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Synthesis of ferrocenyldiimine metal carbonyl complexes and an investigation of the Mo adduct encapsulated in cyclodextrin†

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Cr and Mo tetracarbonyl complexes bearing the diimine ligand *N*,*N*′-bis(ferrocenylmethylene)ethylenediamine (FcNN) have been prepared from the ligand and $M(CO)_6$. Two isomeric forms of $(FcNN)Mo(CO)_4$, corresponding to the *cis*,*cis* and *cis*,*trans* geometries with respect to the C=N bonds of the free ligand, were shown to exist in a 1 : 12.5 ratio by ^{1}H NMR (NOE experiments). By contrast, only the *trans*,*trans* isomer is observed for the Cr complex $(FcNN)Cr(CO)_4$. The compounds $(FcNN)M(CO)_4$ show ferrocene-based irreversible oxidation processes that lead to the deposition of a film at the electrode surface. $(FcNN)Mo(CO)_4$ was immobilised in permethylated β-CD (TRIMEB) by addition of the guest to a solution of TRIMEB in dichloromethane. Removal of the solvent led to the isolation of an inclusion compound with a 2 : 1 host : guest stoichiometry, as evidenced by powder X-ray diffraction, thermogravimetric analysis, FTIR and ^{13}C CP MAS NMR spectroscopy. The electrochemical properties of $(FcNN)Mo(CO)_4$ upon encapsulation are discussed.

Introduction

Cyclodextrins (CDs) are water-soluble cyclic oligosaccharides capable of forming inclusion compounds with a wide range of organic molecules, inorganic ions and metallo-organic species.[1] Suitable guests include transition metal complexes and organometallic compounds bearing hydrophobic ligands such as cyclopentadienyl (Cp = η^5-C_5H_5) and η^6-arene groups.[2] With these ligands, the weaker types of non-covalent bonding, such as van der Waals and charge transfer interactions, assume considerable importance. Encapsulated metallo-organic complexes often exhibit markedly different physical and chemical characteristics compared to the bulk material,[3] for example, in their nonlinear optical,[4] photophysical[5] and electrochemical properties,[6] and ligand substitution/insertion reactions.[7] Cyclodextrins are known to bind ferrocene and its derivatives,[6b–e,8] titanocene and molybdenocene dihalides,[9] aromatic ruthenium complexes,[10] mixed sandwich complexes such as $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)](PF_6)$,[11] and half-sandwich complexes such as $CpFe(CO)_2X$ (X = Cl, Me, CN),[7,12] $[CpFe(CO)_2NH_3](PF_6)$,[13] $CpMn(CO)_3$,[14] $(\eta^6\text{-}C_6H_6)Cr(CO)_3$,[15] $Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2$,[16] $Cp'Mo(\eta^3\text{-}C_6H_7)(CO)_2$ and $[Cp'Mo(\eta^4\text{-}C_6H_8)(CO)_2](BF_4)$ (Cp′ = Cp, Ind).[17] Some of us also reported the preparation of an inclusion compound between β-cyclodextrin and a Lewis base adduct comprising 4-ferrocenylpyridine and methyltrioxorhenium (MTO).[18] Unfortunately, the inclusion compound was not effective as a catalyst for the heterogeneous epoxidation of cyclooctene by hydrogen peroxide.

Most of the cyclodextrin adducts cited above were prepared by mixing an aqueous solution of the host with the solid organometallic compound or a solution of the organometallic in an appropriate organic solvent. This method obviously restricts the range of possible complexes to guests that are not particularly water sensitive. For the encapsulated MTO complex, the poor solubility of the inclusion compound in most solvents precluded its use in homogeneous catalysis, or liquid-phase biphasic catalysis. One possible solution would be to use methylated CDs instead of native CDs. These derivatives exhibit an enhanced water-solubility and are also soluble in many organic solvents.[19] In the present work, we report the synthesis and characterisation of an inclusion compound comprising 2,3,6-tri-*O*-methyl-β-CD (TRIMEB) and a novel molybdenum carbonyl complex of ferrocenyldiimine (FcNN). Only a few metal complexes bearing FcNN ligands have been reported, namely $FcNNCu(OTf)$,[20] $[(FcNN)_2M](ClO_4)_n$ (M = Zn, Co, Ni, Fe),[21] $[(FcNN)M(COD)]ClO_4$ (M = Rh, Ir) and $[(FcNN)RhCl]_2$,[22] several of them useful in catalytic transformations. Since $L_nMo(CO)_x$ complexes have proven to be convenient precursors for the L_nMoO_2 oxides, useful in our studies of olefin epoxidation,[23] we decided to study the complexes of ferrocenyldiimine (FcNN) with Cr and Mo carbonyls as well as the inclusion compound comprising TRIMEB and $(FcNN)Mo(CO)_4$, as a possible precursor for cyclodextrin encapsulated epoxidation catalysts.

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† Dedicated to Professor Dr. Josû J. C. Teixeira-Dias on the occasion of his 60th birthday.

