. In an effort to synthesise 'rigid' calix[4]arenes in the cone conformation a number of groups have introduced bulky substituents on the phenolic hydroxy groups, and this has met with some success, although the partial cone [10] or 1,3-alternate conformations [11] may occasionally be obtained instead. Recently a series of bridged calix[4]arenes having two opposite phenolic units connected by an aliphatic chain were prepared, and shown to adopt the fixed cone conformation in solution [12] and in the solid state [13].

The incorporation of redox-active centres into a calix[4]arene host molecule could lead ultimately to a new class of molecular sensor and/or catalyst with a well defined rigid molecular cavity capable of electrochemically detecting and catalysing redox reactions on an included organic guest substrate [14] (Fig. 1). With this objective in mind, we have investigated the synthesis and electrochemical properties of three such prototype compounds **4**, **5** and **7**, and determined the crystal structure of **5**. A preliminary account of the work has appeared [15].

## Experimental

Reactions were carried out under dry nitrogen and solvents were distilled prior to use from an appropriate drying agent.  $^1\text{H}$  NMR spectra were recorded at 400 and 270 MHz with tetramethylsilane (TMS) as internal standard. Microanalyses were performed by the Birmingham University Chemistry Department Microanalytical Service. Conductivity measurements [16] were carried out with a PT1-58 digital conductivity meter at concentrations of  $10^{-3}$ – $10^{-4}$  M in dry acetonitrile at 20–22°C. Electrochemical measurements were performed with a PAR 174A polarographic analyser. Cyclic voltammetric measurements were carried out in dry acetonitrile solution containing 0.2 M  $n\text{-Bu}_4\text{NBF}_4$  as supporting electrolyte using a platinum bead working electrode with ferrocene internal reference. Values are quoted relative to the saturated calomel reference electrode (SCE). Positive ion fast atom bombardment mass spectrometry was carried out using a primary atom beam of argon (6 keV) on a Kratos MS80 RF mass spectrometer coupled to a Kratos DS55 data system.

Ferrocene carbonylchloride (**1**) [17], *p*-*t*-butylcalix[4]arene (**2**) [18], calix[4]arene (**3**) [19] and cobalticinium carbonylchloride chloride (**6**) [20] were prepared by published procedures.

**Preparation of pentacyclo[19.3.1.1<sup>3,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,27-dioxa-26,28-diol,5,11,17,23-tetrakis(1,1-dimethyl)-25,27-bis(carbonylferrocene) (4)**

*p*-t-Butylcalix[4]arene (**2**) (0.44 g, 0.59 mmol) and triethylamine (0.6 g, 6 mmol) were dissolved in dry toluene (100 cm<sup>3</sup>) and the solution was warmed to 70 °C. Dropwise addition of a solution of ferrocene carbonylchloride (**1**) (0.59 g, 2.37 mmol) in toluene (50 cm<sup>3</sup>) gave an orange-red reaction mixture which was then stirred for 1 h at 70 °C. After cooling to room temperature the mixture was evaporated to dryness, and the residue was taken up in dichloromethane (100 cm<sup>3</sup>). The solution was washed with water (3 × 100 cm<sup>3</sup>), dried over magnesium sulphate, and subjected to column chromatography (alumina, 100% dichloromethane) to give **4** as a powdery orange solid (0.41 g, 83% yield). M.p. > 280 °C decomp., *m/z* 1072 (*M*<sup>+</sup>); IR: 1733 cm<sup>-1</sup> (C=O str.). (Found: C, 74.4; H, 6.8. C<sub>66</sub>H<sub>72</sub>Fe<sub>2</sub>O<sub>6</sub> calcd.: C, 73.9; H, 6.8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.94 (s, 18H, *t*-butyl-H), 1.28 (s, 18H, *t*-butyl-H), 3.47 (d, *J* 10 Hz, 4H, CH<sub>2</sub>), 4.14 (d, *J* 10 Hz, 4H, CH<sub>2</sub>), 4.40 (s, 10H, FcH), 4.62 (t, *J* 2 Hz, 4H, FcH), 5.25 (t, *J* 2 Hz, 4H, FcH), 5.62 (s, 2H, OH), 7.10 (s, 8H, ArH).

