Dimer and Trimer Calix[4]arenes containing Multiple Metallocene Redox-active Centres. Single-crystal X-Ray Structure of a Bis(ferrocene)-Bis(p-t-butylcalix[4]-arene) Hydrophobic Host Molecule‡

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The condensation of 1,1'-bis(chlorocarbonyl)ferrocene (1) and 1,1'-bis(chlorocarbonyl)ruthenocene (2) with p-t-butylcalix[4]arene gave the respective new redox-active metallocene–calix[4]arene dimers (3) and (4). An X-ray diffraction study of (3) shows the two calix[4]arenes to be in cone conformations with a metallocene metal atom transannular Fe ⋯ Fe separation of 5.9 Å. The reaction of 1,1'-bis(chlorocarbonyl)cobaltocenium chloride (5) and p-t-butylcalix[4]arene gave a cobaltocenium–bis(p-t-butylcalix[4]arene) dimer (6). A ferrocene–calix[4]arene trimer (7) was isolated from the reaction of (1) and calix[4]arene. Solution variable-temperature ¹H n.m.r. studies show (3) and (4) to be conformationally mobile with respective low-temperature spectra consistent with either partial cone conformations or *cis* orientation of respective metallocene carbonyl ester moieties. Cyclic voltammetric and coulometric studies in acetonitrile reveal that compound (3) undergoes a reversible two-electron oxidation at +1.24V (*versus* saturated calomel electrode), suggesting the two respective ferrocene moieties are oxidised in one step. Proton n.m.r. complexation studies showed (3) to be incapable of forming a solution host–guest complex with t-butylamine.

The calixarenes are a family of synthetic macrocyclic receptors consisting of cyclic arrays of phenol moieties linked by methylene groups.[1] They possess hydrophobic cavities capable of including molecular guest species in the solid state.[1-3] 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] Additionally, 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]

We have recently initiated a synthetic programme aimed at the incorporation of multiple redox-active centres into calixarene host structural frameworks[9-14] in an effort to produce a new class of molecular sensor and/or catalyst with a well defined rigid molecular cavity able electrochemically to recognise, respond, and catalyse redox reactions on an included organic guest substrate.[15] This paper reports the synthesis of novel di- and tri-topic metallocene calixarene host molecules including the single crystal structure of one as determined by X-ray diffraction analysis. A preliminary account of the work has appeared.[16]

Experimental

Reactions were carried out under dry nitrogen and solvents were distilled prior to use from an appropriate drying agent. Proton n.m.r. spectra were recorded at 400 and 270 MHz with tetramethylsilane as internal standard. Microanalyses were performed by the Birmingham University Chemistry Department Microanalytical Service. Electrochemical measurements were performed with a PAR 174A polarographic analyser. Cyclic voltammetric measurements were carried out in dry acetonitrile solution containing 0.2 mol dm⁻³ NBuⁿ₄BF₄ as supporting electrolyte using a platinum-bead working electrode with ferrocene internal reference. Values are quoted relative to

the saturated calomel reference electrode (s.c.e.). Positive-ion fast atom bombardment mass spectrometry was carried out using a primary atom beam of argon (6 keV, *ca.* 4.6 × 10⁻¹⁶ J) on a Kratos MS80 RF mass spectrometer coupled to a Kratos DS55 data system. 1,1'-Bis(chlorocarbonyl)ferrocene (1),[17] 1,1'-bis(chlorocarbonyl)ruthenocene (2),[17] 1,1'-bis(chlorocarbonyl)-cobaltocenium chloride (5),[18] p-t-butylcalix[4]arene,[19] and calix[4]arene[20] were prepared by published procedures.

Compound (3).—p-t-Butylcalix[4]arene (1.00 g, 1.35 mmol) and triethylamine (0.50 g, 4.95 mmol) were dissolved in dry toluene (500 cm³) and the solution refluxed under nitrogen. Dropwise addition of a solution of 1,1-bis(chlorocarbonyl)-ferrocene (0.43 g, 1.38 mmol) in toluene (100 cm³) over a period of 1 h gave an orange-red reaction mixture which was allowed to cool to room temperature and stirred for an additional 24 h. The solvent was removed *in vacuo* and the residue taken up in dichloromethane (100 cm³). The solution was washed with water (3 × 100 cm³), dried over magnesium sulphate, and subjected to column chromatography (alumina, 98% dichloromethane, 2% methanol) to give compound (3) as an orange solid (0.77 g, 64% yield), m.p. >280 °C (decomp.), m/z 1 773 ([M + H]⁺), 1 745 cm⁻¹ (C=O str.) (Found: C, 75.9; H, 7.3. Calc. for $C_{112}H_{124}Fe_2O_{12}$: C, 75.8; H, 7.0%). ¹H N.m.r. (CDCl₃): δ 0.94 (s, 36 H), 1.31 (s, 36 H), 3.47 (d, *J* 20, 8 H), 4.06 (d, *J* 20, 8 H), 4.99 (t, *J* 2, 8 H), 5.48 (t, *J* 2 Hz, 8 H), 6.79 (s, 8 H), and 7.12 (s, 8 H).

An analogous procedure was used to prepare compound (4) using 1,1'-bis(chlorocarbonyl)ruthenocene (2) instead of (1):

47% yield, m.p. >280 °C (decomp.), m/z 1 863 ($[M + H]^+$), 1 745 cm^{-1} (C=O str.) (Found: C, 71.9; H, 6.5. Calc. for $C_{112}H_{124}O_{12}Ru_2$: C, 72.2; H, 6.7%). ^{1}H N.m.r. (CDCl$_3$): δ 0.96 (s, 36 H), 1.36 (s, 36 H), 3.45 (d, J 20, 8 H), 3.99 (d, J 20 Hz, 8 H), 5.07 (s, 8 H), 5.66 (s, 8 H), 6.77 (s, 8 H), and 7.12 (s, 8 H).

Compound (6).—To a solution of *p*-t-butylcalix[4]arene (0.57 g, 0.77 mmol) and triethylamine (0.48 g, 4.75 mmol) in toluene (100 cm^3) was added dropwise 1,1'-bis(chlorocarbonyl)cobaltocenium chloride (6) (1.00 g, 2.37 mmol) in dry acetonitrile (40 cm^3). The mixture was stirred at room temperature for 24 h, the solvent removed *in vacuo*, and the yellow-brown residue dissolved in dichloromethane (50 cm^3). The solution was shaken with decolourising charcoal, filtered, and evaporated to leave a yellow-brown solid. Column chromatography (Sephadex LH20, 50% water : 50% acetonitrile, followed by 100% acetone) followed by addition of excess of ammonium hexafluorophosphate gave compound (6) as a light brown-yellow powder (0.16 g, 12% yield), m.p. >280 °C (decomp.), m/z 1 536 ($[M - PF_6]^+$); 1 740 cm^{-1} (C=O str.). ^{1}H N.m.r. (CD$_3$CN): δ 1.06 (s, 36 H), 1.24 (s, 36 H), 4.53 (d, J 10, 8 H), 5.01 (8 H, d, J 10), 6.78 (s, 8 H), 6.99 (s, 4 H), 7.13 (d, J 2, 4 H), 7.22 (s, 4 H), and 7.28 (d, J 2 Hz, 4 H).