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Experimental

Materials and methods

Heptakis-2,3,6-tri-*O*-methyl-β-CD was obtained from Fluka. *N*,*N*′-Bis(benzylidene)-1,2-ethylenediamine was prepared using the method described below for *N*,*N*′-bis(ferrocenylmethylene)ethylenediamine. All air-sensitive operations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures, distilled under nitrogen or argon and kept over 4 Å molecular sieves. Ethylenediamine was dried over sodium, distilled under reduced pressure and stored under nitrogen.

Microanalyses were performed at the ITQB (C. Almeida). TGA studies were carried out using a Shimadzu TGA-50 system at a heating rate of 5 K min^{-1} under a static atmosphere of air. Powder XRD data were collected on a Philips X'pert diffractometer using Cu-K$_\alpha$ radiation filtered by Ni (λ = 1.5418 Å). Infrared spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 instrument at the Instituto Superior Técnico, Lisbon, Portugal. Assignments were supported by proton decoupling and NOE difference spectra. ^{13}C solid-state CP MAS NMR spectra were recorded at 125.72 MHz on a (11.7 T) Bruker Avance 500 spectrometer, with a 4.5 μs ^{1}H 90° pulse, 2 ms contact time, a spinning rate of 7 kHz and 12 s recycle delays. Chemical shifts are quoted in parts per million from tetramethylsilane.

The electrochemical measurements were performed with a BAS CV-50W-1000 voltammetric analyser controlled by BAS/Windows data acquisition software, using CH_2Cl_2 solutions containing 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate. Cyclic voltammograms were obtained in a glass cell (BAS MF-1082 in a C-2 cell enclosed in a Faraday cage) using a platinum electrode as the working electrode, a 7.5 cm platinum wire (BAS MW-1032) with a gold-plated connector as the counter electrode, and an Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode. All voltammograms were obtained without IR feedback compensation and the measured potentials were not corrected for liquid junction potentials. All the potentials are reported relative to that of the Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode. Cyclic voltammograms were obtained in the potential range −1.5 to 1.5 V, at 0.2 V s^{-1}. The solutions were purged with argon and kept under an inert atmosphere throughout the measurements. The ferrocenium/ferrocene couple was used as an internal standard: under the experimental conditions used and for the scan rate of 0.2 V s^{-1}, $E_{1/2}$ = 0.46 V, ΔE_p = 0.22 V and i_{pa}/i_{pc} = 1.00.

Synthesis and characterisation

***N*,*N*′-Bis(ferrocenylmethylene)ethylenediamine (FcNN, 1).** Ferrocenecarboxaldehyde (0.59 g, 2.76 mmol) was added to a solution of dry ethylenediamine (83 mg, 1.38 mmol) in dry benzene and the reaction mixture refluxed overnight with a Dean–Stark apparatus for azeotropic distillation until all the water had been removed. The mixture was then evaporated to dryness under reduced pressure to give the pure diimine as a hygroscopic red powder in quantitative yield (1.03 g). Anal. calcd for $C_{24}H_{24}Fe_2N_2$ (452.16): C, 63.75; H, 5.35; N, 6.20; found: C, 63.65; H, 5.03; N, 6.23. IR (KBr, cm^{-1}): 3110 w, 3089 vw, 3081 w, 3071 w, 2913 w, 2894 w, 2829 m, 1640 vs, 1470 w, 1458 w, 1408 w, 1395 vw, 1379 w, 1368 w, 1350 vw, 1327 w, 1280 vw, 1260 vw, 1246 m, 1215 vw, 1193 vw, 1104 m, 1063 w, 1047 w, 1030 w, 1012 m, 1003 m, 957 w, 934 vw, 876 b, 855 sh, 837 sh, 817 s, 765 w, 668 vw, 641 vw, 518 m, 511 m, 487 m, 455 w, 436 w. ^{1}H NMR (C_6D_6, 25 °C): δ = 8.04 (s, 2H, H7,8), 4.63 (m, $^3J_{H1H2}$ = 2 Hz, 4H, H1,4), 4.04 (m, $^3J_{H2H1}$ = 2 Hz, 4H, H2,5), 4.03 (s, 10H, H3,6), 3.83 (s, 4H, H9,10). ^{13}C {^{1}H} NMR (C_6D_6, 25 °C): δ = 161.1, 81.8, 70.3, 69.4, 68.9, 62.9. DEPT (C_6D_6, 25 °C): δ = 161.1 (+), 70.3 (+), 69.4 (+), 68.9 (+), 62.9 (−).

(FcNN)Cr(CO)$_4$ (2). A solution of FcNN (**1**; 0.31 g, 0.68 mmol) and $Cr(CO)_6$ (0.15 g, 0.68 mmol) in dry toluene (8 ml) was refluxed for 12 h. During the reaction, sublimation of $Cr(CO)_6$ occurred, so it was scraped down from the walls from time to time. The precipitate was filtered, washed with hexane, dried under reduced pressure and the excess of $Cr(CO)_6$ was removed by sublimation under vacuum to give the product as an orange powder (0.33 g, 78%). Anal. calcd for $C_{28}H_{24}CrFe_2N_2O_4$ (616.20): C, 54.58; H, 3.93; N, 4.55; found: C, 54.25; H, 4.33; N, 4.53. IR (KBr, cm^{-1}): 3095 vw, 2923 vw, 2851 vw, 1990 s, 1850 vs, 1796 vs, 1621 s, 1445 m, 1411 m, 1246 m, 1106 m, 1004 m, 820 w, 694 m, 650 m, 636 m, 482 m, 471 m, 447 w, 425 w. IR (CH_2Cl_2, cm^{-1}): 2003 s, 1888 vs, 1867 vs, 1817 vs (selected data). ^{1}H NMR ($CDCl_2CDCl_2$, 25 °C): δ = 8.63 (s, 2H, H7,8), 4.58 (m, 4H, H2), 4.55 (m, 4H, H1,4), 4.32 (s, 10H, H3,6), 3.60 (s, 4H, H9,10).