**Preparation of pentacyclo[19.3.1.1<sup>3,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,27-dioxa-26,28-diol,25,27-bis(carbonylferrocene) (5)**

Calix[4]arene (**3**) (0.26 g, 0.62 mmol), triethylamine (0.6 g, 6 mmol) were dissolved in dry toluene (100 ml). Dropwise addition of a solution of ferrocene carbonylchloride (**1**) (0.65 g, 2.62 mmol) in toluene (50 cm<sup>3</sup>) was followed by gentle refluxing of the mixture for 1 h, which gave an orange solution. Removal of the solvent in vacuo and purification by column chromatography (alumina, dichloromethane) gave **5** as orange crystals (0.45 g, 85% yield). M.p. > 280 °C decomp., *m/z* 848 (*M*<sup>+</sup>); IR: 1731 cm<sup>-1</sup> (C=O str.). (Found: C, 71.1; H, 5.0. C<sub>50</sub>H<sub>40</sub>Fe<sub>2</sub>O<sub>6</sub> calcd.: C, 70.8; H, 4.8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.53 (d, *J* 10 Hz, 4H, CH<sub>2</sub>), 4.20 (d, *J* 10 Hz, 4H, CH<sub>2</sub>), 4.38 (s, 10H, FcH), 4.56 (t, *J* 2 Hz, 4H, FcH), 5.30 (t, *J* 2 Hz, 4H, FcH), 6.05 (s, 2H, OH), 6.78–7.15 (m, 12H, ArH).

**Preparation of pentacyclo[19.3.1.1<sup>3,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25-oxa-26,27,28-triol,5,11,17,23-tetrakis(1,1-dimethyl)-25-carbonylcobalticinium hexafluorophosphate (7)**

To a solution of *t*-butylcalix[4]arene (**2**) (0.12 g, 0.16 mmol) and triethylamine (0.10 g, 0.99 mmol) in toluene (100 cm<sup>3</sup>) was added dropwise cobalticinium carbonylchloride chloride (**6**) (1.0 g, 2.65 mmol) in dry acetonitrile (50 cm<sup>3</sup>). The mixture was stirred at room temperature for 24 h, the solvent removed in vacuo, and the yellow-brown residue taken up in dichloromethane (100 cm<sup>3</sup>). The solution was shaken with decolourising charcoal, filtered, shaken with water (3 × 100 cm<sup>3</sup>), dried over magnesium sulphate and evaporated to leave a yellow solid. Column chromatography (Sephadex LH20, acetonitrile) followed by addition of excess ammonium hexafluorophosphate and recrystallisation from dichloromethane/hexane mixture gave **7** as yellow crystals (0.04 g, 25% yield). M.p. > 280 °C; *m/z* 863 (*M* – PF<sub>6</sub>)<sup>+</sup>; IR: 1742 cm<sup>-1</sup> (C=O str.). <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ: 1.18 (m, 36H,

t-butyl-H), 3.48 (d,  $J$  12 Hz, 2H, CH<sub>2</sub>), 3.53 (d,  $J$  12 Hz, 2H, CH<sub>2</sub>), 4.07 (d,  $J$  14 Hz, 2H, CH<sub>2</sub>), 4.22 (d,  $J$  14 Hz, 2H, CH<sub>2</sub>), 5.95 (s, 5H, Cp<sub>2</sub>Co<sup>+</sup>), 6.02 (t,  $J$  2 Hz, 2H, Cp<sub>2</sub>Co<sup>+</sup>), 6.47 (t,  $J$  2 Hz, 2H, Cp<sub>2</sub>Co<sup>+</sup>), 7.13 (d,  $J$  2 Hz, 2H, ArH), 7.14 (s, 2H, ArH), 7.23 (d,  $J$  2 Hz, 2H, ArH), 7.26 (s, 2H, ArH). Conductivity in acetonitrile,  $\Lambda$  148  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, a typical value for a 1/1 electrolyte.

*Crystal data.* [Fe<sub>2</sub>C<sub>50</sub>O<sub>6</sub>H<sub>40</sub>], 0.5CH<sub>2</sub>Cl<sub>2</sub>,  $M = 890.46$ , orthorhombic,  $a$  12.873(13),  $b$  28.964(22),  $c$  22.998(23) Å,  $U$  8574.9 Å<sup>3</sup>,  $F(000) = 3688$ ,  $d_m$  1.38 g cm<sup>-3</sup>,  $d_c$  1.38 g cm<sup>-3</sup>,  $Z = 8$ , Mo- $K_\alpha$  radiation ( $\lambda$  0.7107 Å),  $\mu(\text{Mo-}K_\alpha)$  8.1 cm<sup>-1</sup>, Spacegroup *Pbca*.

A crystal of approximate size 0.25 × 0.3 × 0.3 mm was set up to rotate about the  $a$  axis on a Stoe Stadi2 diffractometer and data were collected via variable width  $\omega$  scan. Background counts were for 20 s and a scan rate of 0.0333°/s was applied to a width of (1.5 + sin  $\mu$ /tan  $\theta$ ). 6668 independent reflections were measured with a  $2\theta$  maximum of 50° of which 1821 with  $I > 2\sigma(I)$  were used in subsequent refinement. The structure was determined by the heavy atom method. The iron

Table 1

Atomic co-ordinates ( $\times 10^4$ ) with estimated standard deviations (e.s.d.'s) in parentheses