The procedure for preparing compound (3) was used to synthesise (7) using calix[4]arene instead of *p*-t-butylcalix[4]arene: 34% yield, m.p. >280 °C (decomp.), m/z 1 987 ($[M + H]^+$); 1 742 cm^{-1} (C=O str.) (Found: C, 72.3; H, 4.5. Calc. for $C_{120}H_{90}Fe_3O_{18}$: C, 72.5; H, 4.6%). ^{1}H N.m.r. (CDCl$_3$): δ 3.59 (d, J 10, 12 H), 4.10 (d, J 10, 12 H), 4.98 (t, J 2, 12 H), 5.31 (t, J 2 Hz, 12 H), and 6.84—7.18 (m, 36 H).

1,1'-*Bis*(p-*t*-*butylphenoxycarbonyl*)*ferrocene* (8).—*p*-t-Butyl-phenol (1.94 g, 12.9 mmol) and triethylamine (2.70 g, 26.7 mmol) were dissolved in toluene (250 cm^3) and the solution warmed to reflux under a nitrogen atmosphere. To this solution was added dropwise 1,1'-bis(chlorocarbonyl)ferrocene (1) (2.00 g, 6.43 mmol) in toluene (50 cm^3) over a period of 10 min. The reaction mixture was allowed to cool to room temperature and stirred for 24 h. The solvent was removed *in vacuo* and the residue column chromatographed (alumina, dichloromethane) to give compound (8) as an orange solid (85% yield), m/z 538 (M^+), 1 735 cm^{-1} (C=O str.) (Found: C, 71.8; H, 6.6. Calc. for $C_{32}H_{34}FeO_4$: C, 71.4; H, 6.4%). ^{1}H N.m.r. (CDCl$_3$): 1.29 (s, 18 H), 4.49 (t, J 2, 4 H), 5.00 (t, J 2, 4 H), 7.13 (d, J 6, 4 H), and 7.34 (d, J 6 Hz, 4 H).

1,1'-*Bis*(p-*t*-*butylphenoxythiocarbonyl*)*ferrocene* (9).—Compound (8) (1.00 g, 1.86 mmol) and Lawessons reagent (*p*-methoxyphenylthionophosphine sulphide dimer) (1.80 g, 4.45 mmol) were dissolved in xylene (50 cm^3) and refluxed under nitrogen for 48 h. The solvent was removed *in vacuo* and dissolved in a mixture of light petroleum (b.p. 40—60 °C, 20 cm^3) and dichloromethane (5 cm^3) and purified by column chromatography (alumina; 90% light petroleum, 10% dichloromethane). Recrystallisation from a mixture of dichloromethane and methanol gave the product (9) as a blood-red solid (25% yield), m/z 570 (M^+) (Found: C, 67.2; H, 6.3. Calc. for $C_{32}H_{34}FeO_2S_2$: C, 67.4; H, 6.0%). ^{1}H N.m.r. (CDCl$_3$): δ 1.33 (s, 18 H), 4.67 (t, J 2, 4 H), 5.14 (t, J 2, 4 H), 7.05 (d, J 6, 4 H), and 7.43 (d, J 6 Hz, 4 H).

Crystallography.—Crystal data. Compound (3), $C_{112}H_{124}$-Fe_2O_{12}·$1.8C_6H_{14}$, $M = 1 929.2$, triclinic, space group $P\bar{1}$, $a = 12.480(6)$, $b = 15.425(6)$, $c = 16.082(7)$ Å, α = 69.48(3), β = 88.87(4), γ = 87.34(4)°, $U = 2 896$ Å^3, $Z = 1$ (the molecule is disposed about a centre of symmetry), $D_c = 1.11$ g cm^{-3}, Cu-K_α radiation, λ = 1.541 78 Å, μ(Cu-K_α) = 24 cm^{-1}, $F(000) = 1 034$.

An irregularly shaped crystal of approximate size 0.5 × 0.3 × 0.3 mm was grown by slow evaporation from dichloromethane–hexane, then taken out of solution and immediately sprayed with lacquer and placed within a capillary tube. Data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω scans. 5 942 Independent reflections (2θ > 100°) were measured, of which 4 869 had $|F_o| > 3σ(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods. A ΔF map revealed the presence of a 0.9 occupancy hexane molecule in two interleaving orientations, producing the effect of two continuous chains running through the crystal. These atoms were refined isotropically with idealised geometry. All other non-hydrogen atoms were refined anisotropically. All four tertiary butyl groups were disordered, that about C(18) into three distinct orientations, and the other three into two discrete orientations. All these groups were idealised, and refined as rigid bodies.