(PhNN)Cr(CO)$_4$ (3). A solution of *N*,*N*′-bis(benzylidene)-1,2-ethylenediamine (0.11 g, 0.68 mmol) and $Cr(CO)_6$ (0.150 g, 0.68 mmol) in dry toluene (8 ml) was refluxed for 12 h. During the reaction sublimation of $Cr(CO)_6$ occurred, so it was scraped down from the walls from time to time. The precipitate was filtered, washed with hexane, dried under reduced pressure and the excess of $Cr(CO)_6$ was removed by sublimation under vacuum. The yield of impure product was 0.1 g (less then 36%). IR (KBr, cm^{-1}): 3060 vw, 3028 vw, 2956 w, 2923 w, 2853 w, 2003 s, 1962 w, 1888 vs, 1862 vs, 1810 vs, 1635 sh, 1618 m, 1599 w, 1577 w, 1492 w, 1450 w, 1437 m, 1384 w, 1329 vw, 1312 vw, 1287 vw, 1262 vw, 1218 w, 1194 vw, 1185 vw, 1159 vw, 1104 sh, 1079 w, 1028 w, 1001 vw, 947 vw, 909 vw, 852 vw, 830 vw, 805 vw, 749 m, 691 s, 650 s, 639 s, 617 vw, 602 w, 558 w, 446 w.

(FcNN)Mo(CO)$_4$ (4). A solution of FcNN (**1**; 0.19 g, 0.43 mmol) and $Mo(CO)_6$ (0.11 g, 0.43 mmol) in dry toluene (8 ml) was refluxed for 1.5 h (until evolution of carbon monoxide had stopped). The precipitate was filtered, washed with hexane and dried under reduced pressure to give the product as an orange powder (0.25 g, 88%). Anal. calcd for $C_{28}H_{24}Fe_2MoN_2O_4$ (660.13): C, 50.94; H, 3.66; N, 4.24; found: C, 50.64; H, 3.95; N, 4.26. IR (KBr, cm^{-1}): 3095 vw, 2918 vw, 2853 vw, 1997 s, 1853 vs, 1813 vs, 1619 s, 1444 m, 1412 m, 1394 w, 1377 m, 1353 w, 1343 w, 1325 w, 1248 m, 1208 m, 1105 m, 1064 sh, 1050 m, 1036 m, 1026 sh, 954 vw, 937 vw, 902 vw, 868 vw, 821 m, 782 w, 755 vw, 668 w, 645 w, 615 w, 603 m, 584 m, 557 w, 517 w, 484 m, 472 m, 433 w, 405 vw, 366 m. IR (CH_2Cl_2, cm^{-1}): 2009 s, 1894 vs, 1869 vs, 1821 vs (selected data). ^{1}H NMR data for isomer **B** (CD_2Cl_2, 25 °C): δ = 8.60 (s, 2H, H7,8), 4.64, 4.59 (c, 8H, H1,2,4,5), 4.32 (s, 10H, H3,6), 3.73 (s, 4H, H9,10). ^{1}H NMR data for isomer **C** (CD_2Cl_2, 25 °C): δ = 8.62 (s, 1H, H7), 8.41 (s, 1H, H8), 5.23 (d, $^3J_{H4H5}$ = 1.8 Hz, 2H, H4), 4.64, 4.59 (c, 6H, H1,2,5), 4.30, 4.28 (s, 10H, H3,6), 3.95 (m, 2H, H10), 3.58 (m, 2H, H9). ^{13}C {^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 207.8, 171.0, 168.1, 73.0, 72.8, 72.2, 72.1, 70.2, 70.1, 70.0, 68.4, 54.5–53.1 (complex signal). ^{13}C CP MAS NMR: δ = 222.1, 209.0 (CO), 171.5, 166.7 (C=N), 80.0, 73.6, 70.5, 69.8, 64.5 (Cp), 54.4 (CH_2).

