

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].

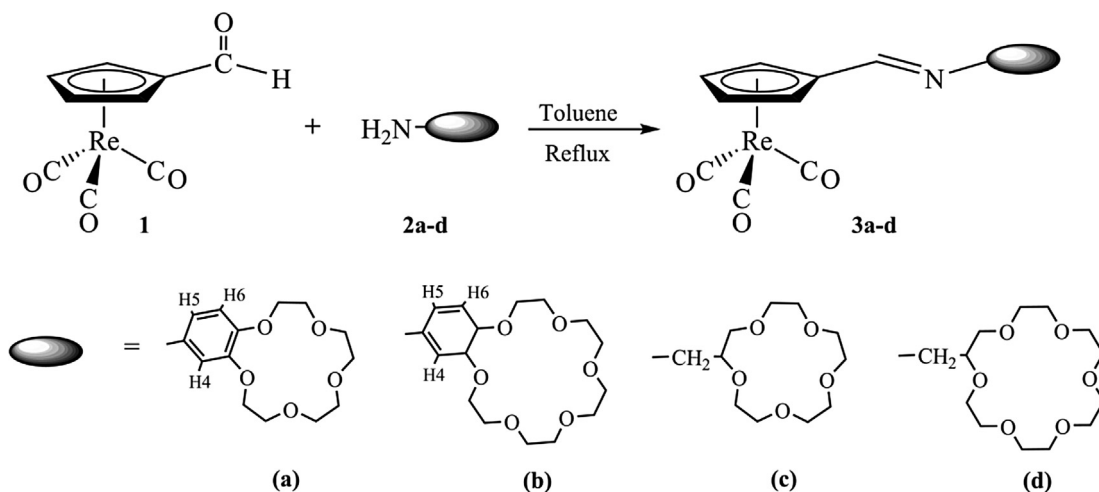
Schiff bases **3a–d** were isolated as pure samples after successive recrystallisations in hexane. Complexes **3b** and **3c** were obtained as solid crystals and characterised using X-ray crystallography (*vide infra*).

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**.

