

NEW HYDROPHOBIC HOST MOLECULES CONTAINING
MULTIPLE REDOX-ACTIVE CENTRES

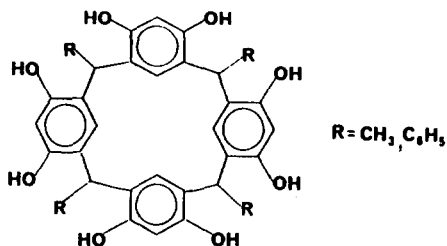
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Abstract

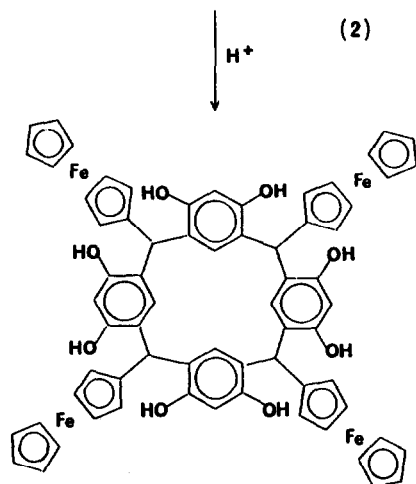
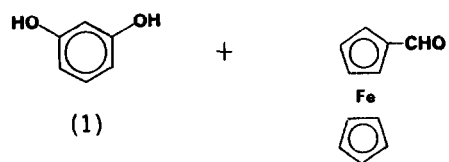
The synthesis of two novel macrocyclic hydrophobic host molecules (4) and (6) containing respectively four and twelve ferrocene redox-active centres is described.

Although there is considerable current interest in the design and synthesis of receptor molecules containing a redox-active centre in close proximity to a crown ether¹⁻³ or cryptand⁴ coordination site, few examples of the incorporation of redox centres into hydrophobic host molecules have been reported.⁵⁻⁷ Interest in these latter molecules stems from the idea of investigating the potential catalytic interactions between the redox-active moiety and an included organic guest substrate. This paper reports the preparation of a new redox-active hydrophobic host molecule (4) that contains four ferrocenyl groups and a novel twelve ferrocenyl group containing analogue (6).

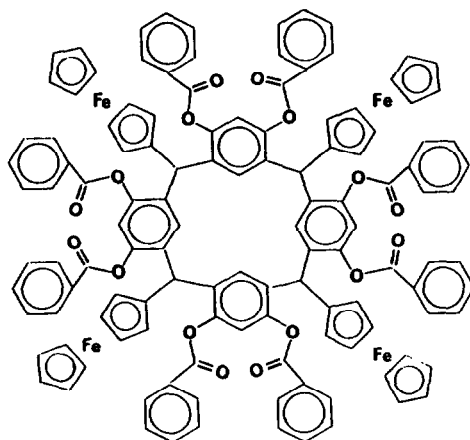
It is well known that reactions of resorcinol with aldehydes under acidic conditions can lead to macrocyclic products of type I.^{8,9} A simple adaptation of this methodology by using a metallocenecarboxaldehyde leads to



respective two step preparations of (4) and (6). The reaction of ferrocenecarboxaldehyde (1) and resorcinol (2) in the presence of hydrochloric acid and ethanol gave initially a black precipitate, insoluble in all common organic solvents tentatively assigned as the phenolic macrocycle (3). Subsequent benzoylation of a suspension of (3) in dry tetrahydrofuran followed by column chromatographic separation gave (4) as an orange crystalline solid, m.p. >250 (10% overall yield for the two steps).

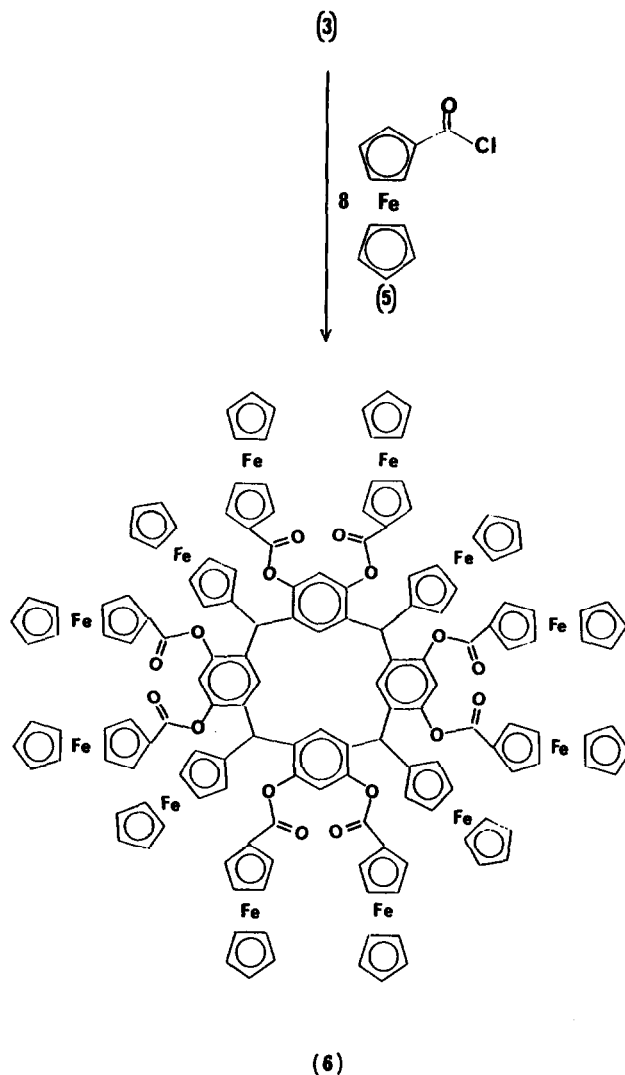


(3)



(4)

An analogous procedure using ferrocenecarbonyl chloride (5) gave (6) as an orange-red crystalline solid m.p. $>250^{\circ}\text{C}$ (10% overall yield).



Elemental analyses, mass spectrometry [(4) $m/z = 2057$, (6) $m/z 2921$] and ^1H and ^{13}C n.m.r. spectroscopy confirmed the proposed structures.^{10,11} It is noteworthy that the ^1H n.m.r. spectrum of (4) in CDCl_3 at ambient temperature reveals two types of ferrocene groups suggesting the solution structure of (4) possesses a C_2 axis of symmetry.^{10,11} Preliminary electrochemical experiments (acetonitrile, S.C.E.) on (4) shows two, two electron reversible oxidation waves at $+0.575$ V and $+0.665$ V corresponding to the oxidation of the respective four ferrocenyl moieties.

These interesting electrochemical observations indicate the future possibility for preparing mixed-valence species which may exhibit exciting new electronic, optical, catalytic and physical properties.

Acknowledgements

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- The result of a single crystal X-ray analysis of (4) is in accordance with the proposed structure. P.D. Beer, E.L. Tite, A.M.Z. Slawin and D.J. Williams, to be reported elsewhere.
- ¹H NMR (CDCl₃) for (4) 3.93 (24H, s), 4.05 (4H s), 4.12 (4H s), 4.23 (4H, s), 5.65 (4H, s), 6.64 (2H, s), 6.73 (2H, s), 6.75 (2H, s), 7.20–7.25 (8H, m), 7.42–7.58 (16H m), 7.82–7.99 (16H, m). ν (C = O) KBr disc = 1735 cm⁻¹.
C₁₂₄H₈₈O₁₆Fe₄ requires C, 72.4, H 4.3
found C, 72.3, H 4.5

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