

## The Synthesis of Metallocene Calix[4]arenes

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**Abstract.** The condensation of 1,1'-bis(chlorocarbonyl)metallocenes and *p*-*tert*-butylcalix[4]arene in toluene leads to novel metallocene calix[4]arenes in which the metallocene subunit bridges the opposite hydroxy groups of the parent calixarene.

**Key words:** Metallocene calix[4]arenes, synthesis, variable temperature NMR studies, electrochemistry.

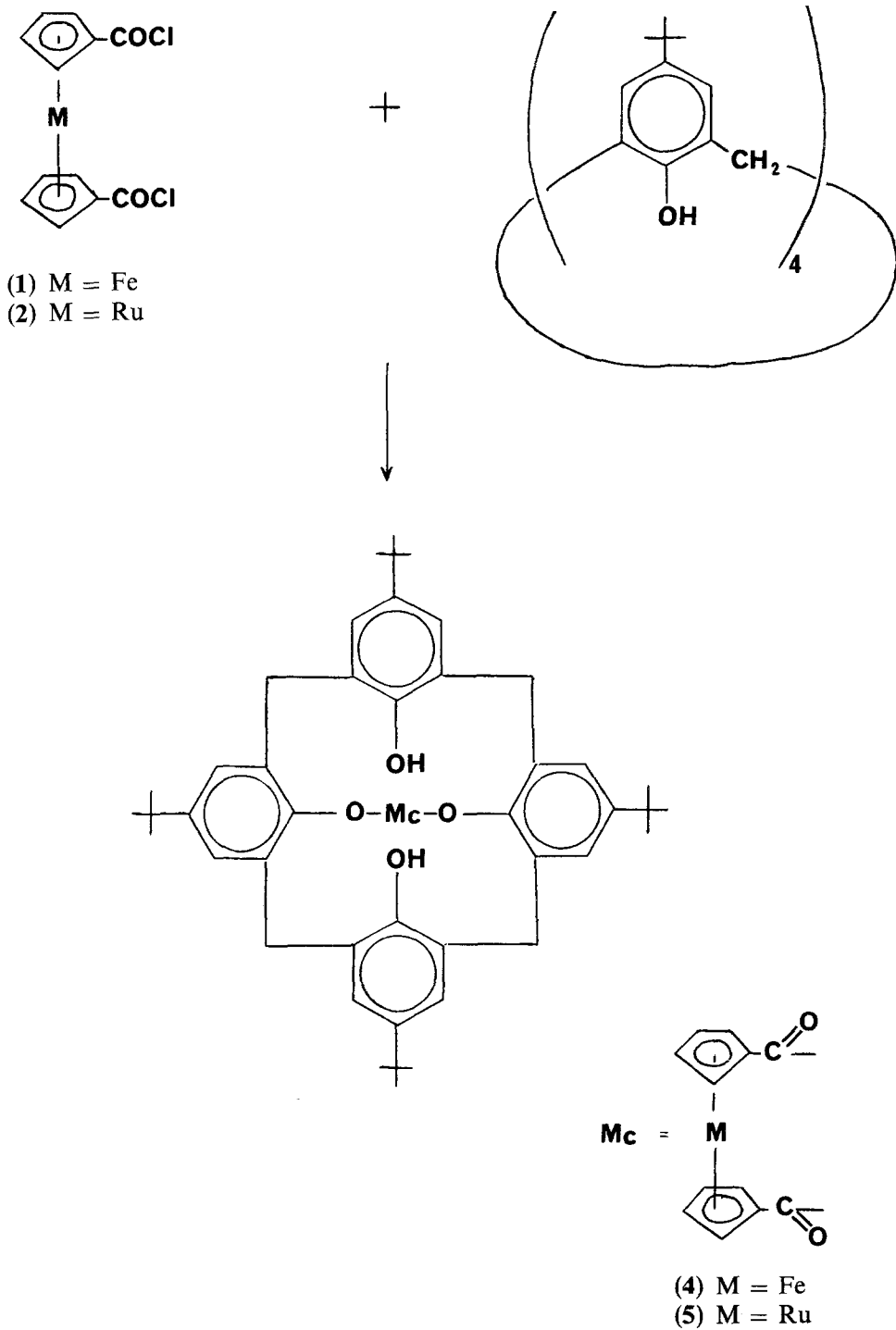
The calixarenes are phenol-formaldehyde cyclic oligomers which possess hydrophobic cavities capable of forming inclusion complexes with aromatic guest molecules in the solid state [1, 2]. They also have the ability to function as ion and molecular carriers as well as enzyme mimics [1, 3, 4].