The hydroxy protons on O(24) and O(47) were located from a ΔF map and refined isotropically. The solvent hydrogen atoms were not located. The positions of the remaining hydrogen atoms were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2 U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by block-cascade full-matrix least squares to $R = 0.078$, $R' = 0.078 [w^{-1} = σ^2(F) + 0.000 40F^2]$. The maximum and minimum residual electron densities in the final ΔF map were 0.43 and -0.37 e Å^{-3} respectively. The mean and maximum shift/error in the final refinement were 0.035 and 0.280 respectively. Computations were carried out on an eclipse S140 computer using the SHELXTL program system.[21] Positional parameters are given in Table 1, bond lengths in Table 2, and bond angles in Table 3.
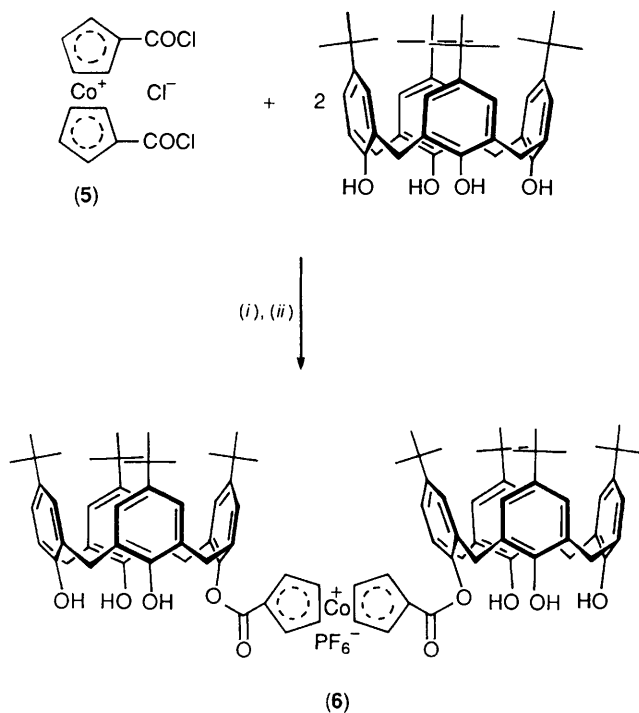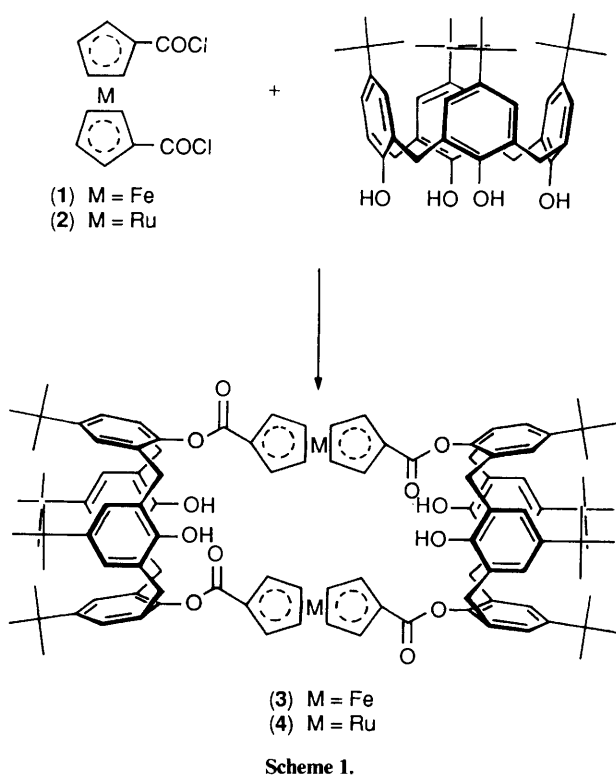
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Syntheses.—The reaction of 1,1'-bis(chlorocarbonyl)ferrocene (1) and 1,1'-bis(chlorocarbonyl)ruthenocene (2)[17] with *p*-t-butylcalix[4]arene[19] in the presence of triethylamine gave, after column chromatography (alumina, CH$_2$Cl$_2$), the respective bis(metallocene)–bis(*p*-t-butylcalix[4]arene) dimers (3) (64% yield, orange crystals) and (4) (47% yield, pale yellow crystals) (Scheme 1). Both compounds were reported in our communication[16] as monomeric species, however the recent availability of the fast atom bombardment mass spectrometry SERC Service at University College Swansea enabled spectra of (3) and (4) to be obtained which revealed respective molecular ion $(M + H)^+$ peaks at m/z 1 773 and 1 863, suggesting dimeric species. This was subsequently confirmed by the single-crystal X-ray determination of (3) which is also reported.

No evidence for the presence of the monomer metallocene calix[4]arene derivatives was found indicating that 1,2- or 1,3-metallocene bridging of the hydroxyl groups of the calix[4]arene is sterically unfavourable. In an analogous synthetic procedure the condensation of 1,1'-bis(chlorocarbonyl)-cobaltocenium chloride (5)[18] and *p*-t-butylcalix[4]arene followed by column chromatography (Sephadex LH20; 50% water, 50% acetonitrile) and excess of ammonium hexafluorophosphate gave the cobaltocenium–bis(*p*-t-butylcalix[4]arene) dimer (6) as a yellow crystalline solid in low yield (Scheme 2). The expected bis(cobaltocenium)–bis(*p*-t-butylcalix[4]arene) compound was not isolated implying the positive charge of the cobaltocenium unit is discouraging and repelling the attachment of a second cobaltocenium moiety to (6).

The reaction of compound (1) with calix[4]arene[20] led to

Scheme 1.

(1) M = Fe
(2) M = Ru

(3) M = Fe
(4) M = Ru

Scheme 2. (i) NEt₃; (ii) NH₄PF₆

(5)

(6)

Scheme 3.

(1)

(7)

Figure 1. Distance d between the transannular 1,3-hydroxyl groups of a calix[4]arene

the isolation of the trimer (7) (34% yield) as a pink powder (Scheme 3). No other product was obtained from this reaction and evidence for the trimer was gained from the fast atom bombardment mass spectrum revealing the $(M + H)^+$ ion at m/z 1 987. A possible rationalisation for the formation of the metallocene–calix[4]arene cyclic oligomers comes from considering the distance of separation of the transannular 1,3-hydroxyl groups in the calix[4]arene starti7g materials. It might
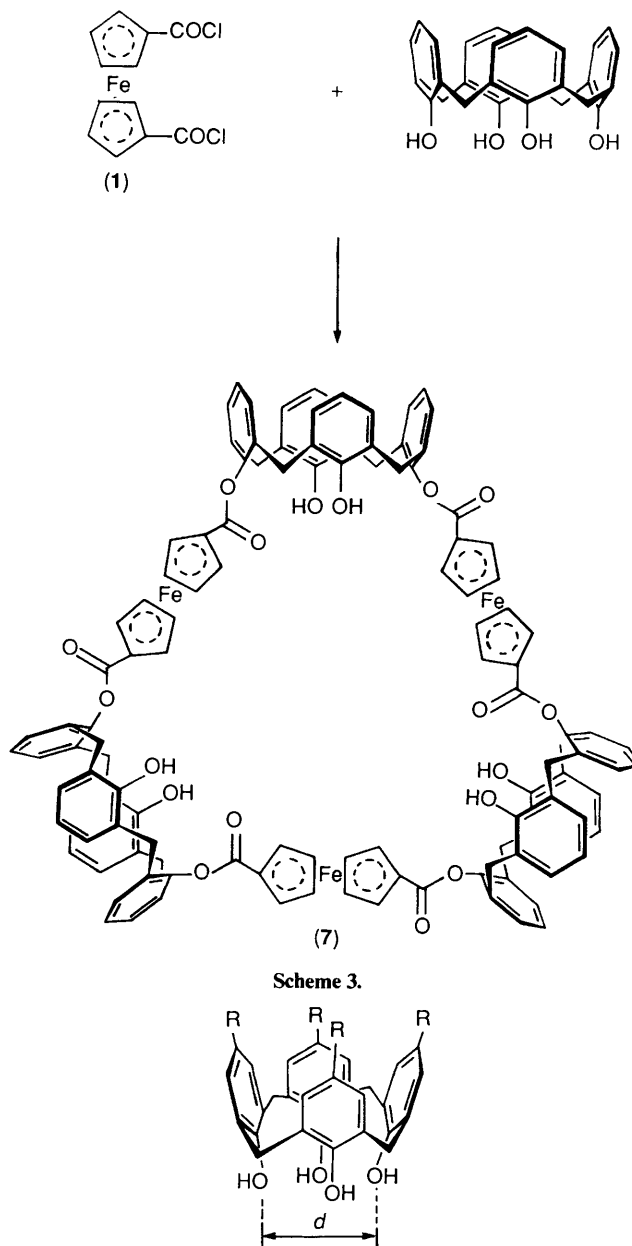
be expected that the more bulky the substituent *para* to a hydroxyl group in a calix[4]arene the smaller is the separation distance d between the transannular 1,3-hydroxyl groups, Figure 1. Thus for *p*-t-butylcalix[4]arene the value of d will be less than that for calix[4]arene, containing no *para* substituent. For any of the metallocene–calix[4]arene systems the synthetic results indicate the distance d is too small * to allow the formation of the 1 + 1 bridged metallocene–calixarene monomer species and consequently higher oligomers are produced. With calix[4]-arene d is of sufficient size to allow the 3 + 3 cyclic oligomer to form in preference to the 2 + 2 species whereas with *p*-t-butylcalix[4]arene because d is smaller the 2 + 2 product is preferred.

