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Preliminary communication

Redox-active dinuclear macrocycles designed to bind and activate small molecules

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Abstract

The syntheses, electrochemistry and preliminary coordination studies of novel redox-active dinucleating macrocyclic molecules $(FcCH_2SCH_2RCH_2SCH_2)_2$ (Fc = ferrocenyl, R = CH_2SCH_2, NC_5H_3) and their acyclic analogues, which incorporate ferrocene subunits into cyclic and acyclic structural frameworks are described.

There is considerable current interest in the synthesis of dinucleating macrocycles designed to bind two metals close to one another [1,2]. Such model systems can be used to study the unique properties of bimetallic centres in biology [3] (magnetic coupling, electron transfer, modified redox properties). They also have the potential to bind and activate small molecules such as olefins, acetylenes, CO, CO_2, etc. between the metal centres for the purpose of bringing about regio- or stereo-specific reactions in a stoichiometric or catalytic fashion [4].

Redox reactions on an included substrate may be facilitated by Lewis acid-substrate activation. Figure 1 depicts the principle of polymetallic activation of a substrate by one such catalytic system. With this in mind, we describe here the syntheses, electrochemical properties and preliminary coordination studies of new dinucleating macrocyclic and acyclic molecules, which incorporate redox-active ferrocene subunits into a cyclic or acyclic structural framework that contain additional recognition sites for transition metal guests.

In application of the methodology derived by Ratajczak and co-workers [5], the macrocyclic species **3** and **5** were prepared by the reaction of 1,1′-bis(hydroxymethyl)ferrocene (**1**) [6] with the appropriate dithiol **2** [7] or **4** in the presence of a catalytic amount of trifluoroacetic acid under high dilution in dichloromethane (Scheme 1). Both macrocycles were obtained as air stable crystalline solids **3** (m.p. 85–87 °C); **5**, (decomp 180 °C) in yields of 10–15%. Analogous synthetic proce-

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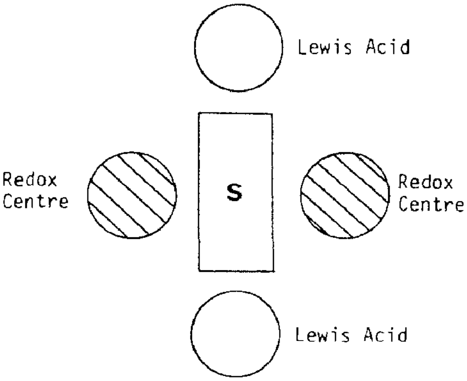
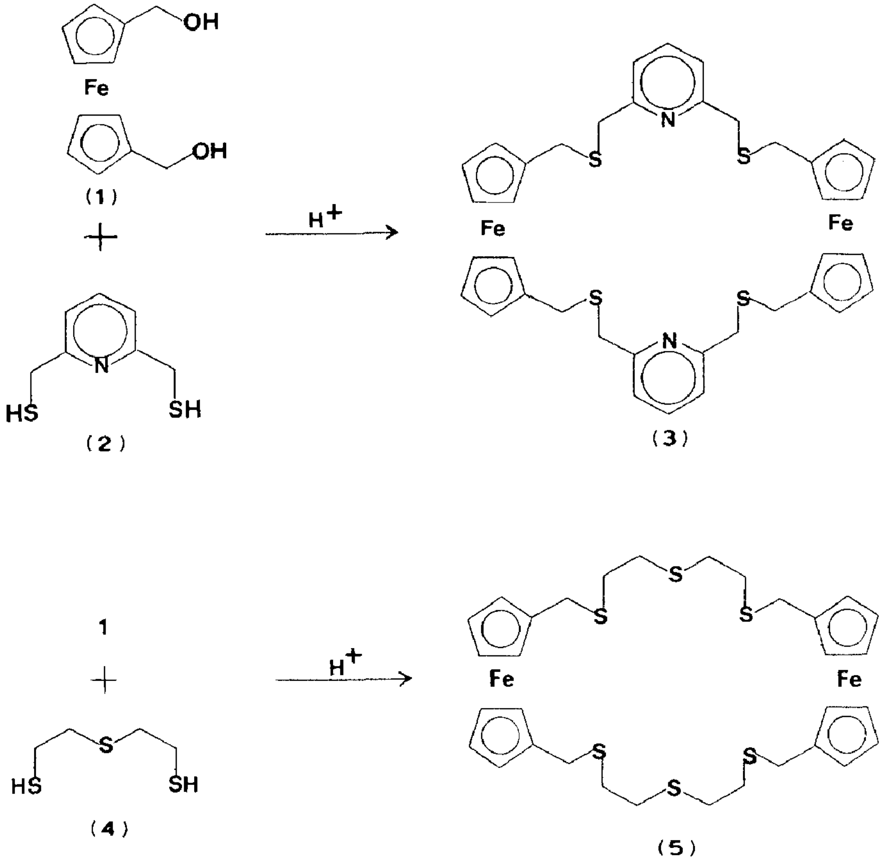