Calix[4]arenes in solution are conformationally mobile and can exist in four discrete forms, the 'cone', 'partial cone', '1,2-alternate' and '1,3 alternate' conformations [1]. Above room temperature these conformations are rapidly interconverting as shown by dynamic <sup>1</sup>H NMR investigations [5]. In an effort to synthesise 'rigid' calix[4]arenes in the cone conformation a number of workers have introduced bulky substituents on the hydroxy groups with some success, although the partial cone[6] or 1,3-alternate conformations [7] may occasionally be obtained instead. Recently the fixed cone conformation has been achieved by the connection of two *para*-positions by an aliphatic chain of appropriate length [8]. This communication reports the first example of a metallocene calix[4]arene in which the metallocene subunit bridges opposite hydroxy groups of *p*-*tert*-butylcalix[4]arene.

The condensation of respective 1,1'-bis(chlorocarbonyl)-metallocenes (1) and (2) [9, 10] with *p*-*tert*-butylcalix[4]arene [11] (3) in the presence of triethylamine gave, after column chromatography (alumina/CH<sub>2</sub>Cl<sub>2</sub>), the ferrocene calix[4]arene (4) (64% yield, orange crystals) and the ruthenocene analogue (5) (47% yield, pale yellow crystals) (Scheme 1). The structures of both new air-stable metallocene calix[4]arenes were verified by elemental analysis and mass spectrometry. The experimental details for their synthesis and characterisation will be reported elsewhere.

The respective 400 MHz <sup>1</sup>H NMR spectra of (4) and (5) in CDCl<sub>3</sub> at room temperature (298 K) display two broad doublets for the methylenes of (4) and (5) typical of an *AB* system, two singlets for the *t*-butyl groups, two metallocene signals 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 NMR data are similar to those shown by the dimethyl derivative of *p*-*tert*-butylcalix[4]arene [12] and by the crowned *p*-*tert*-butylcalix[4]arenes [3, 13]. These compounds are all

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Scheme 1.