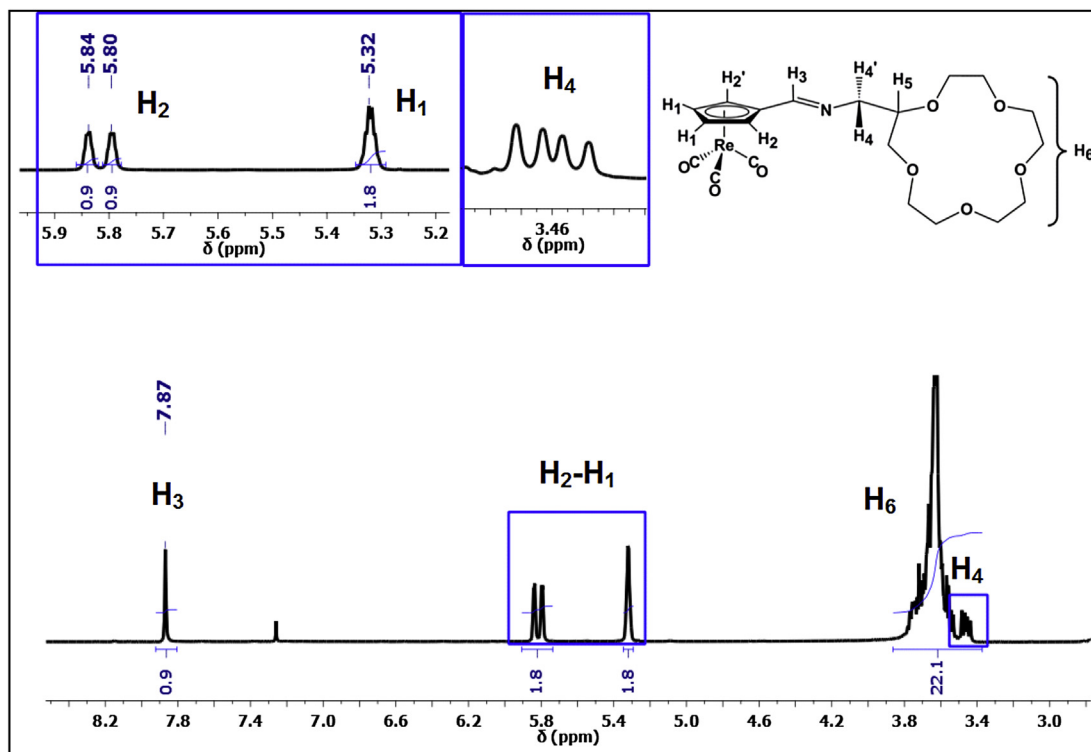


Fig. 1. Proton ^1H NMR spectrum of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH=N-2-methyl-15-crown-5})\text{Re}(\text{CO})_3]$ (**3c**) in CDCl_3 at 298 K.

The mass spectrum of **3a–d** exhibits the presence of a molecular ion and fragments corresponding to the loss of one CO group. In all the cases, a typical fragmentation pattern was observed for the rhenium complexes [16–21].

Crystal structure of **3b** and **3c**

The molecular structures of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH=N-4'-benzo-18-crown-6})\text{Re}(\text{CO})_3]$ (**3b**) and $[(\eta^5\text{-C}_5\text{H}_4\text{-CH=N-2-methyl-15-crown-5})\text{Re}(\text{CO})_3]$ (**3c**) are shown in Figs. 2 and 3, respectively. In addition, the crystal structure and refinement data are reported in Table 1.

The complex **3b** crystallises in the monoclinic space group $P2_1/n$, with two molecules in the asymmetric unit. On the other hand, the complex **3c** crystallizes in the monoclinic space group $P2_1/c$, with only one molecule per asymmetric unit.

The cyrhetrenyl moiety in both the structures exhibits a typical three-legged piano-stool type of structure. The rhenium atom is coordinated with the cyclopentadienyl at ring centroid-rhenium distances of 1.956(4)/1.952(4) and 1.966(7) Å for molecules **3b** and **3c** respectively, in a typical η^5 -coordination fashion. In addition, the Re-CO distances and Re-C-O angles are similar to the values previously reported for cyclopentadienyl functionalised rhenium complexes [22].

The dihedral angle between the C5 ring plane and iminyl group plane are 9.7(4)/7.7(4)° and 5.4(4)° for **3b** and **3c** respectively. Thus, the imine moiety is nearly coplanar with the C5 ring plane. On the other hand, in the molecular structure of **3b**, the benzo ring is rotated by 39.6(7)/34.8(7)° with respect to the C=N group. The structure confirms the *E* configuration assigned tentatively based on the NMR spectral data. The C=N bond length (1.277 Å) agrees well with the values reported for cyrhetrenyl and ferrocenyl imines.

The molecular structures of **3b** and **3c** and the H(7)⋯N(1) bond length of CH(cyclopentadienyl)-nitrogen (2.832(7) for **3b** and

2.879(5) Å for **3c**) can be considered to be a result of weak interactions and is a typical of the bonds formed between CH donors and nitrogen or oxygen acceptors with a bond energy $< 4 \text{ kcal mol}^{-1}$ [23].