Atom	$x$	$y$	$z$	Atom	$x$	$y$	$z$
Fe(1)	4855(1)	2040(1)	3322(1)	O(37)	4405(8)	3633(4)	5539(5)
Fe(2)	4844(2)	2350(1)	5773(1)	C(38)	4322(10)	3398(5)	6050(7)
Cp(11)	3361(9)	2173(4)	3061(6)	O(39)	4466(8)	3569(4)	6515(5)
Cp(12)	3373(11)	1790(6)	3432(6)	Cp(31)	3983(9)	2923(5)	5969(6)
Cp(13)	3737(13)	1945(6)	3978(8)	Cp(32)	3614(9)	2704(4)	5452(5)
Cp(14)	4102(12)	2412(6)	3946(7)	Cp(33)	3320(11)	2249(5)	5604(6)
Cp(15)	3826(9)	2566(5)	3338(6)	Cp(34)	3542(14)	2188(7)	6170(8)
C(6)	3947(9)	3013(4)	3083(6)	Cp(35)	3919(10)	2600(5)	6444(7)
O(7)	3781(9)	3107(4)	2583(5)	C(41)	2643(12)	4253(6)	5494(7)
O(8)	4271(8)	3327(4)	3453(4)	C(51)	2203(10)	4361(5)	4910(6)
C(11)	4456(11)	3780(6)	3249(6)	C(52)	2514(11)	4114(5)	4416(7)
C(12)	5455(10)	3952(5)	3159(6)	C(53)	2146(11)	4228(5)	3877(7)
C(13)	5679(17)	4371(7)	2943(9)	C(54)	1408(16)	4569(7)	3842(10)
C(14)	4909(12)	4660(6)	2844(7)	C(55)	1106(16)	4784(7)	4275(9)
C(15)	3874(13)	4555(6)	2922(7)	C(56)	1448(14)	4703(7)	4843(9)
C(16)	3654(10)	4094(5)	3154(7)	O(57)	3257(7)	3750(4)	4477(4)
C(17)	6390(15)	3639(7)	3329(8)	C(58)	2527(11)	3942(5)	3322(6)
C(21)	6947(13)	3837(6)	3872(8)	Cp(21)	6424(14)	2067(7)	3450(8)
C(22)	7935(14)	4019(6)	3818(9)	Cp(22)	6212(15)	2284(8)	2925(9)
C(23)	8371(16)	4177(7)	4354(9)	Cp(23)	5779(13)	1899(6)	2603(8)
C(24)	7983(13)	4136(6)	4877(9)	Cp(24)	5692(16)	1515(8)	2962(9)
C(25)	7047(12)	3947(6)	4953(7)	Cp(25)	6086(19)	1643(9)	3483(11)
C(26)	6506(13)	3773(6)	4462(8)	Cp(41)	6416(15)	2540(7)	5742(9)
O(27)	5574(7)	3556(4)	4482(4)	Cp(42)	6041(15)	2378(7)	5223(9)
C(28)	6547(12)	3891(6)	5526(7)	Cp(43)	6204(16)	2163(7)	6167(10)
C(31)	5616(12)	4240(6)	5613(7)	Cp(44)	5777(15)	1757(8)	5801(9)
C(32)	5795(16)	4733(7)	5640(8)	Cp(45)	5740(17)	1944(8)	5288(10)
C(33)	4958(13)	5039(7)	5724(7)	Cl(1)	3291(18)	4422(9)	7825(11)
C(34)	3953(13)	4879(6)	5657(7)	Cl(2)	1919(18)	4650(8)	6924(11)
C(35)	3785(15)	4403(8)	5590(8)	C(1)	2860(27)	4383(13)	7125(15)
C(36)	4565(11)	4113(6)	5571(7)				