2TRIMEB · (FcNN)Mo(CO)$_4$ (5). (FcNN)Mo(CO)$_4$ (**4**; 0.046 g, 0.07 mmol) was added stepwise to a solution of TRIMEB (0.20 g, 0.14 mmol) in dichloromethane (1 ml), allowing each fraction to dissolve before adding the next. When guest dissolution was no longer possible, CH_2Cl_2 (10 ml) was added to help dissolve it. The mixture was stirred overnight and then evaporated to dryness under reduced pressure to obtain a bright orange solid product. IR (KBr, cm^{-1}): 2978 s, 2928 s, 2832 s, 2007 m, 1891 m, 1871 m, 1831 m, 1683 m, 1666 w, 1641 w, 1621 m, 1460 m, 1406 w, 1369 m, 1322 w, 1303 w, 1195 sh, 1161 vs, 1141 vs, 1107 vs, 1088 vs, 1071 vs, 1065 sh, 1039 vs, 970 s, 951 s, 910 sh, 856 m, 821 m, 755 m, 736 m, 704 m, 668 vw, 658 vw, 646 vw, 602 w, 575 sh, 553 m, 523 m, 503 sh, 484 w, 472 w, 432 w, 365 w. ^{13}C CP MAS NMR: δ = 170.0, 166.3 (guest, C=N), 99.8, 96.4, 93.1 (TRIMEB, C1), 85.5, 83.2, 82.4, 81.1, 79.4, 77.7, 76.9 (all TRIMEB, C2,3,4), 72.5, 71.7, 70.8, 70.4, 69.8 (TRIMEB, C5,6, and overlapping guest Fc), 63.1, 61.5, 60.7, 60.1, 59.2, 57.7, 56.7 (TRIMEB, O–CH_3), 54.0 (guest, CH_2).

Results and discussion

Synthesis and characterisation of (FcNN)M$(CO)_4$ complexes

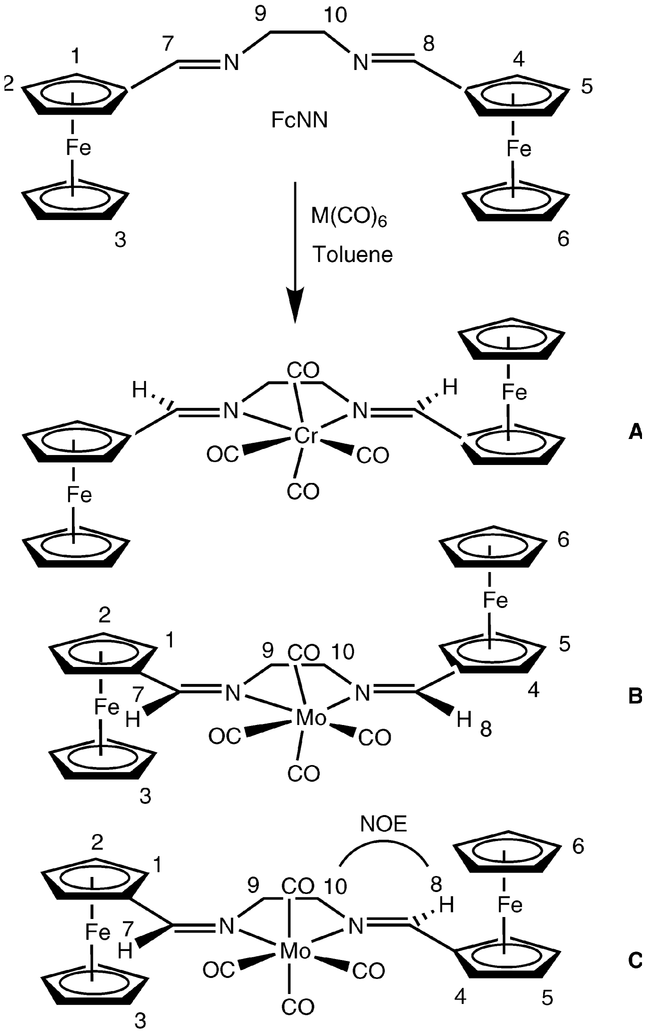
The ligand *N*,*N*′-bis(ferrocenylmethylene)ethylenediamine (FcNN) was prepared in quantitative yield by the condensation of ferrocenecarboxaldehyde and ethylenediamine. If this reaction is carried out in the presence of anhydrous $MgSO_4$ or Na_2CO_3 for the removal of water, yields of 70–75% are obtained.[21,24] We found that quantitative yields are possible when a Dean–Stark apparatus is used for the removal of water through azeotropic distillation. The ^1H NMR spectrum of FcNN in solution showed that the ligand was geometrically pure. Thus, NOE experiments on the imine protons (H7,8) produced a positive enhancement in the signals for the methylene protons (H9,10), indicating the presence of the *trans*,*trans* isomer (Scheme 1). These experiments also allowed assignment of the cyclopentadienyl substituted protons as two multiplets at 4.63 (H1,4) and 4.04 (H2,5) ppm.

Reaction of FcNN with the hexacarbonyls $Cr(CO)_6$ and $Mo(CO)_6$ in refluxing toluene gave the novel polynuclear complexes (FcNN)$Cr(CO)_4$ (**2**) and (FcNN)$Mo(CO)_4$ (**4**) as orange powders (Scheme 1). The chromium complex (PhNN)$Cr(CO)_4$ (**3**) was also prepared, albeit in poor yield and purity (PhNN = *N*,*N*′-bis(benzylidene)-1,2-ethylenediamine). Indeed, we were unable to obtain analytically pure samples but the IR spectrum allowed the desired complex to be identified as the major product.