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* Gutsche and Alam [4] estimated the 'lower rim' transannular distance of calix[4]arenes to be *ca.* 2 Å diameter which is less than the metallocene cyclopentadienyl–cyclopentadienyl interring distance, *ca.* 3.25 Å.[22]
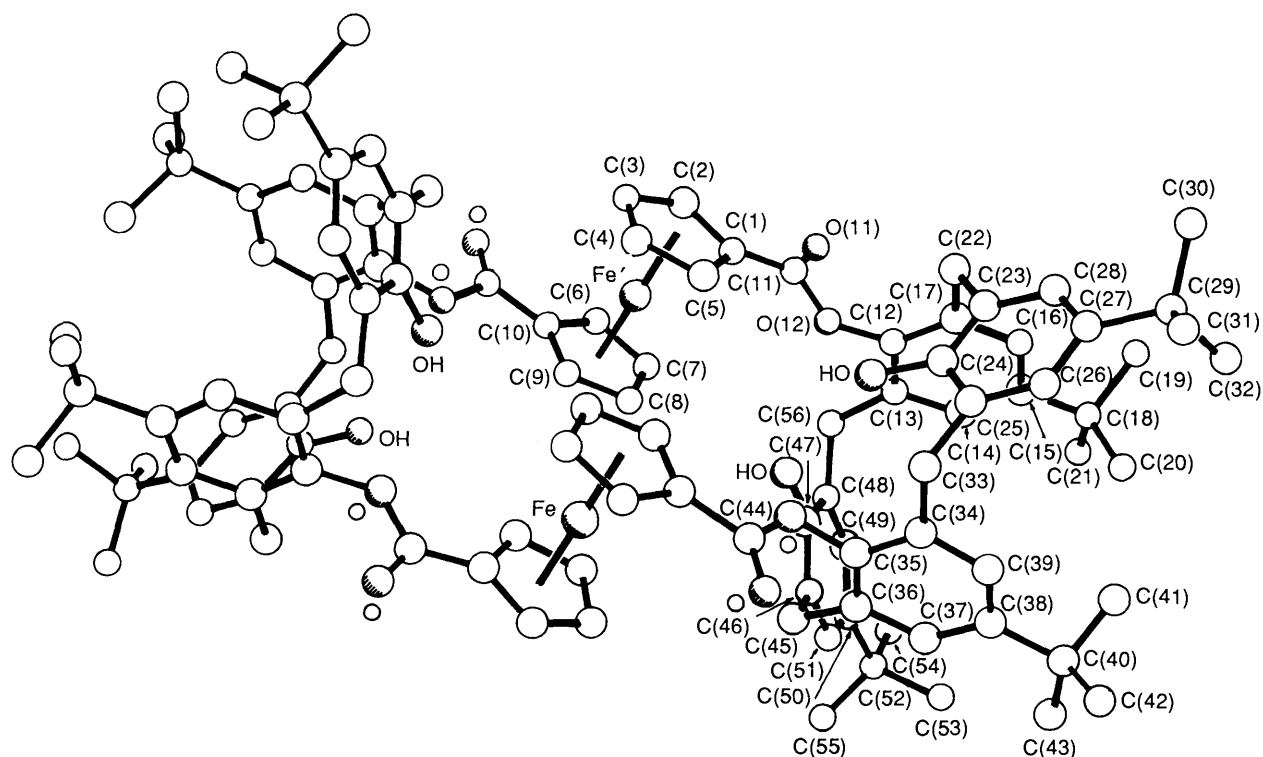
Figure 2. Skeletal representation of the solid-state structure of compound (3)
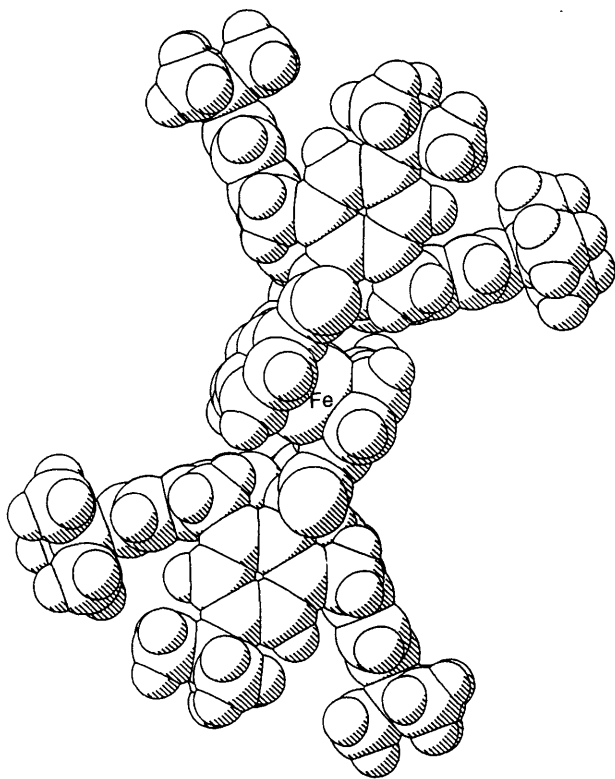

Figure 3. Space-filling representation of the solid-state structure of compound (3)

X-Ray Structural Investigation of Compound (3).—Orange crystals of compound (3) suitable for *X*-ray structural investigations were obtained from a dichloromethane–hexane mixture. Instead of bridging intramolecularly, between opposite

faces of the calixarene ring, the ferrocene unit links to an adjacent macrocycle (and *vice versa*), forming a dimeric structure which is disposed about a crystallographic centre of symmetry (Figure 2). The effect of the ferrocene bridges is to distort each cyclophane ring from optimal C_{4v} to approximate non-crystallographic C_{2v} symmetry. The planes of the two ferrocene-bearing phenol rings are almost parallel to the cyclophane C_2 axis (inclined by 4 and 6°), whereas the other pair of phenol rings are significantly splayed (inclined by 46 and 53° to the molecular axis), Figure 3. The two calixarene rings within each dimer, although necessarily having parallel symmetry axes, are displaced laterally relative to each other by *ca.* 3 Å. Both calix[4]arene moieties are in cone conformations.

The cyclopentadienyl rings within each ferrocene unit are not perfectly eclipsed, being rotated by *ca.* 10° to each other. Each cyclopentadienyl ring is coplanar with its ester substituent and lies nearly normal to the plane of its associated phenyl (dihedral angles of 78 and 86°). There are no significant Fe ⋯ Fe interactions; the transannular Fe ⋯ Fe separation is 5.9 Å.