Table 2

Selected bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

<i>Bond lengths (Å)</i>			
Fe(1)–Cp(11)	2.052(12)	Cp(11)–Cp(12)	1.401(18)
Fe(1)–Cp(12)	2.055(15)	Cp(11)–Cp(15)	1.435(17)
Fe(1)–Cp(13)	2.103(17)	Cp(12)–Cp(13)	1.414(20)
Fe(1)–Cp(14)	2.053(16)	Cp(13)–Cp(14)	1.458(21)
Fe(1)–Cp(15)	2.021(13)	Cp(14)–Cp(15)	1.503(19)
Fe(1)–Cp(21)	2.043(18)	Cp(15)–C(6)	1.429(17)
Fe(1)–Cp(22)	2.096(21)	C(6)–O(7)	1.202(14)
Fe(1)–Cp(23)	2.077(17)	C(6)–O(8)	1.313(14)
Fe(1)–Cp(24)	2.039(20)	O(8)–C(11)	1.414(17)
Fe(1)–Cp(25)	1.992(24)	C(11)–C(12)	1.394(19)
Fe(2)–Cp(31)	2.045(14)	C(11)–C(16)	1.392(19)
Fe(2)–Cp(32)	2.025(12)	C(12)–C(13)	1.345(22)
Fe(2)–Cp(33)	2.021(14)	C(12)–C(17)	1.555(22)
Fe(2)–Cp(34)	1.965(19)	C(13)–C(14)	1.317(23)
Fe(2)–Cp(35)	2.080(15)	C(14)–C(15)	1.378(21)
Fe(2)–Cp(41)	2.098(20)	C(15)–C(16)	1.467(19)
Fe(2)–Cp(42)	1.996(19)	C(16)–C(58)	1.565(19)
Fe(2)–Cp(43)	2.044(21)	C(17)–C(21)	1.549(23)
Fe(2)–Cp(44)	2.098(22)	C(21)–C(22)	1.382(22)
Fe(2)–Cp(45)	1.990(22)	C(21)–C(26)	1.482(22)
		C(22)–C(23)	1.429(24)
		C(23)–C(24)	1.307(24)
		C(24)–C(25)	1.336(20)
		C(25)–C(26)	1.419(21)
		C(25)–C(28)	1.476(21)
<i>Bond angles (°)</i>			
Cp(11)–Fe(1)–Cp(12)	39.9(5)	O(8)–C(11)–C(16)	122.2(13)
Cp(11)–Fe(1)–Cp(13)	66.0(6)	C(12)–C(11)–C(16)	115.4(13)
Cp(12)–Fe(1)–Cp(13)	39.7(5)	C(11)–C(12)–C(13)	125.1(15)
Cp(11)–Fe(1)–Cp(14)	70.2(5)	C(11)–C(12)–C(17)	118.0(13)
Cp(12)–Fe(1)–Cp(14)	70.4(6)	C(13)–C(12)–C(17)	116.9(15)
Cp(13)–Fe(1)–Cp(14)	41.0(5)	C(12)–C(13)–C(14)	118.4(19)
Cp(11)–Fe(1)–Cp(15)	41.26(48)	C(13)–C(14)–C(15)	124.5(19)
Cp(12)–Fe(1)–Cp(15)	69.8(6)	C(14)–C(15)–C(16)	115.8(15)
Cp(13)–Fe(1)–Cp(15)	68.7(6)	C(11)–C(16)–C(15)	120.6(13)
Cp(14)–Fe(1)–Cp(15)	43.3(5)	C(11)–C(16)–C(58)	117.8(13)
Cp(11)–Fe(1)–Cp(21)	164.1(6)	C(15)–C(16)–C(58)	121.6(12)
Cp(12)–Fe(1)–Cp(21)	155.9(7)	C(12)–C(17)–C(21)	110.2(14)
Cp(13)–Fe(1)–Cp(21)	125.3(6)	C(17)–C(21)–C(22)	119.7(17)
		C(17)–C(21)–C(26)	121.0(15)
Cp(14)–Fe(1)–Cp(21)	110.2(6)	C(22)–C(21)–C(26)	118.8(16)
Cp(15)–Fe(1)–Cp(21)	128.1(7)	C(21)–C(22)–C(23)	114.0(18)
Cp(11)–Fe(1)–Cp(22)	126.2(7)	C(22)–C(23)–C(24)	127.9(20)
Cp(12)–Fe(1)–Cp(22)	161.2(7)	C(23)–C(24)–C(25)	120.1(19)
Cp(13)–Fe(1)–Cp(22)	158.0(7)	C(24)–C(25)–C(26)	119.0(16)
Cp(14)–Fe(1)–Cp(22)	121.1(7)	C(24)–C(25)–C(28)	123.7(16)
Cp(15)–Fe(1)–Cp(22)	107.4(7)	C(26)–C(25)–C(28)	117.3(14)
Cp(21)–Fe(1)–Cp(22)	39.2(6)	C(21)–C(26)–C(25)	119.8(15)
Cp(11)–Fe(1)–Cp(23)	109.9(6)	C(21)–C(26)–O(7)	115.4(14)
Cp(12)–Fe(1)–Cp(23)	124.1(6)	C(25)–C(26)–O(7)	124.8(15)
Cp(13)–Fe(1)–Cp(23)	159.6(6)	C(25)–C(28)–C(31)	111.9(13)
Cp(14)–Fe(1)–Cp(23)	158.7(6)		
Cp(15)–Fe(1)–Cp(23)	122.6(6)	Cp(22)–Cp(21)–Cp(25)	114.3(21)

Table 2 (continued)