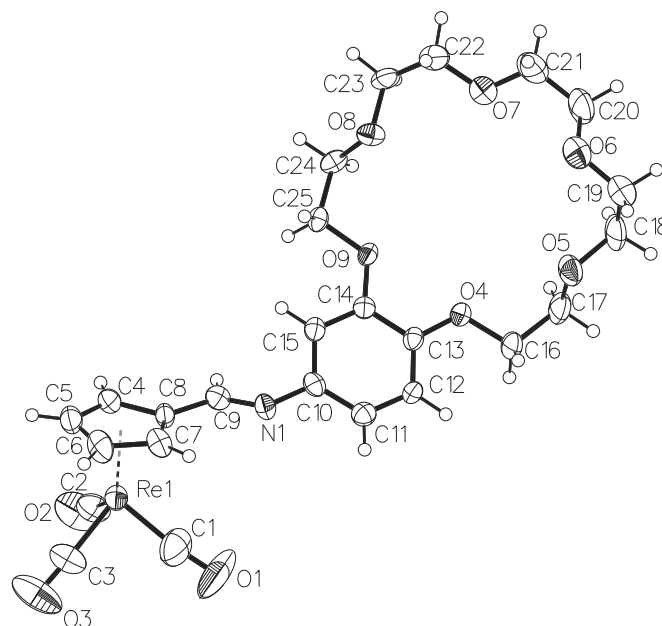


Fig. 2. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH=N-4'-benzo-18-crown-6})\text{Re}(\text{CO})_3]$ (**3b**· H_2O). Selected bond lengths (in Å) and angles (in deg): C(9)–N(1), 1.257(9); N(1)–C(10), 1.418(9); C(8)–C(9), 1.462(9); C(4)–C(5), 1.463(10); C(5)–C(6), 1.381(12); C(6)–C(7), 1.420(11); C(7)–C(8), 1.401(10); C(4)–C(8), 1.419(10); C(8)–C(9)–N(1), 120.6(7); C(9)–N(1)–C(10), 117.3(9); N(1)–C(10)–C(11), 119.8(7); N(1)–C(10)–C(15), 121.7(7).

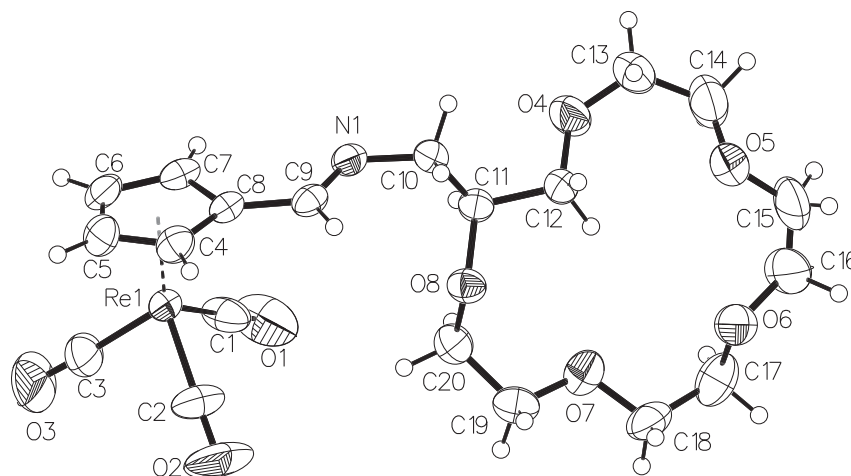


Fig. 3. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH=N-CH}_2\text{-15-crown-5)Re(CO)}_3]$. Selected bond lengths (in Å) and angles (in deg): C(9)–N(1), 1.258(8); N(1)–C(10), 1.451(9); C(8)–C(9), 1.462(9); C(4)–C(5), 1.371(10); C(5)–C(6), 1.410(12); C(6)–C(7), 1.395(11); C(7)–C(8), 1.418(9); C(4)–C(8), 1.422(10); C(8)–C(9)–N(1), 121.5(6); C(9)–N(1)–C(10), 116.8(6); N(1)–C(10)–C(11), 112.1(6).

Table 1
Crystal data and structure refinement for **3b** and **3c**.

