Journal of Organometallic Chemistry, 353 (1988) C10–C12
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

New bis-ferrocene calix[4]arene hydrophobic receptor molecules and crystal structure of one of them

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(Received June 27th, 1988)

Abstract

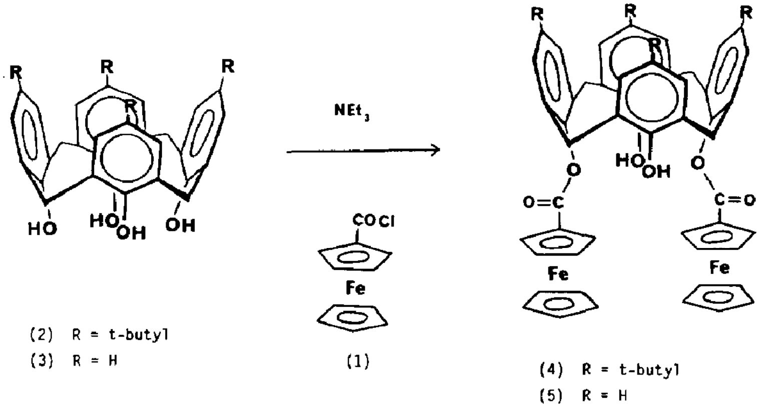
The condensation of ferrocene carbonylchloride (1) with *p*-t-butylcalix[4]arene (2) and calix[4]arene (3) leads to the respective novel redox-active hydrophobic host molecules containing two ferrocene moieties. An X-ray diffraction study of one of the products shows that the calix[4]arene is in a cone conformation.

The calixarenes are phenol-formaldehyde cyclic oligomers which possess hydrophobic cavities capable of forming inclusion complexes with a variety of neutral organic guest molecules in the solid state [1,2]. They also have the ability to function as ion and molecular carriers as well as enzyme mimics [1,3,4]. Although in solution the calix[4]arenes are known to be conformationally mobile [1], this flexibility can be reduced by derivatisation of the phenolic groups [5]. The incorporation of redox-active centres into this class of host molecule may lead to a new type of molecular sensor and/or catalyst with a well-defined molecular cavity capable of detecting and catalysing redox reactions on an included organic guest substrate [6]. We report here the preparation of two such compounds **4** and **5**, and the structure of **5** as determined by X-ray diffraction.

The reaction of an excess of ferrocene carbonylchloride (1) [7] with *p*-t-butylcalix[4]arene (2) [8] and calix[4]arene (3) [9] in the presence of triethylamine gave the respective 1,3-substituted bis-ferrocene calix[4]arenes (4) (83% yield, decomposes > 280 ° C, orange crystals) and **5** (70% yield, decomposes > 280 ° C, orange crystals). The structures of both of these new air-stable compounds were characterised by elemental analysis, mass spectrometry, and ^1H and ^{13}C NMR spectroscopy.

Orange crystals of **5** suitable for X-ray structural investigation were obtained from a dichloromethane/hexane mixture.

0022-328X/88/$03.50

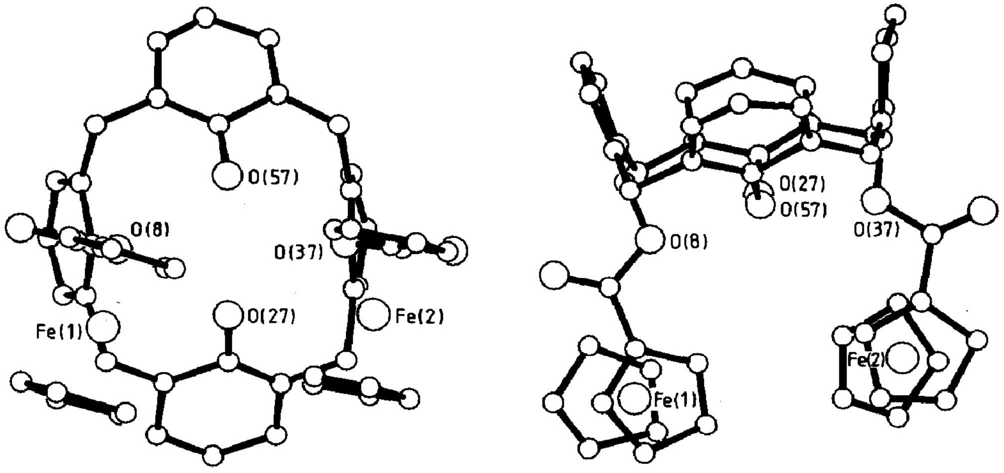


(2) R = t-butyl
(3) R = H

(1)

(4) R = t-butyl
(5) R = H

The structure consists of discrete molecules of 5 * (shown in Fig. 1a and 1b) together with $0.5CH_2Cl_2$. The calix[4]arene is in a cone conformation [1,5]; the angle between the phenyl rings attached to O(8) and O(37) is 26.4 and between



(a) (b)

Fig. 1. Two views of the crystal structure of (5) showing the shape of the calixarene cavity.

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* *Crystal data* for 5, $[Fe_2C_{50}O_6H_{40}]$, $0.5CH_2Cl_2$, $M = 890.46$, orthorhombic, a 12.873(13), b 28.964(22), c 22.998(23) Å, U 8574.9, $F(000) = 3688$, D_m 1.38 g cm^{-3}, D_c 1.38 g cm^{-3}, $Z = 8$, Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α 8.1 cm^{-1}, Space group *Pbca*.

1826 independent reflections above background ($I > 2\sigma(I)$) were measured on a diffractometer. The structure was determined by heavy atom methods (the molecule together with a dichloromethane at half-occupancy) and refined by full-matrix least-squares (Fe, anisotropic, C, O, Cl, H (in fixed positions) isotropic, to R 0.095 (R_w 0.097)). The hydrogen atoms on the two –OH groups could not be located.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

those attached to O(27) and O(57) 72.5°. There are several close 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 3.05 Å; the exception O(8)...O(37) being 4.85 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 2 sites.

Variable temperature solution ^{1}H NMR studies ($CDCl_3$) over the temperature range +50 °C to −50 °C reveal no change in the respective methylene AB pair of doublet absorptions of **4** and **5** suggesting a 'rigid' cone conformation, similar to the solid state structure of **5**, is adopted by both host molecules in solution.

The electrochemical properties of **4** and **5** were investigated in acetonitrile solution by cyclic voltammetry and coulometry. Both compounds exhibit reversible two electron oxidations at +0.90 V (S.C.E.), which suggests that the respective two ferrocene moieties present in both receptors become oxidised in one step. Solution complexation experiments of **4** and **5** with organic guests are currently under investigation.

We thank the SERC for an 'earmarked' studentship to A.D.K., for use of the high field NMR service at the University of Warwick and The Research Corporation Trust, L and D Blond for additional financial support.

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