There are weak intramolecular hydrogen bonds (both of 3.03 Å) between the hydroxyl groups and the ether oxygen atoms of the ester groups.

Variable-temperature ^{1}H *N.M.R. Studies of Compounds* (3) *and* (4).—The parent 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', conformations.[1] It was of interest therefore to establish using variable-temperature ^{1}H n.m.r. spectroscopy whether the respective room-temperature solution conformations of (3) and (4) were rigid on the n.m.r. time-scale and ultimately favourable for possible guest inclusion.

The respective 400-MHz ^{1}H n.m.r. spectra of compounds (3) and (4) in CDCl$_3$ at room temperature (298 K) display two broad doublets for the methylenes typical of an AB system, two singlets for the t-butyl groups, two metallocene signals,

Table 1. Atom co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for compound (3)

Atom	x	y	z	Atom	x	y	z
Fe	−15(1)	6 608(1)	−1 658(1)	C(34)	−713(4)	5 848(4)	3 904(3)
C(1)	474(4)	7 339(4)	−917(4)	C(35)	−1 211(4)	5 354(4)	3 470(3)
C(2)	1 116(5)	7 540(5)	−1 701(5)	O(35)	−572(3)	4 970(2)	2 934(2)
C(3)	1 605(5)	6 691(6)	−1 679(6)	C(36)	−2 324(5)	5 298(4)	3 463(4)
C(4)	1 292(6)	5 984(5)	−905(5)	C(37)	−2 910(5)	5 731(4)	3 951(4)
C(5)	576(5)	6 376(4)	−427(4)	C(38)	−2 461(5)	6 221(4)	4 420(4)
C(6)	−834(5)	7 127(4)	−2 819(4)	C(39)	−1 359(5)	6 267(4)	4 380(3)
C(7)	−1 507(5)	7 102(5)	−2 103(5)	C(40)	−3 147(4)	6 702(4)	4 942(3)
C(8)	−1 554(5)	6 193(5)	−1 522(4)	C(41)	−2 613(4)	6 502(4)	5 856(3)
C(9)	−890(5)	5 630(4)	−1 876(4)	C(42)	−4 302(4)	6 348(4)	5 082(3)
C(10)	−450(4)	6 205(4)	−2 679(4)	C(43)	−3 188(4)	7 760(4)	4 420(3)
C(11)	−177(4)	8 047(4)	−718(3)	C(41a)	−4 093(4)	7 263(4)	4 358(3)
O(11)	−295(4)	8 840(3)	−1 167(3)	C(42a)	−2 436(4)	7 369(4)	5 194(3)
O(12)	−651(3)	7 685(2)	95(2)	C(43a)	−3 592(4)	5 977(4)	5 797(3)
C(12)	−1 297(4)	8 290(3)	404(3)	C(44)	−276(5)	4 046(4)	3 275(4)
C(13)	−2 409(4)	8 265(3)	347(3)	O(44)	−577(4)	3 553(3)	3 978(3)
C(14)	−3 012(5)	8 835(4)	695(4)	C(45)	−2 875(5)	4 863(4)	2 886(4)
C(15)	−2 574(5)	9 399(4)	1 086(4)	C(46)	−3 493(4)	5 586(4)	2 146(4)
C(16)	−1 469(5)	9 381(4)	1 138(3)	C(47)	−2 970(4)	6 182(4)	1 408(4)
C(17)	−814(4)	8 826(3)	813(3)	O(47)	−1 876(3)	6 071(2)	1 303(2)
C(18)	−3 274(4)	10 017(3)	1 474(4)	C(48)	−3 519(4)	6 891(4)	768(4)
C(19)	−2 943(4)	11 030(3)	1 012(4)	C(49)	−4 619(5)	6 998(4)	873(4)
C(20)	−3 042(4)	9 706(5)	2 482(4)	C(50)	−5 174(5)	6 433(4)	1 599(4)
C(21)	−4 487(4)	9 953(3)	1 329(4)	C(51)	−4 587(4)	5 724(4)	2 222(4)
C(19a)	−4 270(4)	9 488(3)	1 939(4)	C(52)	−6 389(3)	6 638(3)	1 713(4)
C(20a)	−3 642(4)	10 923(3)	724(4)	C(53)	−7 017(3)	6 638(3)	891(4)
C(21a)	−2 603(4)	10 253(3)	2 160(4)	C(54)	−6 510(3)	7 610(3)	1 793(4)
C(19b)	−4 292(4)	10 382(3)	898(4)	C(55)	−6 844(3)	5 907(3)	2 560(4)
C(20b)	−2 632(4)	10 846(3)	1 491(4)	C(53a)	−7 018(3)	5 738(3)	1 959(4)
C(21b)	−3 606(4)	9 429(3)	2 433(4)	C(54a)	−6 844(3)	7 358(3)	841(4)
C(22)	407(4)	8 762(4)	968(3)	C(55a)	−6 507(3)	7 039(3)	2 471(4)
C(23)	653(4)	8 341(4)	1 944(3)	C(56)	−2 938(4)	7 580(4)	12(4)
C(24)	511(4)	7 403(3)	2 413(3)	C(57)	5 425(7)	459(6)	4 611(6)
O(24)	194(3)	6 837(2)	1 970(2)	C(58)	4 760(7)	1 039(6)	3 793(6)
C(25)	699(4)	7 025(4)	3 315(3)	C(59)	5 368(7)	1 908(6)	3 258(6)
C(26)	1 036(5)	7 589(4)	3 748(4)	C(60)	4 719(7)	2 455(6)	2 417(6)
C(27)	1 195(5)	8 524(4)	3 312(4)	C(61)	5 360(7)	3 281(6)	1 840(6)
C(28)	987(5)	8 876(4)	2 415(4)	C(62)	4 634(7)	3 929(6)	1 098(6)
C(29)	1 550(6)	9 155(4)	3 810(4)	C(63)	5 328(7)	4 630(6)	403(6)
C(30)	2 137(6)	9 992(4)	3 164(4)	C(64)	4 741(9)	417(8)	4 565(8)
C(31)	2 304(6)	8 611(4)	4 592(4)	C(65)	5 415(9)	1 201(8)	3 948(8)
C(32)	526(6)	9 506(4)	4 176(4)	C(66)	4 760(9)	1 739(8)	3 108(8)
C(30a)	1 391(6)	8 690(4)	4 826(4)	C(67)	5 355(9)	2 612(8)	2 563(8)
C(31a)	877(6)	10 079(4)	3 472(4)	C(68)	4 672(9)	3 179(8)	1 753(8)
C(32a)	2 753(6)	9 348(4)	3 605(4)	C(69)	5 382(9)	3 872(8)	1 068(8)
C(33)	486(4)	6 010(4)	3 823(3)	C(70)	4 664(9)	4 639(8)	415(8)

and two aromatic absorptions. On warming to 55 °C (328 K) the two doublets sharpen and at 100 °C (373 K) in toluene the respective AB systems are still observed. These n.m.r. observations are similar to those found for the 1,3-disubstituted dimethyl ether[23] and crown derivatives of p-t-butylcalix[4] arene,[24] which have been demonstrated to exist in 'flattened' cone conformations.

