



Synthesis, reactivity, electrochemical behaviour, and molecular structure of crown ether cyrhetrene complexes



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ABSTRACT

Cyrhetrenyl crown ether complexes $[(\eta^5\text{-C}_5\text{H}_4\text{CH=N-M})\text{Re}(\text{CO})_3]$ (where M = 4-benzo-15-crown-5 (**3a**), 4-benzo-18-crown-6 (**3b**), 2-methyl-15-crown-5 (**3c**), or 2-methyl-18-crown-6 (**3d**)) were synthesised from cyrhetrenylcarboxaldehyde (**1**) and the corresponding crown ether amines **2a–d**. All the complexes were characterised by IR spectroscopy, ¹H and ¹³C NMR spectroscopies, and mass spectrometry. The stereochemistry for imine compounds **3a–d** were determined using the ¹H and ¹³C NMR spectroscopy data, which indicated that these complexes have the anti-(*E*) conformation. This was also confirmed by the X-ray crystal structures of **3b** and **3c** in the solid state. Additionally, the electrochemical behaviours of **1** and **3a–d** were studied.

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Introduction

Organometallic complexes containing cyclopentadienyl-functionalised ligands ($\eta^5\text{-C}_5\text{H}_4\text{R}$) have received considerable attention mainly because the functional group R (e.g., phosphine, amine, alkene, and sulfide) can act as a donor or spectator ligand. Such groups are known as *hemilabile* ligands and have interesting applications in homogeneous catalysis, such as in olefin polymerisation [1–4], hydrogenation of ketones [5], and alcohol oxidation [6]. Biomolecules linked to a pentagonal ring have also found applications in biomedicine. For instance, Orvig et al. reported the synthesis of several cyclopentadienyl-glucosamine-conjugated rhenium and technetium tricarbonyl complexes and were evaluated them as substrates of hexokinase inhibitors [7]. Meanwhile, Nordlander et al. reported on the synthesis of cymantrene and cyrhetrene 4-aminoquinoline conjugates and evaluated their biological activity against malaria, leishmaniasis, and trypanosomiasis [8]. Recently, Madureira reported on the synthesis and evaluation of the leishmanicidal activity of ferrocenyl N-heterocyclic complexes [9].

Another important class of cyclopentadienyl-functionalised metal complexes are those substituted with a crown ether or azamacrocyclic units. These type of compounds which are typically coupled with redox active organometallic fragments such as ferrocene (most commonly used) and crown ethers, azamacrocycles or nitrogen–sulfur mixed-macrocycles have attracted the attention of several research groups, owing to their applications as redox-responsive chemosensors [10]. The use of such complexes in molecular recognition and host–guest interaction applications has been demonstrated.

The design strategy for these systems as chemosensors are dictated by the following two well known properties: (i) macrocyclic receptors have certain advantages over acyclic structures, which provide more selective complexation to metal ions and (ii) the inclusion of various donor atoms in the macrocycles can be used to control the selectivity [11]. In addition, the selectivity can be enhanced by combining ring of different sizes or by properly arranging the donor atoms in the macrocyclic fragments. From an electrochemical point of view, ferrocene and to a lower extent cobaltocenes containing macrocyclic fragments, have been widely used as redox centres for cation and anion detection [12]. Crown ethers mainly coordinate with alkali and alkaline-earth ions, whereas, the binding sites on the azamacrocycles or mixed

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macrocycles are more appropriate for coordination with transition metal ions.

Other types of systems involving the synthesis of phthalocyanines functionalised with aza-macrocylic fragments have been recently reported by Bıyıklıođlu. These species can be used as precursors in the syntheses of the zinc (II) and cobalt (II) derivatives. Spectroscopic and electrochemical studies have been performed in water and other polar organic solvents, which show that these complexes undergo redox processes involving the ligand [13]. To the best of our knowledge the only previous example of a rhenium (I) tricarbonyl complex linked to an azacrown ether moiety was reported by Moore et al. This complex, [(bpy)Re(CO)₃(4-(4-aza-15-crown-5-styr-yl)pyridine)]⁺ can act as a photo-switchable device and its protonation can be used to control the *trans*–*cis* photoisomerisation reaction [14]. Further, in other studies, the excited states have been characterized and the structure and bonding of complexes in which a metal cation (Li⁺, Na⁺, Ca²⁺, Ba²⁺) is bound to the azacrown have been determined. There is evidence that these systems release the metal cation upon excitation [15].

In this work, we report the synthesis and electrochemical behaviour of new cyrhetrenyl tricarbonyl complexes functionalised with 4'-benzo-crown or 2-methyl-crown ether fragments, bridged by an imine linker.