| | 3b | 3c |
|--|--|--|
| Empirical formula | $\text{C}_{50}\text{H}_{58}\text{N}_2\text{O}_{19}\text{Re}_2$ | $\text{C}_{20}\text{H}_{26}\text{NO}_8\text{Re}$ |
| Formula weight | 1363.38 | 594.63 |
| Temperature/K | 296.15 | 297(2) |
| Crystal size/mm | $0.269 \times 0.034 \times 0.025$ | $0.28 \times 0.24 \times 0.01$ |
| $\lambda/\text{Å}$ | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| a (Å) | 21.4489(11) | 14.5701(13) |
| b (Å) | 11.9635(6) | 19.1499(17) |
| c (Å) | 22.6648(11) | 8.2442(7) |
| α (°) | 90 | 90 |
| β (°) | 103.2740(10) | 94.748(1) |
| γ (°) | 90 | 90 |
| Volume (Å ³) | 5660.5(5) | 2292.4(3) |
| Z | 4 | 4 |
| ρ_{calc} (mg/mm ³) | 1.600 | 1.723 |
| μ/mm^{-1} | 4.343 | 5.344 |
| $F(000)$ | 2696.0 | 1168.0 |
| 2θ range for data collection (°) | 4.142–53.016 | 3.52–55.6 |
| Index ranges | $-26 \leq h \leq 26, -15 \leq k \leq 15, -28 \leq l \leq 28$ | $-18 \leq h \leq 19, -25 \leq k \leq 24, -10 \leq l \leq 10$ |
| Reflections collected | 264,544 | 18,787 |
| Independent reflections | 11,684 [$R(\text{int}) = 0.3490$] | 5117 [$R(\text{int}) = 0.0299$] |
| Data/restraints/parameters | 11,684/0/665 | 5117/1/271 |
| Goodness-of-fit on F^2 | 0.950 | 1.204 |
| Final R indexes [$I > 2\sigma(I)$] | $R_1 = 0.0527, wR_2 = 0.0849$ | $R_1 = 0.0439, wR_2 = 0.0979$ |
| Final R indexes [all data] | $R_1 = 0.14225, wR_2 = 0.1001$ | $R_1 = 0.0592, wR_2 = 0.1026$ |
| Largest diff. peak/hole/e Å ⁻³ | 1.00/–0.75 | 1.14/–0.37 |

Electrochemical behaviour of organometallic complexes

With the aim of determining the electronic effect of the organic fragment (4'-benzo or 2-methyl) located between the iminic nitrogen and the crown ether moiety, we conducted electrochemical characterization experiments using low scan rate cyclic voltammetry, with 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile as the supporting electrolyte, for both the cyrhetrenyl aldehyde precursor (**1**) and complexes **3a–d**.

Fig. 4 shows the cyclic voltammograms (CVs) of the precursor $[(\eta^5\text{-C}_5\text{H}_4\text{CHO)Re(CO)}_3]$ (**1**) and complexes **3a–d** measured in the potential range of -1.00 to $+1.70$ V. Irreversible redox processes were observed for both types of complexes. The CV of **1** shows the occurrence of typical redox processes that are characteristic of this type of complexes. A single-electron oxidation was observed at

1.29 V and was assigned to the $[(\eta^5\text{-C}_5\text{H}_4\text{CHO)Re(CO)}_3]^0 \Rightarrow [(\eta^5\text{-C}_5\text{H}_4\text{CHO)Re(CO)}_3]^+$ metal-centred process, which under the experimental conditions was irreversible. We verify experimentally, in an indirect way, the one-electron oxidation process character of the complex **1**. We performed additional experiments of CV in the same conditions of Fig. 4 adding equal concentrations (1 mM) of ferrocene and cyrhetrene complex (**1**). Both compounds exhibited single oxidation waves involving similar electrical charge values; 10.9 C for ferrocene and 9.1 C for cyrhetrene complex (**1**) (see Fig. S11). The CV of **1** also showed a barely visible broad irreversible cathodic wave at about -0.51 V. Our first attempt was to attribute this cathodic wave to the electrochemical reduction of the dimeric species $[(\eta^5\text{-C}_5\text{H}_4\text{CHO)Re(CO)}_3]_2^+$, which was formed by the radical coupling of the oxidised product [24]. But the excessive degree of irreversibility, given by the ΔE_p around 1.5 V, between the