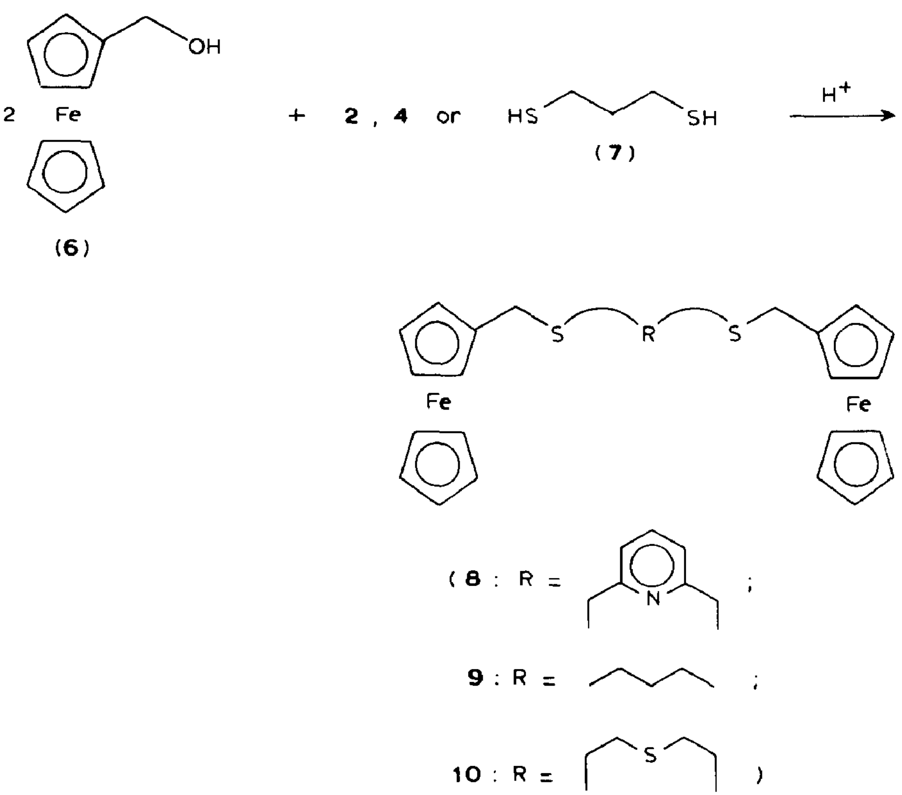
Fig. 1. Depiction of the principle of catalytic polymetallic activation of an included substrate S by a redox active dinuclear macrocyclic system.

dures using hydroxymethylferrocene (**6**) [8] and various dithiols, (**2**, **4**, **7**) as starting materials and acid catalysis were used to prepare the new acyclic bis-ferrocenyl compounds **8**–**10** in reasonable yields; Scheme 2.

The structures of all these new air stable compounds were characterised by elemental analyses, fast atom bombardment mass spectrometry (FABMS), and ^{1}H NMR spectroscopy.



Scheme 1



Scheme 2

The electrochemical properties of **3**, **5** and **8**–**10** were investigated in dry dichloromethane solution by cyclic voltammetry and coulometry with [n-Bu$_4$N]BF$_4$ as the supporting electrolyte, a platinum bead working electrode, and a standard calomel electrode (SCE) as reference (Table 1). All the compounds exhibit reversible two electron oxidations, suggesting that both the ferrocenyl moieties become oxidised in one step.

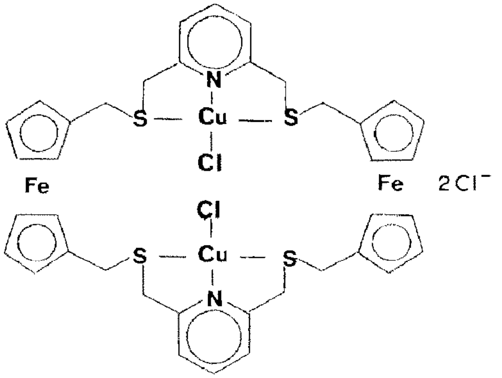
Preliminary coordination studies have been carried out on **3**, **8** and **9**. Addition of $CuCl_2 \cdot 2H_2O$ to a methanol solution of **3** gave the novel dinuclear macrocyclic complex **11**, which was characterised by elemental analysis and FABMS. Reaction

Table 1

Electrochemical data [a]

Compound	E_{pa} (V)	E_{pc} (V)
3	0.57	0.47
5	0.62	0.52
8	0.57	0.47
9	0.63	0.52
10	0.64	0.55

[a] Obtained from cyclic voltammetry studies in dry dichloromethane solvent containing 0.2 *M* n-Bu$_4$NBF$_4$ as supporting electrolyte. Solutions were ca. 2×10^{-3} *M* in compound and potentials were determined with reference to SCE. Coulometric studies revealed each reversible redox couple to be a two electron oxidation process.



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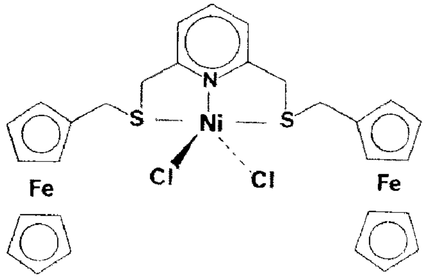

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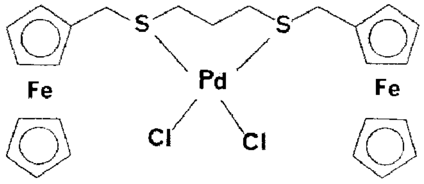

(13)

of $NiCl_2 \cdot 6H_2O$ with **8** in methanol/ethyl acetate solvent mixture gave a green complex (**12**) in near quantitative yield. The palladium(II) complex **13** was prepared from **9** and $(C_6H_5CN)_2PdCl_2$.

We are currently extending our coordination studies to the synthesis of related dinuclear and mononuclear transition metal complexes of potential catalytic interest.

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