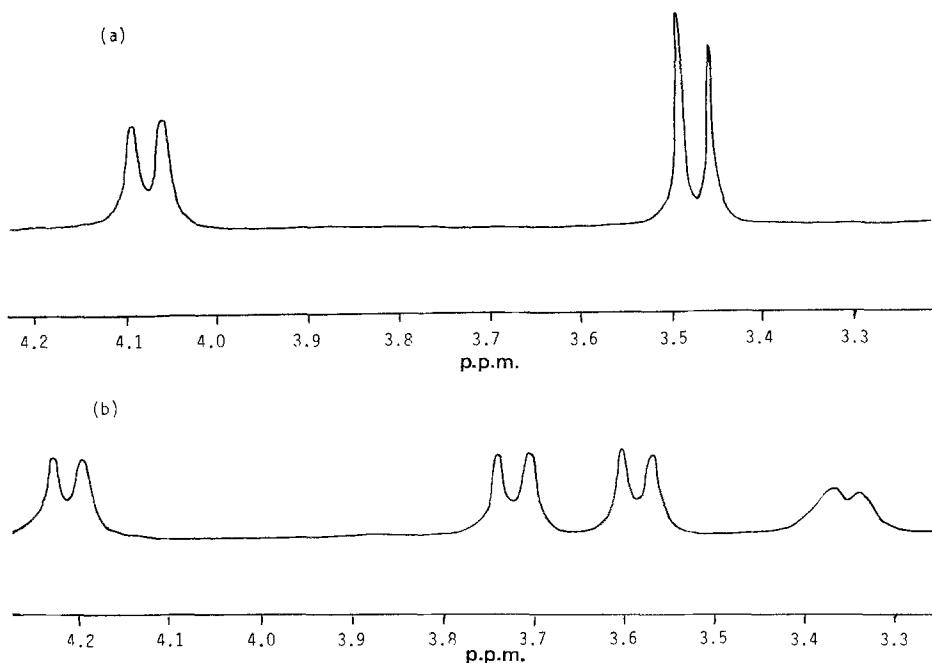


Fig. 1.  $^1\text{H}$  NMR spectrum of the methylene protons of ferrocene calix[4]arene (**4**) at (a) 25 °C (298 K) and (b) -100 °C (173 K) ( $\text{CD}_2\text{Cl}_2$ )

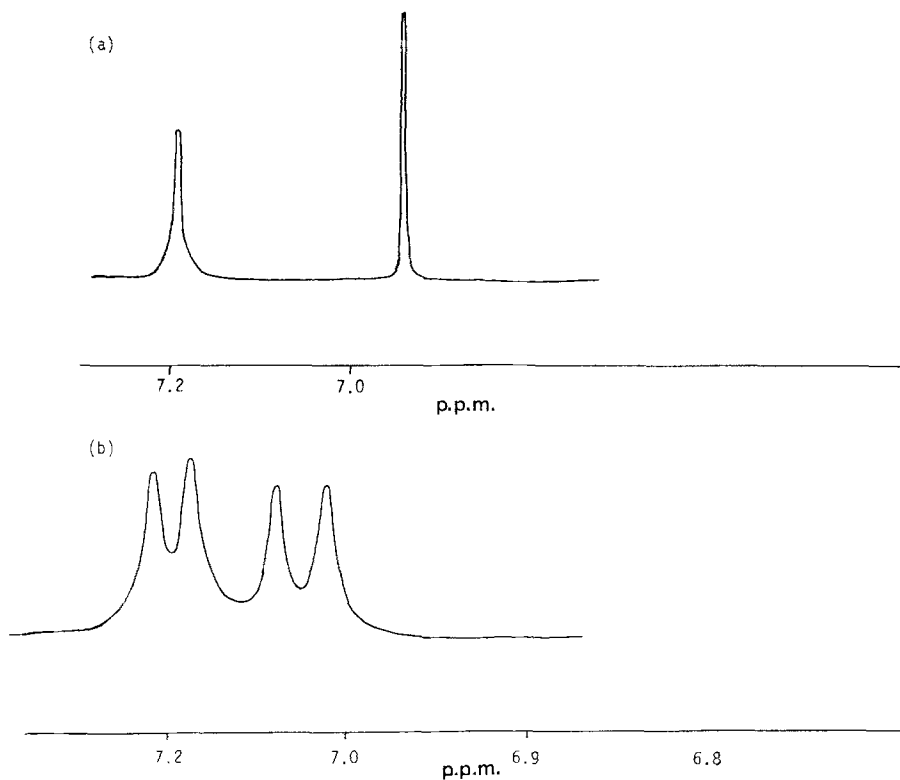


Fig. 2.  $^1\text{H}$  NMR spectrum of the aromatic protons of ferrocene calix[4]arene (**4**) at (a) 25 °C (298 K) and (b) -100 °C (173 K) ( $\text{CD}_2\text{Cl}_2$ ).

(1,3)-calix[4] arene derivatives and have been proved to exist in a "flattened" cone conformation.

