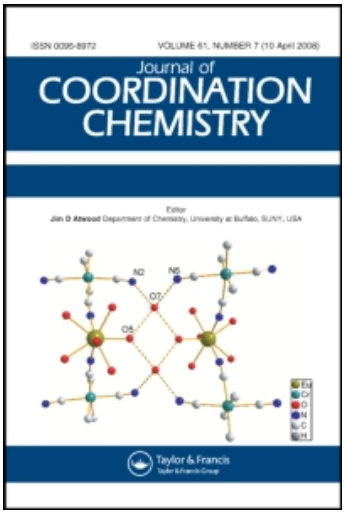

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Synthesis and Characterisation of New Redox-Active Hydrophobic Host Molecules

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SYNTHESIS AND CHARACTERISATION OF NEW REDOX-ACTIVE HYDROPHOBIC HOST MOLECULES

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Abstract The synthesis of the first cobalticinium calix[4]-arene and a macrocyclic resorcinol-ferrocenecarboxaldehyde condensation product is reported.

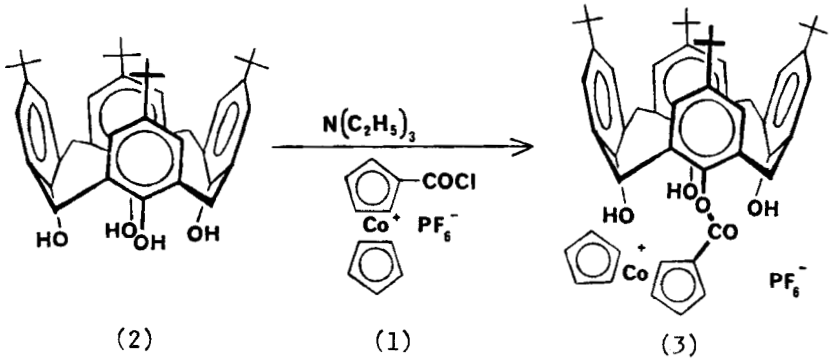
Keywords: Redox-active, resorcinol, ferrocenecarboxaldehyde

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 ether[1-3] or cryptand[4] coordination site, few examples of the covalent attachment of redox centres to known hydrophobic host molecules have been reported.[5,6] Potential interest in these latter molecules stems from the idea of investigating the catalytic interactions between the redox-active moiety and an included organic guest substrate.

We have recently begun a research programme constructing redox-active hydrophobic host molecules by appending the metallocene redox centres ferrocene and ruthenocene to p-tert-butylcalix[4]arene.[7] As an extension to this initial work we report here the synthesis of the first cobalticinium calix[4]arene (3) and a macrocyclic resorcinol-ferrocenecarboxaldehyde condensation product (7).

COBALTICINIUM CALIX[4]ARENE (3)

The condensation of chlorocarbonyl cobalticinium (1)[8] with p-tert-butylcalix[4]arene (2) in the presence of triethylamine followed by the addition of an excess amount of sodium hexafluorophosphate gave the cobalticinium calix[4]arene (3) PF_6 salt as a yellow crystalline solid. Scheme 1.

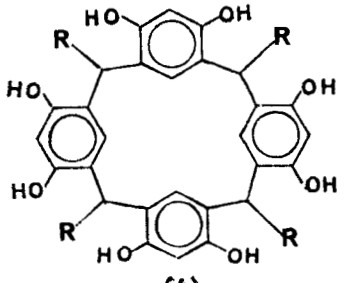


(2) (1) (3)

The structure of this new host molecule was confirmed by elemental analysis, conductivity measurements (= 148 $\Omega^{-1}cm^2mol^{-1}$) and mass spectrometry. The 270 MHz ^1H n.m.r. spectrum of (3) in CD_3CN at ambient temperature displays two t-butyl signals (2:1 relative integration), two pairs of AB doublets for the methylene protons and four aromatic absorptions indicative of a mono-substituted calix[4]arene.[9]

RESORCINOL-FERROCENECARBOXALDEHYDE CONDENSATION PRODUCTS (7)

Hogberg has recently described[10,11] the synthesis of two stereo-isomeric macrocycles of the same general structure (4) by the acid catalysed condensation of resorcinol and benzaldehyde or acetaldehyde.

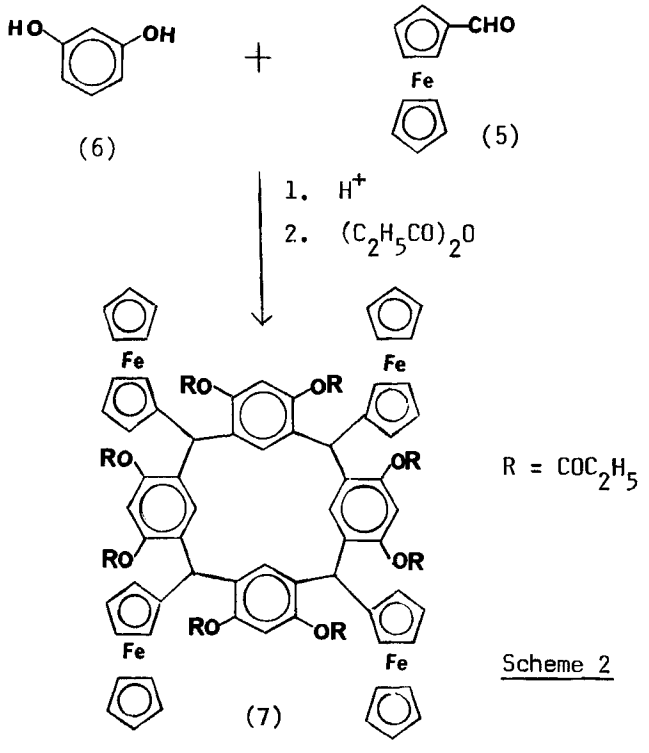


R = Me, Ph

(4)

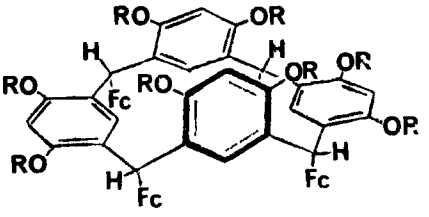
We have adapted this method to the preparation of a new macrocyclic redox-active hydrophobic host molecule (7). The

reaction of ferrocenecarboxaldehyde (5) and resorcinol (6) in the presence of hydrochloric acid gave initially a black precipitate which was propionylated to give (7) as a dark brown purple solid. Scheme 2.



Scheme 2

Elemental analyses, infrared and mass spectral data confirm the proposed structure. The ^1H n.m.r. spectrum of (7) in $CDCl_3$ at ambient temperature is very similar to the all cis, boat conformation, of the reported propionylated resorcinol-acetaldehyde condensation product (8),[10] indicating the four ferrocenyl groups are in axial positions (9).



(9)

Fc = Ferrocenyl
R' = COC_2H_5

Dynamic multinuclear n.m.r. and electrochemical studies of (3) and (7) are in progress.

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