However, unexpectedly on cooling the respective samples to −50 (223) (CDCl₃) and −100 °C (173 K) (CD₂Cl₂) another pair of AB doublets appear (Figure 4) along with four singlets for the metallocene protons, four singlets for aromatic protons (Figure 5), and two hydroxyl signals. The t-butyl protons now appear as at least three singlets, one of which remains broad even at −100 °C (Figure 6). Two possible rationalisations may account for this variable-temperature n.m.r. behaviour. At low temperatures (−100 °C) the respective ¹H n.m.r. spectra of compounds (3) and (4) are consistent with a partial cone conformation.[23] Alternatively the ¹H n.m.r. spectra may be explained by considering only the intramolecular rotation of the respective metallocene carbonyl groups. At room temperature

and above the carbonyl group is rotating rapidly on the n.m.r. time-scale about the metallocene cyclopentadienyl–carbonyl carbon bond. On cooling, this intramolecular fluxional process slows down and more complicated spectra result. The fact that two hydroxyl protons are observed at the lowest temperatures suggests the absence of a C_2 axis in the respective molecules. This result coupled with molecular model considerations imply that at low temperatures the respective carbonyl groups attached to the metallocene subunits are cis to one another. Acyl groups in simple acylferrocenes are known to exhibit this type of fluxional behaviour.[25] Unfortunately corroborative evidence from ¹³C n.m.r. spectra could not be obtained because of the poor solubility of both compounds (3) and (5) in organic solvents.

In an effort to test this latter explanation further, attempts were made to convert the ester linkages of compounds (3) and (4) into ether bonds using the synthetic strategy[26] shown in Scheme 4. The viability of this preparative route was first investigated using the 'model' compound (8) prepared from (1) and p-t-butylphenol. Refluxing (8) with Lawessons reagent in

Table 2. Bond lengths (Å) with e.s.d.s in parentheses

Fe–C(1)	2.024(7)	Fe–C(2)	2.045(7)	C(29)–C(31)	1.550	C(29)–C(32)	1.550
Fe–C(3)	2.030(7)	Fe–C(4)	2.041(7)	C(29)–C(30a)	1.550	C(29)–C(31a)	1.549
Fe–C(5)	2.032(7)	Fe–C(6)	2.031(6)	C(29)–C(32a)	1.550	C(33)–C(34)	1.523(8)
Fe–C(7)	2.024(6)	Fe–C(8)	2.037(6)	C(34)–C(35)	1.375(9)	C(34)–C(39)	1.388(8)
Fe–C(9)	2.032(7)	Fe–C(10)	2.039(7)	C(35)–O(35)	1.420(7)	C(35)–C(36)	1.396(8)
C(1)–C(2)	1.426(9)	C(1)–C(5)	1.418(8)	O(35)–C(44)	1.371(6)	C(36)–C(37)	1.377(9)
C(1)–C(11)	1.452(9)	C(2)–C(3)	1.409(12)	C(36)–C(45)	1.513(9)	C(37)–C(38)	1.383(9)
C(3)–C(4)	1.399(10)	C(4)–C(5)	1.415(11)	C(38)–C(39)	1.379(9)	C(38)–C(40)	1.529(9)
C(6)–C(7)	1.402(10)	C(6)–C(10)	1.421(8)	C(40)–C(41)	1.550	C(40)–C(42)	1.550
C(7)–C(8)	1.389(9)	C(8)–C(9)	1.424(10)	C(40)–C(43)	1.550	C(40)–C(41a)	1.550
C(9)–C(10)	1.404(7)	C(10)–C(44a)	1.444(9)	C(40)–C(42a)	1.550	C(40)–C(43a)	1.550
C(11)–O(11)	1.186(6)	C(11)–O(12)	1.363(6)	C(44)–O(44)	1.185(6)	C(44)–C(10a)	1.444(9)
O(12)–C(12)	1.416(7)	C(12)–C(13)	1.397(8)	C(45)–C(46)	1.511(7)	C(46)–C(47)	1.393(7)
C(12)–C(17)	1.386(8)	C(13)–C(14)	1.386(9)	C(46)–C(51)	1.381(8)	C(47)–O(47)	1.382(6)
C(13)–C(56)	1.521(9)	C(14)–C(15)	1.375(9)	C(47)–C(48)	1.376(7)	C(48)–C(49)	1.390(8)
C(15)–C(16)	1.382(8)	C(15)–C(18)	1.541(8)	C(48)–C(56)	1.505(7)	C(49)–C(50)	1.384(8)
C(16)–C(17)	1.381(8)	C(17)–C(22)	1.542(8)	C(50)–C(51)	1.386(7)	C(50)–C(52)	1.555(7)
C(18)–C(19)	1.549	C(18)–C(20)	1.550	C(52)–C(53)	1.550	C(52)–C(54)	1.550
C(18)–C(21)	1.550	C(18)–C(19a)	1.550	C(52)–C(55)	1.550	C(52)–C(53a)	1.550
C(18)–C(20a)	1.549	C(18)–C(21a)	1.549	C(52)–C(54a)	1.550	C(52)–C(55a)	1.550
C(18)–C(19b)	1.550	C(18)–C(20b)	1.549	C(57)–C(58)	1.538	C(58)–C(59)	1.541
C(18)–C(21b)	1.550	C(22)–C(23)	1.505(7)	C(59)–C(60)	1.543	C(60)–C(61)	1.537
C(23)–C(24)	1.396(7)	C(23)–C(28)	1.381(9)	C(61)–C(62)	1.538	C(62)–C(63)	1.539
C(24)–O(24)	1.380(7)	C(24)–C(25)	1.382(7)	C(63)–C(63a)	1.602(16)	C(64)–C(65)	1.541
C(25)–C(26)	1.373(10)	C(25)–C(33)	1.525(7)	C(64)–C(64a)	1.650(21)	C(65)–C(66)	1.541
C(26)–C(27)	1.387(8)	C(27)–C(28)	1.378(8)	C(66)–C(67)	1.540	C(67)–C(68)	1.538
C(27)–C(29)	1.544(10)	C(29)–C(30)	1.550	C(69)–C(70)	1.540	C(70)–C(70a)	1.651(21)