Compound **4** is stable and does not decompose at room temperature, in the solid state, even after several weeks. However, it is not very soluble in polar solvents such as $CHCl_3$ and CH_2Cl_2, and is completely insoluble in nonpolar solvents such as *n*-hexane. The IR spectra of **2** and **4** in CH_2Cl_2 show four carbonyl stretching modes in the range 1817–2009 cm^{-1}, typical of *cis*-$ML_2(CO)_4$ molecules.[25] Upon complexation, a shift in the C=N stretching frequency takes place from 1640 cm^{-1} in the free ligand (FcNN) to 1621 cm^{-1} in **2** and 1619 cm^{-1} in **4**.

A closely related counterpart of the ligand FcNN is 1,4-diazabutadiene (Fc-DAB): Fc–N=CHCH=N–Fc. A comparison between these ligands can now be made since Bildstein *et al.* reported data for the complexes (Fc-DAB)$M(CO)_4$.[26] Comparison of the IR spectra (KBr) of (Fc-DAB)$M(CO)_4$ and (FcNN)$M(CO)_4$ shows that the former is a stronger π-acid, increasing the values of the ν(CO) stretching frequencies by 10–35 cm^{-1} relative to those of (FcNN)$M(CO)_4$. The ν(CO) stretching frequencies for **3** are shifted *ca.* 13 cm^{-1} to higher frequencies relative to those for **2** (KBr), showing the expected influence of the phenyl substituent, which is a stronger electron acceptor than the ferrocenyl group. Comparison of the ν(CO) stretching frequencies for the complexes (FcNN)$Mo(CO)_4$ and (H_2C=NCH_2CH_2N=CH_2)$Mo(CO)_4$ (in CH_2Cl_2 solution)[27] shows that the former is only a slightly better π-acceptor, producing a shift of 1–9 cm^{-1} to higher frequencies.

The ^1H NMR chemical shifts of the imine protons in **4** are slightly deshielded [$\delta(^1H)$ 8.41–8.62] compared with those of the free ligand FcNN [$\delta(^1H)$ 8.04]. A similar trend was observed for the corresponding ^{13}C chemical shifts. Two isomeric forms were identified by ^1H NMR, corresponding to the *cis*,*cis* and *cis*,*trans* geometries with respect to the C=N bonds of the free ligand. These species co-exist in solution in an approximately 1 : 12.5 ratio (*cis*,*cis* : *cis*,*trans*). In fact, due to hindered rotation about the double bonds, three possible isomers with pseudo-C_s or C_2 (**A** and **B**) and C_1 (**C**) symmetries can be drawn for this compound (Scheme 1). The whole ^1H spectrum was assigned by homonuclear decoupling experiments and NOE difference spectra. The proton spectrum of the mixture shows two sets of peaks. One set consisting of peaks at 8.60 (H7,8), 4.64, 4.59 (H1,2,4,5), 4.32 (H3,6) and 3.73 (H9,10) has a pattern compatible with the existence of a mirror plane or a C_2 axis in the molecule, and must therefore correspond to isomers **A** or **B**. Since the nitrogen atoms have a planar geometry, NOE experiments on the H9,10 singlet enabled us to distinguish between the two symmetrical forms. In fact, saturation of the peak at 3.73 ppm did not show any spatial proximity between the H9,10 protons and H7,8, indicating the presence of isomer **B**. The present data does not allow a definitive statement to be made about the existence of conformers C_s or C_2, or indeed whether the two are in fast exchange with one another on the NMR time scale.



Scheme 1 Preparation of (FcNN)$M(CO)_4$ [M = Cr (**2**), Mo (**4**)], showing the three possible isomers and the numbering scheme used for the NMR assignments. C_s and C_2 conformers are possible for isomers **A** and **B**; only the C_2 conformers are represented.

The other set of signals at 8.62, 8.41, 5.23, 4.64, 4.59, 4.30, 4.28, 3.95 and 3.58 ppm attests to the existence of a structure with a chiral metal center, and corresponds to isomer **C**. Once again, the NOE difference spectrum showed the absence of an interaction between the multiplet at 3.58 ppm (H9) and either peak in the vinylic region, while irradiation of the other methylenic protons (H10) at 3.95 ppm gave, as expected, a positive NOE peak at 8.41 ppm (H8). A series of other experiments, in particular, the NOE enhancements observed at the cyclopentadienyl resonances upon irradiation of the H4, H7 and H8 protons, confirmed these assignments. The CH_2 protons of isomer **C** give rise to an AA′MM′ system, denoting a restricted rotation in the molecule. The stereochemical hindrance in the movement of the ferrocenyl group that is oriented towards the metal is probably responsible for this observation. The four diastereotopic equatorial and axial protons appear then as two groups of complex signals (3.95 and 3.58 ppm for H10 and H9, respectively). The rapid rotation around the Fe–Cp axis averages out the inherent chemical shift differences of non-substituted Cp hydrogens, rendering the protons of each of the rings magnetically equivalent.