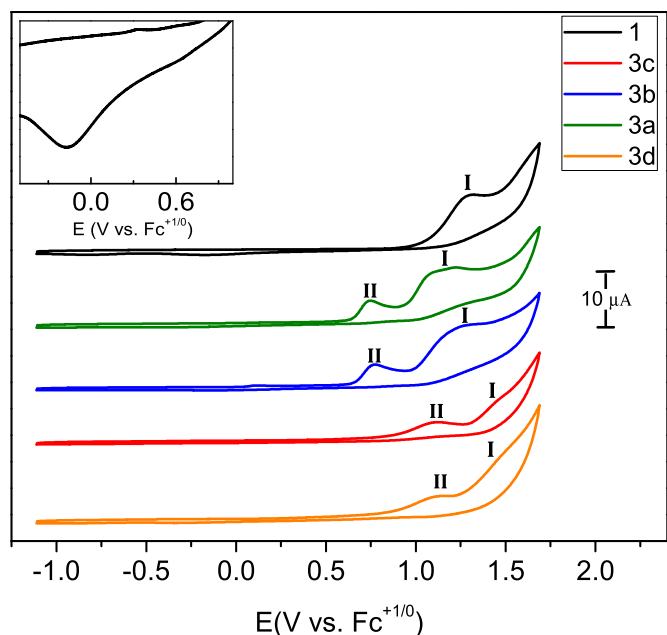


Fig. 4. Cyclic voltammograms of $(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{Re}(\text{CO})_3$ (**1**) and **3a–d** in 0.1 M solution of Bu_4NBF_4 in CH_3CN ; scan rate: 50 mV s^{-1} , complex concentration: 10^{-3} M .

metal-centred electrooxidation and reduction observed processes seems to suggest that these processes are not be related to each other, and the reduction wave could be attributed to the reduction of uncharacterized products generated during the scan.

In all the cases, the CVs showed positive anodic waves due to the Re(II)/Re(I) redox processes (I in Fig. 4). By comparing the CVs of **3a** and **3b** (with peaks at 1.22 and 1.20 V respectively) it can be concluded that the size of the crown ether did not change the anodic peak potential significantly. In contrast, the metal centred redox processes of complexes **3c** and **3d** shifted to positive potentials by about 0.28 V compared to the benzo derivatives **3a–b**. This shift was probably due to the electronic effect of the CH_2 group bound directly to the iminyl nitrogen in **3a–b**, which are efficiently transferred to the metal centre.

Similar electrochemical behaviours were also observed for the less intense anodic waves at potentials of 0.74 (**3a**), 0.76 (**3b**), 1.10 V (**3c**) and 1.14 (**3d**), which were attributed to the oxidation of the organic moiety (II). In addition to the electronic effects, the positive shift in the anionic potential shift of both the metal-centred and the imine redox processes can be attributed to the intramolecular formation of a five-member ring by involving the iminic nitrogen and the H_7 of the Cp ring (Fig. 3). Likely to the greater electronic delocalization of the imine-phenyl moiety, which could make the imine harder to oxidize [25].

Conclusion

A family of four new cyrhetrene imine crown ether complexes was synthesised with good to moderated yields and fully characterised. The NMR spectra indicated that these compounds adopted an anti-(*E*) conformation in solution, which was also confirmed by X-ray crystallography data for two of the complexes. The methylene linker in **3c–d** exhibited diastereotopic behaviour, as determined from the 2D NMR data. The CVs of **3a–d**, showed positive anodic waves arising from the Re(II)/Re(I) redox process (I). Based on the anodic wave potentials (15-crown-5 vs 18-crown-6), it was concluded that the size of the crown ether did not change the anodic potential significantly. Nevertheless, the metal centred redox processes of complexes **3c–d** were shifted by around 0.28 V

in the positive direction compared to benzo derivatives **3a–b**, which was attributed to electronic effects and the intramolecular formation of a five member ring involving iminic nitrogen and one proton of the pentagonal ring.