Table 3. Bond angles (°) with e.s.d.s in parentheses

|							
C(2)–C(1)–C(5)	108.9(6)	C(2)–C(1)–C(11)	122.4(5)	C(31a)–C(29)–C(32a)	109.5	C(25)–C(33)–C(34)	111.2(4)
C(5)–C(1)–C(11)	128.7(5)	C(1)–C(2)–C(3)	106.3(6)	C(33)–C(34)–C(35)	122.7(5)	C(33)–C(34)–C(39)	119.7(5)
C(2)–C(3)–C(4)	109.4(7)	C(3)–C(4)–C(5)	108.4(7)	C(35)–C(34)–C(39)	117.4(5)	C(34)–C(35)–O(35)	118.2(5)
C(1)–C(5)–C(4)	106.9(5)	C(7)–C(6)–C(10)	107.6(5)	C(34)–C(35)–C(36)	122.5(6)	O(35)–C(35)–C(36)	119.0(5)
C(6)–C(7)–C(8)	109.2(6)	C(7)–C(8)–C(9)	107.6(6)	C(35)–O(35)–C(44)	118.3(4)	C(35)–C(36)–C(37)	116.7(6)
C(8)–C(9)–C(10)	108.0(5)	C(6)–C(10)–C(9)	107.6(5)	C(35)–C(36)–C(45)	122.2(5)	C(37)–C(36)–C(45)	120.9(5)
C(6)–C(10)–C(44a)	123.8(5)	C(9)–C(10)–C(44a)	128.5(5)	C(36)–C(37)–C(38)	123.8(6)	C(37)–C(38)–C(39)	116.4(6)
C(1)–C(11)–O(11)	127.2(5)	C(1)–C(11)–O(12)	110.6(4)	C(37)–C(38)–C(40)	121.9(5)	C(39)–C(38)–C(40)	121.7(6)
O(11)–C(11)–O(12)	122.2(5)	C(11)–O(12)–C(12)	117.9(4)	C(34)–C(39)–C(38)	123.2(6)	C(38)–C(40)–C(41)	108.4(3)
O(12)–C(12)–C(13)	118.0(5)	O(12)–C(12)–C(17)	119.3(5)	C(38)–C(40)–C(42)	111.3(3)	C(41)–C(40)–C(42)	109.5
C(13)–C(12)–C(17)	122.4(5)	C(12)–C(13)–C(14)	116.2(6)	C(38)–C(40)–C(43)	108.7(3)	C(41)–C(40)–C(43)	109.5
C(12)–C(13)–C(56)	122.2(5)	C(14)–C(13)–C(56)	121.3(5)	C(42)–C(40)–C(43)	109.5	C(38)–C(40)–C(41a)	109.7(3)
C(13)–C(14)–C(15)	123.8(5)	C(14)–C(15)–C(16)	117.4(6)	C(38)–C(40)–C(42a)	108.5(3)	C(41a)–C(40)–C(42a)	109.5
C(14)–C(15)–C(18)	122.2(5)	C(16)–C(15)–C(18)	120.4(6)	C(38)–C(40)–C(43a)	110.3(3)	C(41a)–C(40)–C(43a)	109.5
C(15)–C(16)–C(17)	122.3(6)	C(12)–C(17)–C(16)	117.9(5)	C(42a)–C(40)–C(43a)	109.5	O(35)–C(44)–O(44)	122.4(6)
C(12)–C(17)–C(22)	121.9(5)	C(16)–C(17)–C(22)	120.0(5)	O(35)–C(44)–C(10a)	110.8(4)	O(44)–C(44)–C(10a)	126.8(5)
C(15)–C(18)–C(19)	107.9(3)	C(15)–C(18)–C(20)	108.2(3)	C(36)–C(45)–C(46)	111.1(5)	C(45)–C(46)–C(47)	121.2(5)
C(19)–C(18)–C(20)	109.5	C(15)–C(18)–C(21)	112.3(3)	C(45)–C(46)–C(51)	120.4(5)	C(47)–C(46)–C(51)	118.2(4)
C(19)–C(18)–C(21)	109.4	C(20)–C(18)–C(21)	109.5	C(46)–C(47)–O(47)	120.3(4)	C(46)–C(47)–C(48)	121.4(5)
C(15)–C(18)–C(19a)	109.5(3)	C(15)–C(18)–C(20a)	110.1(2)	O(47)–C(47)–C(48)	118.3(4)	C(47)–C(48)–C(49)	118.2(5)
C(19a)–C(18)–C(20a)	109.5	C(15)–C(18)–C(21a)	108.7(3)	C(47)–C(48)–C(56)	121.2(5)	C(49)–C(48)–C(56)	120.5(4)
C(19a)–C(18)–C(21a)	109.5	C(20a)–C(18)–C(21a)	109.5	C(48)–C(49)–C(50)	122.6(5)	C(49)–C(50)–C(51)	117.0(5)
C(15)–C(18)–C(19b)	109.7(3)	C(15)–C(18)–C(20b)	110.0(3)	C(49)–C(50)–C(52)	120.0(5)	C(51)–C(50)–C(52)	123.0(5)
C(19b)–C(18)–C(20b)	109.5	C(15)–C(18)–C(21b)	108.7(2)	C(46)–C(51)–C(50)	122.6(5)	C(50)–C(52)–C(53)	110.0(3)
C(19b)–C(18)–C(21b)	109.5	C(20b)–C(18)–C(21b)	109.5	C(50)–C(52)–C(54)	107.5(3)	C(53)–C(52)–C(54)	109.5
C(17)–C(22)–C(23)	110.5(4)	C(22)–C(23)–C(24)	121.1(5)	C(50)–C(52)–C(55)	110.9(3)	C(53)–C(52)–C(55)	109.5
C(22)–C(23)–C(28)	121.2(5)	C(24)–C(23)–C(28)	117.6(5)	C(54)–C(52)–C(55)	109.5	C(50)–C(52)–C(53a)	110.6(3)
C(23)–C(24)–O(24)	119.8(5)	C(23)–C(24)–C(25)	121.0(6)	C(50)–C(52)–C(54a)	110.0(3)	C(53a)–C(52)–C(54a)	109.5
O(24)–C(24)–C(25)	119.2(4)	C(24)–C(25)–C(26)	118.9(5)	C(50)–C(52)–C(55a)	107.7(4)	C(53a)–C(52)–C(55a)	109.4
C(24)–C(25)–C(33)	120.1(5)	C(26)–C(25)–C(33)	121.0(5)	C(54a)–C(52)–C(55a)	109.5	C(13)–C(56)–C(48)	109.3(5)
C(25)–C(26)–C(27)	122.4(5)	C(26)–C(27)–C(28)	116.9(6)	C(57)–C(58)–C(57)	109.4	C(58)–C(59)–C(60)	108.7
C(26)–C(27)–C(29)	121.9(5)	C(28)–C(27)–C(29)	121.2(5)	C(59)–C(60)–C(61)	109.2	C(60)–C(61)–N(62)	109.3
C(23)–C(28)–C(27)	123.2(5)	C(27)–C(29)–C(30)	110.0(3)	C(61)–C(62)–C(63)	109.3	C(62)–C(63)–C(63a)	114.8(6)
C(27)–C(29)–C(31)	110.8(3)	C(30)–C(29)–C(31)	109.5	C(65)–C(64)–C(64a)	122.5(8)	C(64)–C(65)–C(66)	109.1
C(27)–C(29)–C(32)	107.6(4)	C(30)–C(29)–C(32)	109.5	C(65)–C(66)–C(67)	109.0	C(66)–C(67)–C(68)	109.1
C(31)–C(29)–C(32)	109.5	C(27)–C(29)–C(30a)	111.2(3)	C(67)–C(68)–C(69)	109.2	C(68)–C(69)–C(70)	109.3
C(27)–C(29)–C(31a)	108.7(3)	C(30a)–C(29)–C(31a)	109.5	C(69 –C(70)–C(70a)	113.4(8)		
C(27)–C(29)–C(32a)	108.5(4)	C(30a)–C(29)–C(32a)	109.5				
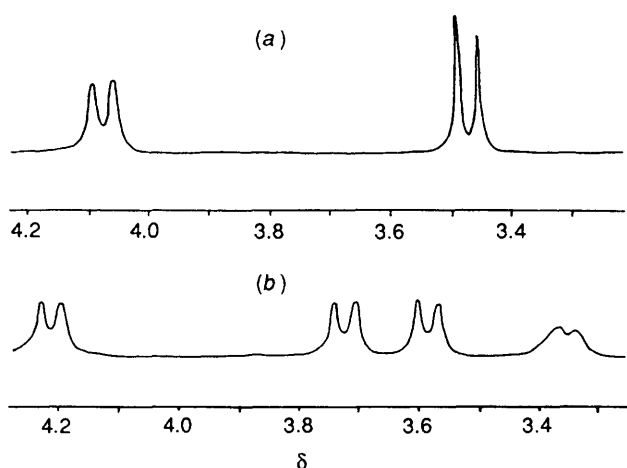
Figure 4. Proton n.m.r. spectrum of the methylene protons of compound (3) at (a) 25 (298) and (b) −100 °C (173 K) (CD₂Cl₂)