Results and discussion

Synthesis of the imine complexes **3a–d**

The cyrhetrenyl crown ether complexes [(η⁵-C₅H₄CH=N-M)Re(CO)₃] (where M = 4'-benzo-15-crown-5 (**3a**), 4'-benzo-18-crown-6 (**3b**), 2-methyl-15-crown-5 (**3c**), or 2-methyl-18-crown-6 (**3d**)) were synthesised using a procedure similar to that described previously in literature for cyrhetrenylimine derivatives [16]. That procedure involved condensation of the cyrhetrenylcarboxaldehyde (**1**) and the corresponding crown ether amines **2a–d** (Scheme 1). The reaction mixtures were refluxed overnight with a 4 Å molecular sieve to remove the water formed during the reaction. The IR spectra (CH₂Cl₂ solution) measured after this procedure showed the disappearance of the peaks corresponding to the starting material and the appearance of new absorption bands from the corresponding imines **3a–b**, i.e. ν_{C=N} stretching around 1630 cm⁻¹. As expected, the ν_{C=N} band for the methylene derivatives **3c–d** was observed at higher frequency (~1650 cm⁻¹)

compared to **3a–b** owing to an increase of the electron density in **3c–d** due to the presence of the electron donating CH₂-crown moiety. The frequencies for both ν_{C=N} and ν_{CO} observed in this study are in a good agreement with the values reported for the related complexes [16–20].

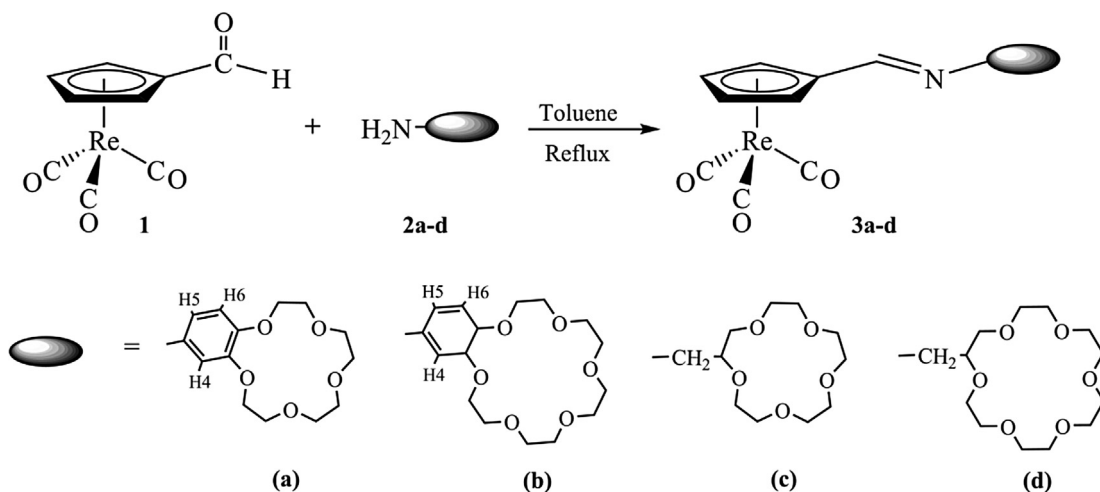
Schiff bases **3a–d** were isolated as pure samples after successive recrystallisations in hexane. Complexes **3b** and **3c** were obtained as solid crystals and characterised using X-ray crystallography (*vide infra*).

The ¹H NMR spectra of **3a–b** (Fig. S.I.) indicated the presence of one singlet at about 8.0 ppm, which was assigned to the iminic protons, and two multiplets which were attributed to the cyclopentadienyl protons. Three resonances were also observed for these compounds. A doublet of doublet centered at around δ: 7.18 (J_{HH} 2.4 and 8.7 Hz) was unequivocally assigned to proton H₅. The one doublet at δ: 6.98 (J_{HH} 8.7 Hz) was assigned to proton H₆, whereas the doublet observed at δ: 7.39 (J_{HH} 2.4 Hz) was attributed to proton H₄ based on the combination of 1D and 2D NMR spectral data.

Furthermore, the ¹³C NMR spectra of **3a–d** showed a singlet corresponding to equivalent CO ligands that δ: ~193. At lower frequencies, the ¹³C NMR spectra also exhibited a single resonance around 152 ppm, which was assigned to iminic carbon. The location of this resonance is in good agreement to that reported by related organometallic Schiff bases, having the *E* isomer. Further proof of the stereochemistry was provided by the X-ray crystal structures of **3b** and **3c** (*vide infra*) [16,21,22].

In contrast, the ¹H NMR spectra for **3c–d** in the 5–6 ppm region showed the presence of three resonances in a 1:1:2 intensity ratio (Fig. 1). This unusual pattern could potentially be produced by the interaction of a lone pair of the iminyl nitrogen atom with the hydrogen of the pentagonal ring. Such interactions can be explained by considering an increase in the basicity of the iminyl nitrogen due to the electron donor effect of the methylene group attached to it. Further evidences will be discussed in the X-ray crystallography section.

In addition, the ¹H NMR spectrum of **3c** showed a doublet centred at δ: 3.46 (J_{HH} = 6.6 and 12.2 Hz), which was assigned to one of the diastereotopic protons of the methylene group (H₄). The other one (H_{4'}) overlapped with the resonances attributed to a crown ether fragment. Furthermore, the ¹H–¹³C HSQC 2D NMR spectrum showed that the singlet at 62.7 ppm was due to the diastereotopic protons (H₄ and H_{4'}) (Fig. S.I.). The same behaviour was observed for **3d**.



Scheme 1. Synthesis of cyrhetrene imine **3a–d**.

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