<i>Bond angles (°)</i>			
Cp(21)–Fe(1)–Cp(23)	63.6(6)	Fe(1)–Cp(22)–Cp(21)	68.4(11)
Cp(22)–Fe(1)–Cp(23)	40.7(6)	Fe(1)–Cp(22)–Cp(23)	69.0(10)
Cp(11)–Fe(1)–Cp(24)	121.2(7)	Cp(21)–Cp(22)–Cp(23)	99.8(18)
Cp(12)–Fe(1)–Cp(24)	106.2(7)	Fe(1)–Cp(23)–Cp(22)	70.4(10)
Cp(13)–Fe(1)–Cp(24)	123.8(7)	Fe(1)–Cp(23)–Cp(24)	68.8(10)
Cp(14)–Fe(1)–Cp(24)	159.0(7)	Cp(22)–Cp(23)–Cp(24)	110.1(18)
Cp(15)–Fe(1)–Cp(24)	156.5(7)	Fe(1)–Cp(24)–Cp(23)	71.7(11)
Cp(21)–Fe(1)–Cp(24)	64.2(8)	Fe(1)–Cp(24)–Cp(25)	68.5(14)
Cp(22)–Fe(1)–Cp(24)	68.5(8)	Cp(23)–Cp(24)–Cp(25)	106.0(22)
Cp(23)–Fe(1)–Cp(24)	39.4(6)	Fe(1)–Cp(25)–Cp(21)	73.3(14)
Cp(11)–Fe(1)–Cp(25)	155.4(8)	Fe(1)–Cp(25)–Cp(24)	72.3(14)
Cp(12)–Fe(1)–Cp(25)	120.8(8)	Cp(21)–Cp(25)–Cp(24)	109.4(24)
Cp(13)–Fe(1)–Cp(25)	109.6(8)	Fe(2)–Cp(41)–Cp(42)	66.4(11)
Cp(14)–Fe(1)–Cp(25)	123.7(8)	Fe(2)–Cp(41)–Cp(43)	67.0(11)
Cp(15)–Fe(1)–Cp(25)	162.5(8)	Cp(42)–Cp(41)–Cp(43)	104.9(19)
Cp(21)–Fe(1)–Cp(25)	37.7(7)	Fe(2)–Cp(42)–Cp(41)	74.6(12)
Cp(22)–Fe(1)–Cp(25)	67.2(9)	Fe(2)–Cp(42)–Cp(45)	70.3(12)
Cp(23)–Fe(1)–Cp(25)	65.1(8)	Cp(41)–Cp(42)–Cp(45)	109.2(21)
Cp(24)–Fe(1)–Cp(25)	39.2(7)	Fe(2)–Cp(43)–Cp(41)	70.9(11)
Cp(15)–C(6)–O(7)	125.4(12)	Fe(2)–Cp(43)–Cp(44)	69.9(11)
Cp(15)–C(6)–O(8)	113.4(11)	Cp(41)–Cp(43)–Cp(44)	105.4(18)
O(7)–C(6)–O(8)	121.2(13)	Fe(2)–Cp(44)–Cp(43)	66.2(11)
C(6)–O(8)–C(11)	118.9(11)	Fe(2)–Cp(44)–Cp(45)	67.0(13)
O(8)–C(11)–C(12)	122.4(13)	Cp(43)–Cp(44)–Cp(45)	100.9(21)
		Fe(2)–Cp(45)–Cp(42)	70.8(13)
		Fe(2)–Cp(45)–Cp(44)	76.1(14)
		Cp(42)–Cp(45)–Cp(44)	119.2(24)
		Cl(1)–C(1)–Cl(2)	121.0(26)

Table 3

Least squares planes calculations for the calix[4]arene atoms within the planes are coplanar within experimental error. Deviations (Å) of selected non-contributing atoms from the planes are given

Plane 1 Cp(11)–Cp(15) inclusive

Deviations C(6) – 0.04, O(7) 0.03, O(8) – 0.18, C(11) – 0.19

Plane 2 Cp(21)–Cp(25) inclusive

Deviations C(38) – 0.04, O(37) 0.09, O(39) – 0.25, C(36) – 0.14

Plane 3 Cp(31)–Cp(35) inclusive Plane 4 Cp(41)–Cp(45) inclusive

Plane 5 C(11)–C(16) inclusive

Deviations O(8) – 0.05, C(17) 0.15

Plane 6 C(21)–C(26) inclusive

Deviations C(17) – 0.04, O(27) – 0.08, C(28) 0.01

Plane 7 C(31)–C(36) inclusive

Deviations C(28) – 0.09, O(37) 0.09

Plane 8 C(41)–C(46) inclusive

Deviations C(41) 0.05, O(57) – 0.05, C(58) – 0.02

Angles (°)