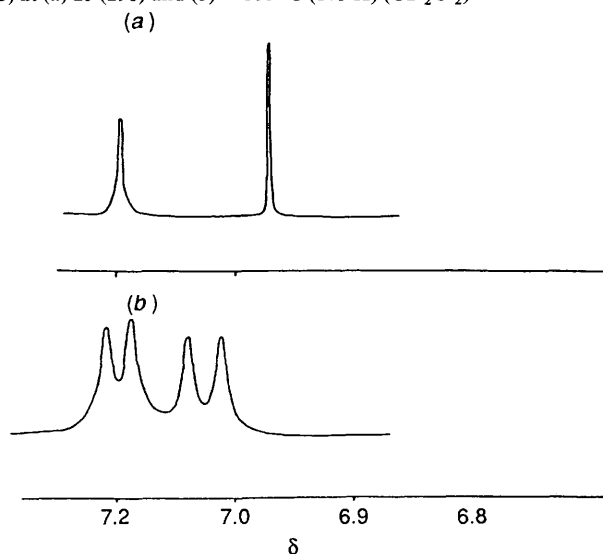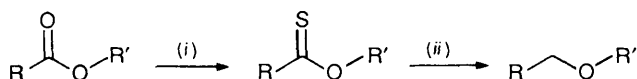Figure 6. Proton n.m.r. spectrum of the t-butyl protons of compound (3) at −100 °C (173 K) (CD₂Cl₂)

Figure 5. Proton n.m.r. spectrum of the aromatic protons of compound (3) at (a) 25 (298) and (b) −100 °C (173 K) (CD₂Cl₂)

Scheme 4. (i) Lawessons reagent; (ii) Raney nickel

(8)

(9)

xylene gave, after chromatographic purification, the desired bis(thioester) intermediate (9) in 25% yield as a blood-red powder. However applying this procedure to (3) or (4) gave no trace of thioester products despite the use of increased reaction times; the starting materials were reisolated. Sterically the carbonyl groups of (3) and (4) are not so accessible to thionisation as in (8) and this may be the primary reason for the reactions failure.

Poor solubility of compounds (6) and (7) in common organic solvents precluded variable-temperature n.m.r. studies of these compounds.

Electrochemical Studies.—The electrochemical properties of compound (3) and the model compound (8) were investigated in acetonitrile solution by cyclic voltammetry and coulometry. Compound (3) exhibits a reversible two-electron oxidation at +1.24 V (*versus* saturated calomel electrode, s.c.e.) which suggests that the respective two ferrocene moieties become
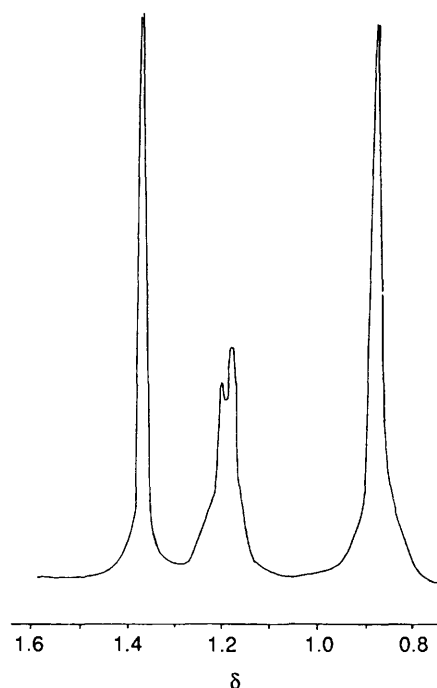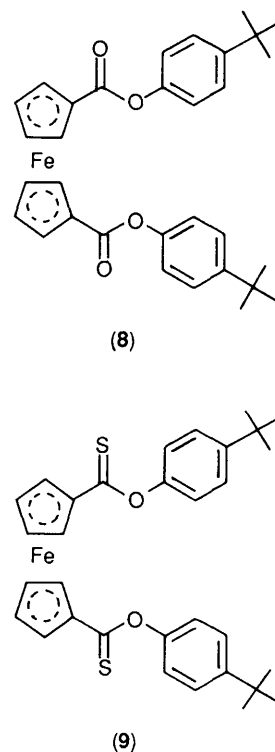
oxidised in one step. Compound (8) exhibits a reversible one-electron oxidation at +1.20 V (s.c.e).

Proton N.M.R. Solution Complexation Studies.—High-field ¹H n.m.r. spectroscopy has been used by Bauer and Gutsche[27] to demonstrate the solution complexation of t-butylamine by allylcalix[4]arene, the changes in the chemical shift values of both the calixarene host and amine guest being monitored.

Addition of stoicheiometric amounts of t-butylamine to room-temperature acetonitrile solutions of compound (3) had little effects ($\Delta\delta \leqslant 0.05$) on the respective ^{1}H chemical shifts for either the host (3) or amine guest, implying that there is no host–guest complexation under these conditions. These disappointing observations may reflect the conformational mobility of (3) negating amine guest inclusion in either of the respective calix[4]arene host cavities.

Conclusion

A novel synthetic route to preparing various metallocene–calix[4]arene cyclic oligomers has been established. The dimeric species (3) and (4) have been shown to be conformationally mobile on the n.m.r. time-scale and this finding may account for the failure of (3) to form inclusion complexes with t-butylamine. Future work is directed at preparing water-soluble metallocene calixarenes in order to use the 'hydrophobic effect'[28] as the driving force for inclusion of organic guest species.

Acknowledgements

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