Other diimine complexes $Mo(CO)_4(RH{=}NCH_2CH_2N{=}RH)$ (R = Ph, 2-C_4H_3O), also prepared from the pure *trans*,*trans* isomer of the ligand and $Mo(CO)_6$, have been shown to be mixtures of *trans*,*trans* (predominant) and *cis*,*trans* isomers.[28] A similar isomerisation has also been reported for the related complexes $(R_2NCH_2CH_2N{=}R')M(CO)_4$.[27] In both cases the driving force for this isomerisation was assigned to steric reasons disfavouring the *trans*,*trans* arrangement for the bulkier imine substituents. Interestingly, however, in *fac*-$[Mo(CO)_3(NCMe)(PhH{=}NCH_2CH_2N{=}PhH)]$ the ligand adopts a *trans*,*trans* geometry.[28] The ^1H NMR spectrum of $(FcNN)Cr(CO)_4$ (**2**) presented five peaks (three singlets and two multiplets), consistent with the formation of a symmetrical compound. NOE experiments on the vinylic protons (H7,8) showed a positive effect on the methylenic hydrogens (H9,10), in agreement with the presence of the *trans*,*trans* isomer (**A**). Moreover, the multiplet at δ 4.55 ppm was also affected and is thus assigned to H1,4. The smaller size of the fragment $Cr(CO)_4$ relative to $Mo(CO)_4$ may be responsible for the absence of isomerisation in $(FcNN)Cr(CO)_4$.

Synthesis and characterisation of the TRIMEB inclusion compound

Since the guest compound $(FcNN)Mo(CO)_4$ (**4**) is sensitive to water, inclusion was carried out by co-dissolution in dichloromethane. This is a rather uncommon technique that has worked particularly well in this case due to the high solubility of the methylated cyclodextrin, TRIMEB, in the organic solvent. Still, some water is required in order to prevent the CD cavity from collapsing and so the solvent was used as received, without drying. An initial host : guest ratio of 2 : 1 was used and, after evaporation of the solvent, an orange compound was obtained, designated as 2TRIMEB · $(FcNN)Mo(CO)_4$ (**5**). Fig. 1 shows the powder XRD patterns for TRIMEB, the tetracarbonyl complex **4** and the inclusion compound **5**. Compound **5** is microcrystalline and exhibits no reflections ascribed to either pure TRIMEB or non-included **4**. The formation of a new phase is a good indication for the presence of a true inclusion compound.[29]

The three components TRIMEB, **4** and **5**, as well as a 2 : 1 physical mixture of TRIMEB and **4**, were also studied by thermogravimetry (Fig. 2). The complex **4** shows an initial mass loss from about 100–180 °C assigned to disruption of the Mo–CO bonds and subsequent loss of CO. Following this, there is a rather unusual feature, a mass gain, associated with the formation of molybdenum oxides. There is a mass maximum around 212 °C, followed by decomposition of the material. TRIMEB starts to melt and decompose at about 165 °C, and at 500 °C nearly 100% mass loss is complete. The physical mixture features a combined result of these thermogravimetric processes. In fact, there is a small step (2.5% loss) starting just below 100 °C, corresponding to the initial fragmentation of **4**. At higher temperatures, the onset of TRIMEB decomposition is masked by the mass gain of **4** such that no significant alterations are observed up to 215 °C, after which both components start to decompose. The TG trace of the inclusion compound **5** features a 2% mass loss from room temperature up to *ca.* 80 °C due to dehydration, followed by another loss of 3% up to 220 °C, after which decomposition begins. There is no step characteristic of the initial fragmentation of non-included **4**. Above 220 °C the TG trace is similar to that of the mixture and the residual mass at 500 °C is also the same.

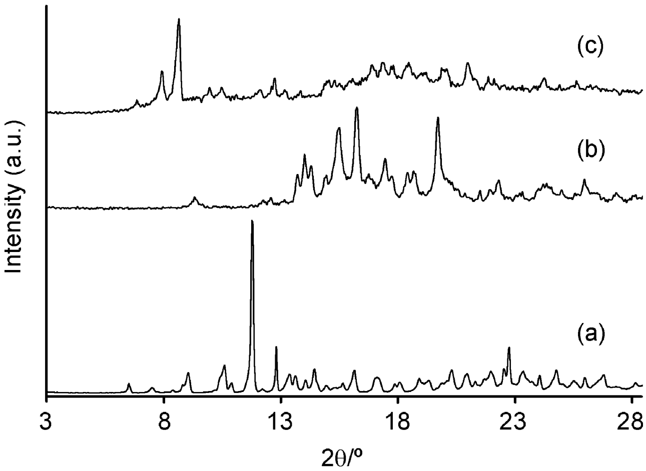


Fig. 1 Powder XRD patterns of (a) TRIMEB, (b) $(FcNN)Mo(CO)_4$ (**4**) and (c) the inclusion compound 2TRIMEB · $(FcNN)Mo(CO)_4$ (**5**).