between Cp rings bonded to the same iron atom

1 and 2 0.9; 3 and 4 2.5

between Cp rings bonded to different iron atoms

1 and 3 5.5; 1 and 4 7.4; 2 and 3 5.6; 2 and 4 7.3

Angles between Cp rings and adjacent phenyl rings

1 and 5 70.8; 3 and 7 78.5

Angles between phenyl rings

5 and 6 79.4, 5 and 7 26.6, 5 and 8 81.4

6 and 7 79.1, 6 and 8 72.5, 7 and 8 77.4

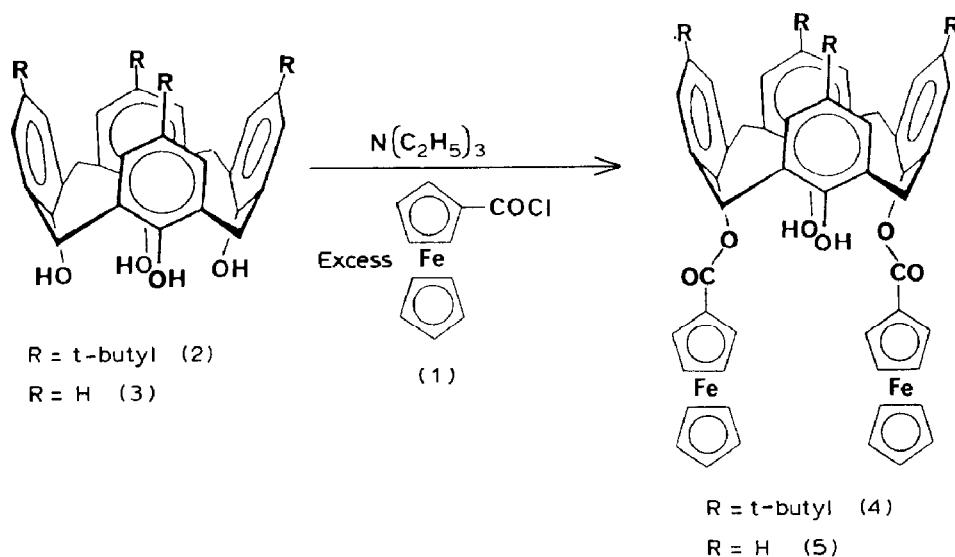
atoms were given anisotropic thermal parameters but the remaining atoms were refined isotropically. The hydrogen atoms bonded to carbon were placed in calculated positions with fixed thermal parameters. The two hydrogen atoms bonded to oxygen could not be located. The dichloromethane molecule was given half-occupancy. The structure was given a weighting scheme in the form  $w = 1/[\sigma^2(F) + 0.003F^2]$ . The final  $R$  value was 0.071 ( $R_w = 0.075$ ). In the final cycle of refinement all shift/error ratios were  $< 0.3\sigma$ . The final difference Fourier map showed no peaks greater than  $1.5 \text{ eA}^{-3}$ .

Calculations were carried out by use of SHELX 76° and some of our own programs on the Amdahl V7 computer at the University of Reading. Positional parameters are given in Table 1, bond lengths and bond angles in Table 2, and details of least squares planes in Table 3. Lists of structure factors, anisotropic temperature factors, and hydrogen atom coordinates are available from the authors.

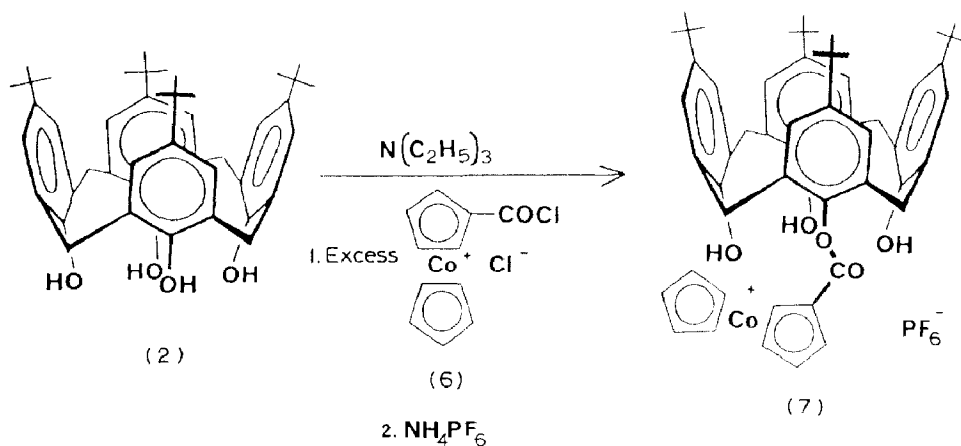
## Results and discussion

### Syntheses

The reaction of an excess of ferrocene carbonylchloride (**1**) [17] with *p*-*t*-butylcalix[4]arene (**2**) [18] and calix[4]arene (**3**) [19] in the presence of triethylamine gave, after column chromatography (alumina,  $\text{CH}_2\text{Cl}_2$ ), the respective regioselective 1,3-disubstituted bis-ferrocene calix[4]arenes (**4**) (83% yield, decomposes  $> 280^\circ\text{C}$ , orange crystals) and **5** (70% yield, decomposes  $> 280^\circ\text{C}$ , orange crystals) (Scheme 1). It is noteworthy that no evidence for the presence of tris- and tetra-substituted ferrocenylcalix[4]arene isomers was found, suggesting that adjacent 1,2-*cis* substitution is sterically unfavourable. Indeed, related 1,3-disubstituted dimethyl ether [11], crown ether [21] and spherand [22] calix[4]arenes have also been regioselectively synthesised. In an analogous synthetic procedure the condensation of an excess of