Experimental

General methods

All the reactions were carried out using the standard Schlenk technique under nitrogen atmosphere. All the solvents were purified and dried by conventional methods and were distilled under nitrogen prior to use. 4'-Aminobenzo-15-crown-5, 4'-aminobenzo-18-crown-6, 2-aminomethyl-15-crown-5, and 2-aminomethyl-18-crown-6 (Aldrich) were used as-received. $[(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{Re}(\text{CO})_3]$ was synthesised following procedures described in literature [26]. IR spectra were recorded in solution (using a CaF_2 cell) on a Perkin–Elmer FT-65 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 400 instrument. All the ^1H NMR chemical shifts were referenced to the chemical shifts of residual solvent resonances, whereas the ^{13}C NMR chemical shifts were referenced to the solvent peaks. Mass spectra were recorded on a GCMS-QP5050A Shimadzu instrument. Cyclic voltammetric (CV) studies were carried out at room temperature using a potentiostat (Metrohm Autolab potentiostat) in a three-electrode cell configuration with a 2 mm Pt electrode, a Pt coil counter electrode, and a Ag/Ag^+ reference electrode. The inner solutions employed for the Ag/Ag^+ reference electrodes were prepared with the same organic solvents as the electrochemical solutions, and calibrated against metallic lithium in the same solution. The working electrode was polished with 0.3 and $0.05 \mu\text{m}$ alumina slurries, rinsed with distilled water (18 M Ω cm) and acetone, and dried prior to use. All electrolyte solutions were thoroughly pre-purged using purified nitrogen gas before use. The measurements were carried out at 50 mV/s scan rate in dry and deoxygenated $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NBF}_4$. The ferrocenium/ferrocene ($\text{Fc}^{+/0}$) couple served as internal reference. All the potentials are expressed against $\text{Fc}^{+/0}$.

Preparation

Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH=N-4'-benzo-15-crown-5})\text{Re}(\text{CO})_3]$ (**3a**)

4'-Aminobenzo-15-crown-5 (78 mg, 0.276 mmol) was added to a solution of $(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{Re}(\text{CO})_3$ (100 mg, 0.276 mmol) in dry toluene (15 mL). The reaction mixture was refluxed for 12 h with a 4 Å molecular sieve. Following this procedure, the IR spectrum of the solution was measured and showed the disappearance of the starting material (i.e., 2033s, 1940, 1694w cm^{-1} disappeared) and the appearance of the new CO absorptions bands attributed to **3a**. The reaction mixture was filtered through Celite and the solvent was concentrated under reduced pressure. Compound **3a** was obtained as a yellow oily liquid. (yield: 150 mg, 0.239 mmol, 87%). IR [CH_2Cl_2 , cm^{-1}] $\nu(\text{CO})$: 2026 (s) 1937 (s) $\nu(\text{C=N})$: 1636 (w). ^1H NMR (CDCl_3) δ : 3.76 (m, 8H, CH_2); 3.91 (m, 4H, CH_2); 4.15 (m, 4H, CH_2); 5.41 (t, 2H, $J_{\text{HH}} = 2.2 \text{ Hz}$, C_5H_4); 5.95 (t, 2H, $J_{\text{HH}} = 2.2 \text{ Hz}$, C_5H_4); 6.68 (dd, 1H, $J_{\text{HH}} = 2.4$; 8.4 Hz, $\text{C}_6\text{H}_3\text{O}_2$); 6.71 (d, 1H, $J_{\text{HH}} = 2.4 \text{ Hz}$, $\text{C}_6\text{H}_3\text{O}_2$); 6.85 (d, 1H, $J_{\text{HH}} = 8.4 \text{ Hz}$, $\text{C}_6\text{H}_3\text{O}_2$); 8.07 (s, 1H, CH=N). ^{13}C NMR (CDCl_3): 69.4; 69.8; 69.9; 70.0; 70.9; 71.0; 71.5; 71.6 (8s, CH_2); 85.3 (s, C_5H_4); 86.1 (s, C_5H_4); 100.6 (s, C_{ipso} , C_5H_4); 108.1 (s, $\text{C}_6\text{H}_3\text{O}_2$); 113.2 (s, $\text{C}_6\text{H}_3\text{O}_2$); 114.9 (s, $\text{C}_6\text{H}_3\text{O}_2$); 145.2 (s, $\text{C}_6\text{H}_3\text{O}_2$); 148.5 (s, $\text{C}_6\text{H}_3\text{O}_2$); 150.0 (s, $\text{C}_6\text{H}_3\text{O}_2$); 150.8 (s, CH=N); 193.2 (s, CO). Mass spectrum (based on ^{187}Re) m/z : 629 [M^+].

Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH=N-4'-benzo-18-crown-6})\text{Re}(\text{CO})_3]$ (**3b**)

4'-Aminobenzo-18-crown-6 (90 mg, 0.276 mmol) was added to a solution of $(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{Re}(\text{CO})_3$ (100 mg, 0.276 mmol) in dry

toluene (15 mL). The reaction mixture was refluxed overnight, with a 4 Å molecular sieve. The solvent was pumped off and the solid was recrystallised successively from hexane at $-18\text{ }^{\circ}\text{C}$ to yield white crystals of **3b**, (155 mg, 0.247 mmol, 89%). IR [CH_2Cl_2 , cm^{-1}] $\nu(\text{CO})$: 2025 (s) 1931 (s) $\nu(\text{C}=\text{N})$: 1636 (w). ^1H NMR (CDCl_3) δ : 3.69 (br. s, 4H, CH_2); 3.75 (m, 8H, CH_2); 3.93 (m, 4H, CH_2); 4.17 (m, 4H, CH_2); 5.43 (t, 2H, $J_{\text{HH}} = 2.1\text{ Hz}$, C_5H_4); 5.96 (t, 2H, $J_{\text{HH}} = 2.1\text{ Hz}$, C_5H_4); 6.68 (dd, 1H, $J_{\text{HH}} = 2.3$; 8.4 Hz, $\text{C}_6\text{H}_3\text{O}_2$); 6.73 (d, 1H, $J_{\text{HH}} = 2.3\text{ Hz}$, $\text{C}_6\text{H}_3\text{O}_2$); 6.86 (d, 1H, $J_{\text{HH}} = 8.4\text{ Hz}$, $\text{C}_6\text{H}_3\text{O}_2$); 8.07 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3): 69.4; 69.8; 69.9; 70.0; 70.9; 71.0; 71.5; 71.5 (8s, CH_2); 85.3 (s, C_5H_4); 86.1 (s, C_5H_4); 100.6 (s, C_{ipso} , C_5H_4); 108.1 (s, $\text{C}_6\text{H}_3\text{O}_2$); 113.2 (s, $\text{C}_6\text{H}_3\text{O}_2$); 114.9 (s, $\text{C}_6\text{H}_3\text{O}_2$); 145.2 (s, $\text{C}_6\text{H}_3\text{O}_2$); 148.5 (s, $\text{C}_6\text{H}_3\text{O}_2$); 150.0 (s, $\text{C}_6\text{H}_3\text{O}_2$); 150.8 (s, $\text{CH}=\text{N}$); 193.2 (s, CO). Mass spectrum (based on ^{187}Re) m/z : 673 [M^+].

Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH}=\text{N-2-methyl-15-crown-5})\text{Re}(\text{CO})_3]$ (**3c**)

To a solution of $(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{Re}(\text{CO})_3$ (100 mg, 0.276 mmol) in dry toluene (15 mL), 2-aminomethyl-15-crown-5 (69 mg, 0.276 mmol) was added and the reaction mixture was refluxed overnight with a 4 Å molecular sieve. The complex **3c**, was obtained as a yellow oily solid after evaporation of the solvent (140 mg, 0.235 mmol, 85%). IR [CH_2Cl_2 , cm^{-1}] $\nu(\text{CO})$: 2026 (s) 1932 (s) $\nu(\text{C}=\text{N})$: 1650 (w). ^1H NMR (CDCl_3) δ : 3.46 (dd, 1H, $J_{\text{HH}} = 6.6$; 12.2 Hz, NCH_2); 3.65 (m, 18H, CH_2); (Overlap, m, 1H, NCH_2); 3.75 (m, 1H, CH); 5.32 (m, 2H, C_5H_4); 5.79 (m, 1H, C_5H_4); 5.84 (m, 1H, C_5H_4); 7.87 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3) δ : 62.7 (s, NCH_2); 70.4 (9s, CH_2); 70.5; 70.6; 70.8; 70.9; 71.0; 72.0 (s, CH_2); 79.0 (s, CH); 84.5 (s, C_5H_4); 84.9 (s, C_5H_4); 85.9 (s, C_5H_4); 86.0 (s, C_5H_4); 99.5 (s, C_{ipso} , C_5H_4); 154.8 (s, $\text{CH}=\text{N}$); 193.1 (s, CO). Mass spectrum (based on ^{187}Re) m/z : 595 [M^+]; 567 [$\text{M}^+ - \text{CO}$].

Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{-CH}=\text{N-2-methyl-18-crown-6})\text{Re}(\text{CO})_3]$ (**3d**)

To a solution of $(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{Re}(\text{CO})_3$ (100 mg, 0.276 mmol) in dry toluene (15 mL), 2-aminomethyl-18-crown-6 (81 mg, 0.276 mmol) was added and the reaction mixture was refluxed overnight with a 4 Å molecular sieve. The complex **3d**, was obtained as a yellow oily solid after evaporation of the solvent (144 mg, 0.226 mmol, 82%). IR [CH_2Cl_2 , cm^{-1}] $\nu(\text{CO})$: 2026 (s) 1932 (s) $\nu(\text{C}=\text{N})$: 1650 (w). ^1H NMR (CDCl_3) δ : 3.53 (dd, 1H, $J_{\text{HH}} = 6.7$; 12.0 Hz, NCH_2); 3.56–3.74 (m, 23H, CH_2); 3.67 (Overlap, m, 1H, NCH_2); 3.77 (m, 1H, CH); 5.34 (m, 2H, C_5H_4); 5.82 (m, 1H, C_5H_4); 5.86 (m, 1H, C_5H_4); 7.90 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3) δ : 62.4 (s, NCH_2); 70.1 (s, CH_2); 70.7; 70.8; 70.9; 71.0 (s, broad, CH_2); 72.3 (s, CH_2); 78.8 (s, CH); 84.3 (s, C_5H_4); 84.5 (s, C_5H_4); 85.9 (s, C_5H_4); 86.0 (s, C_5H_4); 99.7 (s, C_{ipso} , C_5H_4); 154.8 (s, $\text{CH}=\text{N}$); 193.1 (s, CO). Mass spectrum (based on ^{187}Re) m/z : 639 [M^+]; 611 [$\text{M}^+ - \text{CO}$].

X-ray structural characterisation of **3b** and **3c**

Crystals suitable for X-ray diffraction measurements were obtained by hexane solution of **3b**. The X-ray diffraction intensity data were collected at room temperature on a Bruker D8 QUEST Photon 100 CMOS area detector diffractometer equipped with TRIUMPH graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$). The data obtained was corrected for Lorentz and polarization effects. In addition, multi-scan absorption corrections were applied with the SADABS program [27]. Using Olex2 [28], the structure was solved with the ShelXS [29] structure solution program using the Patterson Method and refined with the ShelXL [29] refinement package using the least squares minimization methodology. Hydrogen was included at the calculated positions and refined with positional and thermal riding parameters.

A disorder model for the crystallisation solvent was not found because partial desolvation occurs in the crystal. Therefore, the Olex2 solvent mask routine was used to remove the intensity

contributions from the disordered solvent molecules. The final refinement of the structure of **3b** was carried out using the intensities modified by the Olex2 solvent mask. Consequently, the intensity data factor $R(\text{int})$ had an unexpectedly large value (35%). All the attempts for obtaining a new single crystal of **3b** were unsuccessful.

Suitable yellow crystals for the X-ray diffraction experiments were obtained by the slow diffusion of hexane into concentrated dichloromethane solution of **3c**. The intensity data were collected at (296(2) K) on a Bruker SMART CCD area detector diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) using narrow frames (0.3° in ω). The cell parameters were refined from the observed setting angles and detector positions of strong reflections (4806 refl., $2\theta < 56.56^\circ$). The data were corrected for Lorentz and polarization effects. In addition, multi-scan absorption corrections were applied with SADABS program [27]. The structures were solved by the Patterson method and completed by successive difference Fourier syntheses [30]. Refinement, by full-matrix least squares on F^2 with SHELXL97 [30], was carried out including the isotropic and subsequent anisotropic displacement parameters for all the non-hydrogen atoms. Hydrogen atoms were included at calculated positions and refined with positional and thermal riding parameters. Atomic scattering factors, corrected for anomalous dispersion, were used in the implementation of the refinement program [30].

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Appendix A. Supplementary material

CCDC 1042323 and 1028264 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2015.04.031>.

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