The ^{13}C CP MAS NMR spectra of TRIMEB, $(FcNN)Mo(CO)_4$ (**4**) and the inclusion compound 2TRIMEB · $(FcNN)Mo(CO)_4$ (**5**) are shown in Fig. 3. Like the parent compound β-CD, TRIMEB gives rise to several resonances for each type of carbon atom. By reference to reported solution spectra,[30] the different carbon resonances are assigned to C1 (93–102 ppm), C2,3,4 (74–88 ppm), C5,6 (68–73 ppm) and O–CH_3 (54–64 ppm). When the guest **4** is included in TRIMEB to form compound **5**, the multiplicity of host resonances is reduced. In fact, some of the signals for the same type of carbon, C1 for example, coalesce into one sharper signal while others remain unchanged. For the parent β-CD this feature has

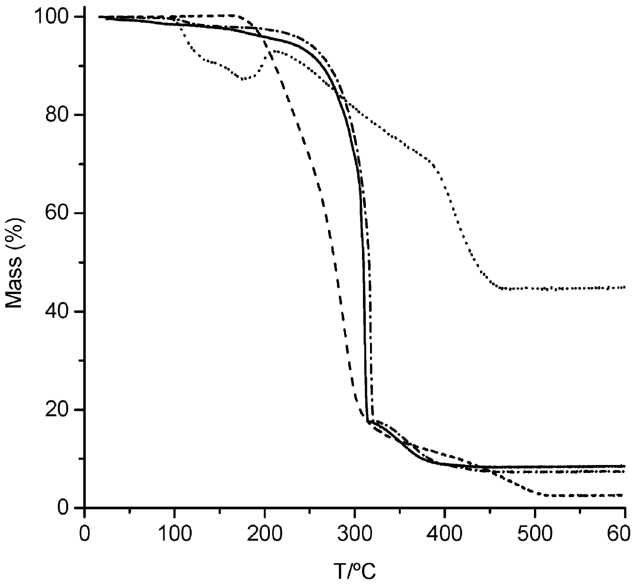


Fig. 2 Thermogravimetric profiles of TRIMEB (– – – –), the tetracarbonyl complex **4** (· · · · · ·), a 2 : 1 physical mixture of TRIMEB and **4** (– — – —) and the inclusion compound **5** (——).

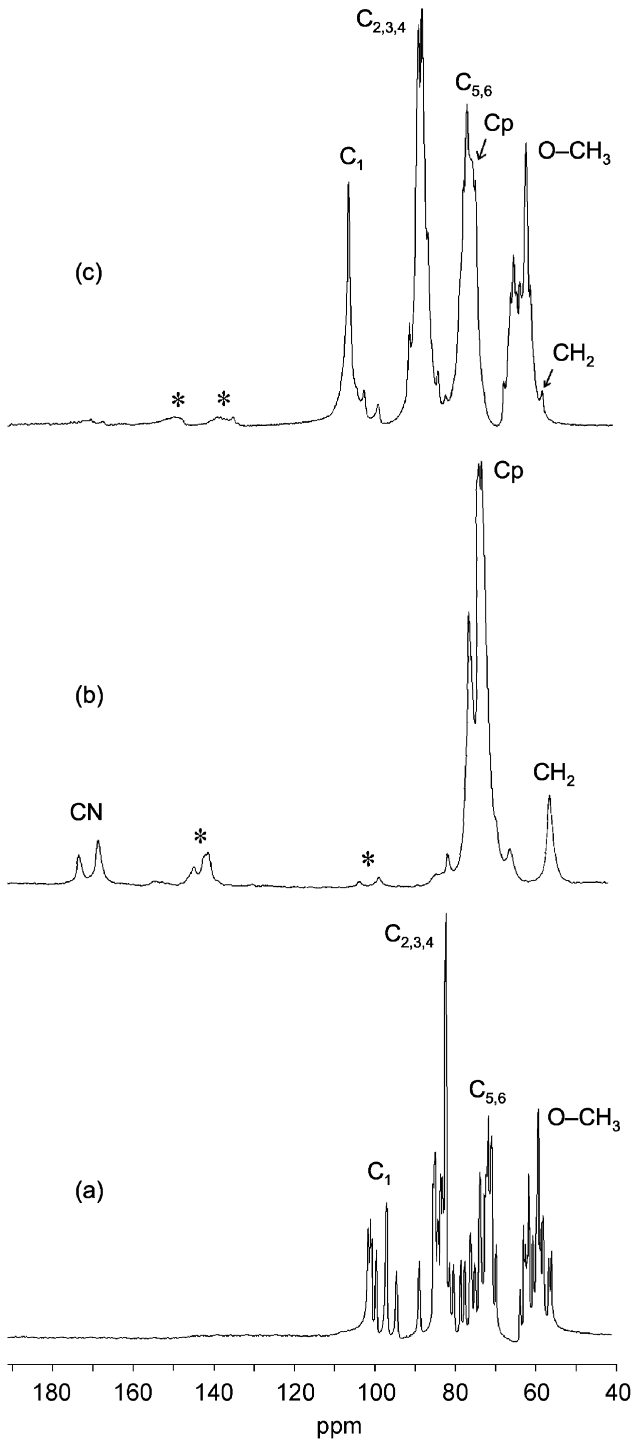


Fig. 3 Solid-state ^{13}C CP MAS NMR spectra of (a) TRIMEB, (b) (FcNN)Mo(CO)$_4$ (**4**) and (c) inclusion compound 2TRIMEB·(FcNN)Mo(CO)$_4$ (**5**). Spinning sidebands are denoted by *.

been associated with the effect of the included guest upon the symmetry of the host and a similar effect may be occurring in the present TRIMEB inclusion compound.[9b,12b,16–18] Additional peaks in the ^{13}C NMR spectrum are readily assigned to the resonances of the carbon atoms of the guest molecule. The –CH=N–CH$_2$– subunit gives rise to peaks at 54.0 (CH$_2$), 166.3 and 170.0 (C=N) ppm, unshifted compared with those observed for pure **4**, while the resonances for the cyclopentadienyl carbons of ferrocenyl groups overlap with those for C5,6 of the host. The C=N peaks were very weak and are therefore not easily observed in Fig. 3(c).