Scheme 1



Scheme 2

cobalticinium carbonylchloride chloride (6) [20] and *p*-*t*-butylcalix[4]arene (2) [18] followed by column chromatography (sephadex LH20, acetonitrile) and excess ammonium hexafluorophosphate gave the monosubstituted cobalticinium calix[4]arene hexafluorophosphate salt (7) as a yellow crystalline solid. Scheme 2. No other products, such as the expected bis 1,3-disubstituted analogue, were isolated. Sterically, cobalticinium and ferrocene moieties are of very similar size and molecular dimensions [23], which implies that it is the positive charge of the former that is discouraging and repelling the attachment of a second cobalticinium fragment to the calix[4]arene. The structures of all these new air-stable compounds were characterised by elemental analyses, fast atom bombardment mass spectrometry (FABMS) and <sup>1</sup>H NMR spectroscopy (see Experimental), and in the case of 7 conductivity measurements [16] in acetonitrile ( $\Lambda$  148  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) which is within the range of values for 1/1 electrolytes.

#### *X-Ray structural investigation of 5*

Orange crystals of 5 suitable for X-ray structural investigations were obtained from a dichloromethane/hexane mixture. The structure consists of discrete molecules of the calix[4]arene together with a molecule of dichloromethane solvent with half-occupancy. The structure of the calix[4]arene is shown by itself in Fig. 2 but with the dichloromethane in Fig. 3. There are three contacts between chlorine atoms and hydrogen atoms of the calix[4]arene less than 3.0 Å. The positions of the carbon atoms suggest that there are weak hydrogen bonds of the type C-H...Cl. Distances are H(411)...Cl(2) ( $x, y, z$ ) 2.76 (C(41)...Cl(2) 3.60 Å), H(15)...Cl(2) ( $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$ ) 2.70 (C(15)...Cl(2) 3.40 Å), H(12)...Cl(1) ( $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ) 2.88 (Cp(12)...Cl(1) 3.78 Å).

These three contacts between the calix[4]arene and different dichloromethanes are illustrated in Fig. 3. As is apparent from Fig. 3, the dichloromethane is not located within the cavity of the calix[4]arene. This molecule (Fig. 2 and 3) has an irregular cone conformation; the angle between the phenyl rings attached to O(8) and O(37) is 26.6° and between those attached to O(27) and O(57) 72.5°.

There are several close intramolecular contacts between the four oxygen atoms (O(8), O(37), O(27), O(57)); five (of the six) O...O distances are between 2.87 and



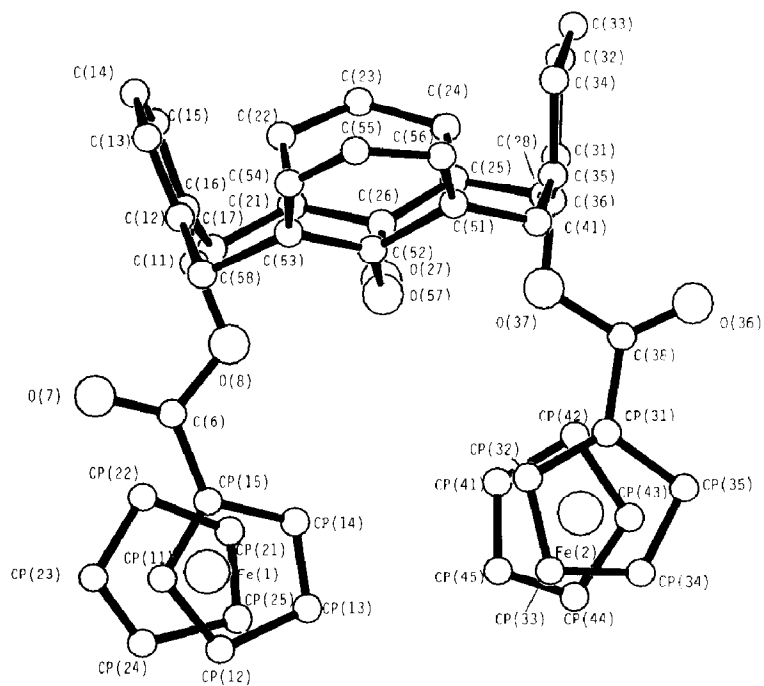


Fig. 2. Structure of **5**.