However, unexpectedly on cooling the respective samples ( $\text{CDCl}_3$ ) to  $-50^\circ\text{C}$  (223 K) and  $-100^\circ\text{C}$  (173 K) ( $\text{CD}_2\text{Cl}_2$ ) another pair of *AB* doublets appear (Figure 1) along with four singlets for the metallocene protons, four singlets for aromatic protons (Figure 2) and two hydroxyl signals. The *t*-butyl protons now consist of at least three singlets, one of which remains broad even at  $-100^\circ\text{C}$  (Figure 3). Two possible ratio-

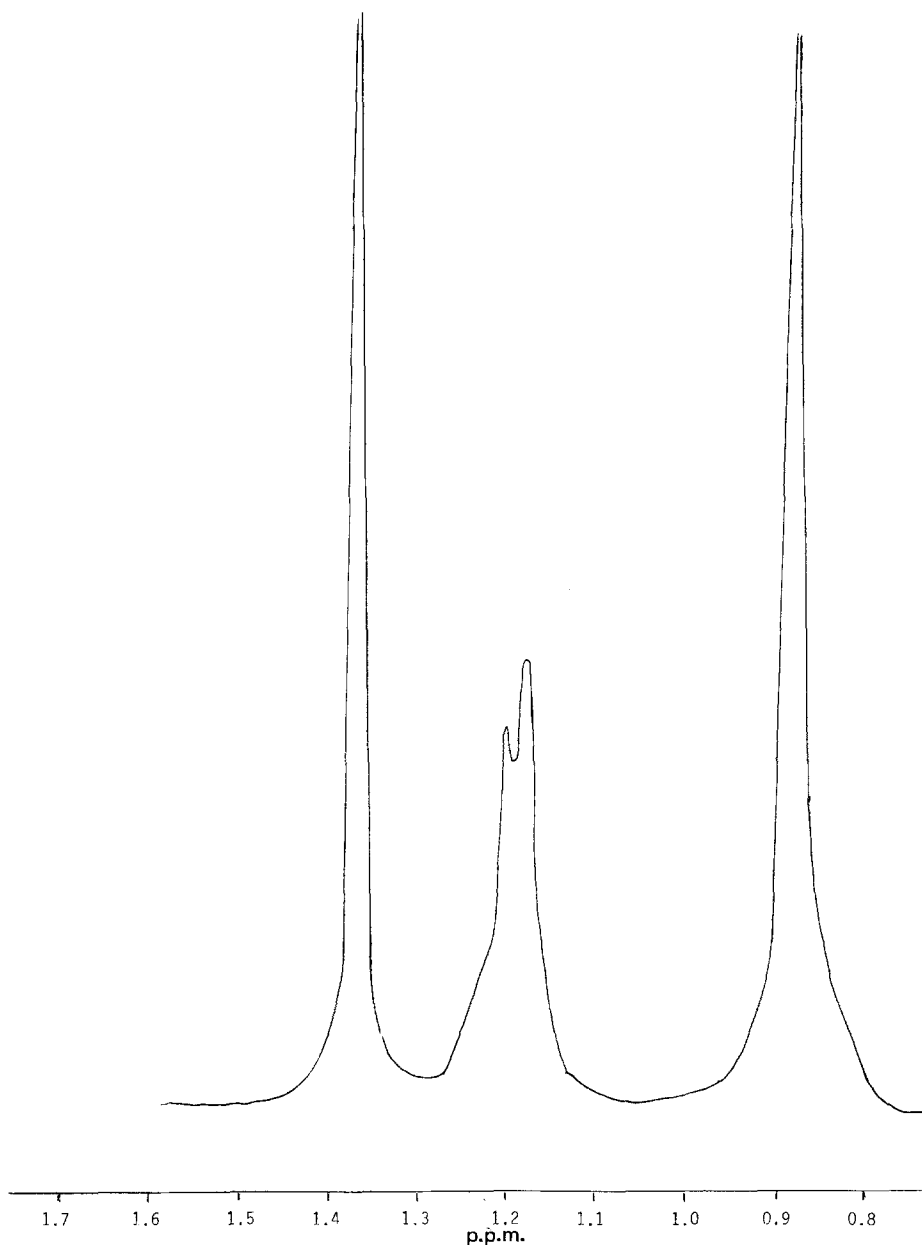


Fig. 3.  $^1\text{H}$  NMR spectrum of the *t*-butyl protons of calix[4]arene (4) at  $-100^\circ\text{C}$  ( $\text{CD}_2\text{Cl}_2$ ).