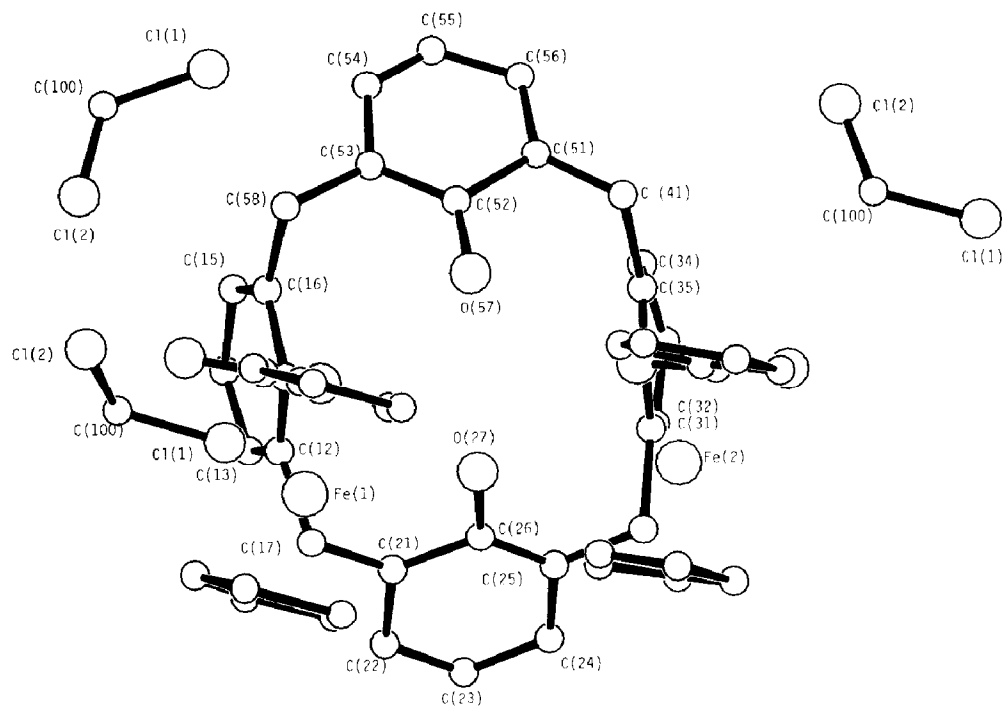


Fig. 3. Structure of **5** with dichloromethane.

3.04 Å; [viz. O(8)...O(27) 2.98, O(8)...O(57) 2.96, O(27)...O(37) 2.87, O(27)...O(57) 3.04, O(37)...O(57) 2.87], the exception O(8)...O(37) being 4.88 Å. These values of the O...O distances and the C–O...O angles indicate that the two hydrogen atoms on O(27) and O(57) could both be hydrogen bonded to either O(8) or O(37). The hydrogens were not located in a difference Fourier map and each may be disordered between two sites. The proposed hydrogen bond formation may impose severe restrictions on possible guests within the cavity. There are no significant intermolecular contacts between calix[4]arene molecules.

The geometry of the dicyclopentadieneiron moieties are as expected. The cyclopentadiene groups are approximately eclipsed (Fig. 2). Fe–C distances range from 1.965(19)–2.103(22) Å. The cyclopentadiene rings are nearly parallel to each other (all angles of intersection less than 10°, see Table 3). Rings 1 and 3 make angles of 70.8, 78.5° with the phenyl rings to which they are attached via the O–C(=O) group. No doubt these large twists are due to the steric constraints of the molecule.

#### *Electrochemical studies*

The electrochemical properties of **4**, **5** and **7** were investigated in acetonitrile solution by cyclic voltammetry and coulometry. The compounds **4** and **5** exhibits reversible two electron oxidations at +0.90 V (versus standard calomel electrode SCE) which suggests that the respective two ferrocene moieties present in both receptors become oxidised in one step. The cobalticinium receptor **7** exhibits a reversible one electron reduction at –0.45 V (SCE).

#### *<sup>1</sup>H NMR solution complexation studies*

Gutsche and co-workers have recently demonstrated by use of high field <sup>1</sup>H NMR spectroscopy the solution complexation of t-butylamine by allyl calix[4]arene, the changes in the chemical shift values of both the calixarene host and the amine guest in acetonitrile being monitored [24]. Initially variable temperature <sup>1</sup>H NMR studies over the temperature range +50 to –50 °C (CD<sub>3</sub>CN) were used to establish whether the room temperature solution conformation of the respective metallocene calix[4]arene was favourable for possible guest inclusion.

No change in the respective methylene AB pair of doublet absorptions of **4**, **5** and **7** were observed, suggesting that a ‘rigid’ cone cavity conformation, similar to the solid state structure of **5**, is adopted by these host molecules in solution.

Addition of stoichiometric amounts of t-butylamine and benzylamine to room temperature acetonitrile solutions of **4**, **5** and **7** had little effect ( $\Delta\delta < 0.05$  ppm) on the respective <sup>1</sup>H chemical shifts for either the calix[4]arene host or amine guest, implying that there is no host-guest complexation under these conditions. These observations are disappointing, and in the case of **4** and **7** may reflect unfavourable steric interactions between t-butyl groups of host and t-butyl or benzyl methylene groups of the amine guests.

Future work is being directed at synthesising water soluble metallocene calixarenes in an effort to utilise the ‘hydrophobic effect’ [25] as the driving force for inclusion of organic guest species.

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