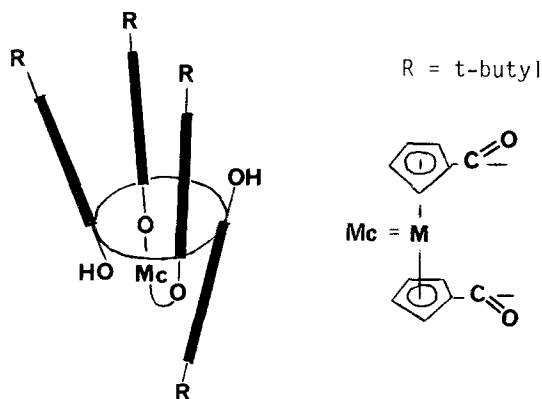


Fig. 4. Partial cone conformation of the metallocene calix[4]arenes.

nalizations may account for this variable temperature NMR behaviour. At low temperatures ( $-100\text{ }^{\circ}\text{C}$ ) the respective  $^1\text{H}$  NMR spectra of (4) and (5) are consistent with a partial cone conformation [7]. See Figure 4.

Alternatively the  $^1\text{H}$  NMR 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 fast on the NMR timescale 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. See Figure 5.

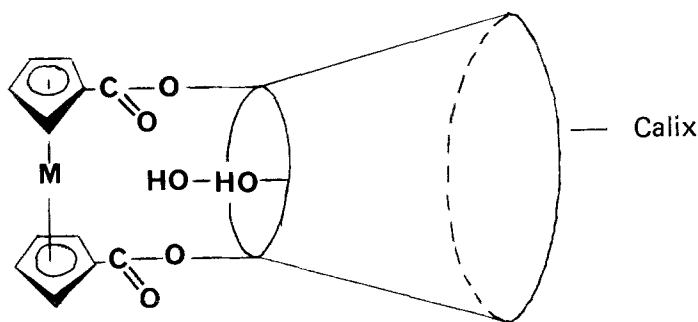


Fig. 5. Metallocene carbonyl groups shown in the *cis* configuration.

Acyl groups in simple acylferrocenes are known to exhibit this type of fluxional behaviour [14]. Unfortunately corroborative evidence from  $^{13}\text{C}$  NMR spectra could not be obtained because of poor solubility of both (4) and (5) in organic solvents. The results of preliminary electrochemical investigations on (4) and on a model

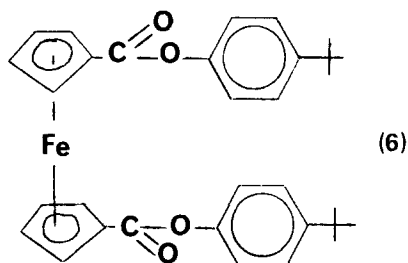


Table I. Electrochemical data

| Compound                       | (4)  | (6)  |
|--------------------------------|------|------|
| $E_{1/2}$ Volts <sup>a</sup>   | +1.2 | +1.2 |
| $\Delta E_p$ <sup>b</sup> (mV) | 80   | 100  |

<sup>a</sup> Obtained in  $\text{CH}_2\text{Cl}_2$  solution containing 0.2 M  $\text{Bu}_4\text{N}^+\text{BF}_4^-$  as supporting electrolyte. Solutions were ca.  $5 \times 10^{-3}$  M in compound and potentials were determined with reference to ferrocene as internal standard but are quoted relative to Ag wire reference electrode.

<sup>b</sup> Separation between anodic and cathodic peak potentials of cyclic voltammograms at a scan rate of  $200 \text{ mv sec}^{-1}$ .

compound (6) are reported in the Table I. Large anodic  $E_{1/2}$  values are found for both compounds.

Solution complexation experiments of the metallocene calix[4]arenes with organic guests are currently under investigation.

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