The KBr IR spectrum of 2TRIMEB·(FcNN)Mo(CO)$_4$ (**5**) showed several absorption bands assigned to the guest species in addition to the characteristic bands of the host. In particular, the retention of a *cis*-MoL$_2$(CO)$_4$ structure was confirmed by four bands in the expected ν(CO) stretching region at 2007, 1891, 1871 and 1831 cm^{-1}. By contrast, only three CO bands were discernible for the non-included complex in the solid state, with frequencies 10–20 cm^{-1} lower than the corresponding bands for **5**. Indeed, the observed frequencies for **5** are close to those for **4** dissolved in dichloromethane (2009, 1894, 1869 and 1821 cm^{-1}). These results indicate that the guest complexes are isolated from each other in the cyclodextrin cavities as in solution. Similar phenomena were reported previously for molybdenum(II) dicarbonyl complexes encapsulated in β-CD.[16,17]

Electrochemical studies

The cyclic voltammograms (CV) of the free ligand FcNN (**1**) and the corresponding (FcNN)M(CO)$_4$ [M = Cr (**2**), Mo (**4**)] complexes are depicted in Fig. 4. A reductive electrochemical behaviour was not detected for any of the compounds in the potential range 0 to −1.4 V; on the contrary they show an oxidative electrochemical behaviour in the potential range of 0 to 1.4 V.

The free ligand FcNN exhibits one reversible ($i_{pa}/i_{pc} = 1.00$) oxidation process, with $E_{1/2} = 0.55$ V and $\Delta E_p = 0.10$ V. It is conceivable that this process might involve a single two-electron event, corresponding to the formation of the Fe^{III}/Fe^{III} dication. The one-electron oxidation of the two metal centres is not separated, indicating the absence of electronic interaction between the Fc centres. This behaviour is different from the related ligand Fc-DAB, which shows in the cyclic voltammogram two one-electron oxidation processes that are separated by 0.060 V from the two iron centres.[26]

The cyclic voltammograms of the complexes (FcNN)M(CO)$_4$ (**2**,**4**) show different features that can be assigned to the Fc units and to the M(CO)$_4$ moieties [Fig. 4(b,c)]. The CV of (FcNN)Cr(CO)$_4$ (**2**) shows a quasi-reversible Cr-centred process at $E_{1/2} = 0.27$ V, with $\Delta E_p = 0.09$ V [Fig. 4(b)]. In the related complex (Fc-DAB)Cr(CO)$_4$,[26] the

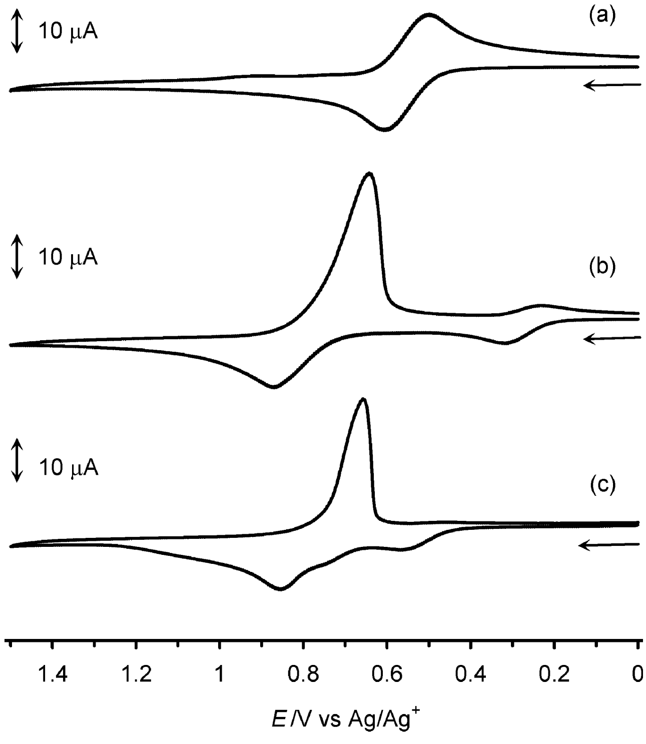


Fig. 4 Cyclic voltammograms of (a) FcNN (**1**), (b) (FcNN)Cr(CO)$_4$ (**2**) and (c) (FcNN)Mo(CO)$_4$ (**4**) in CH$_2$Cl$_2$ with 0.1 mol dm^{-3} NBu$_4$PF$_6$; scan rate 0.25 V s^{-1}; potential range 0 to 1.5 V *vs.* Ag/AgCl (1 mol dm^{-3} NaCl).

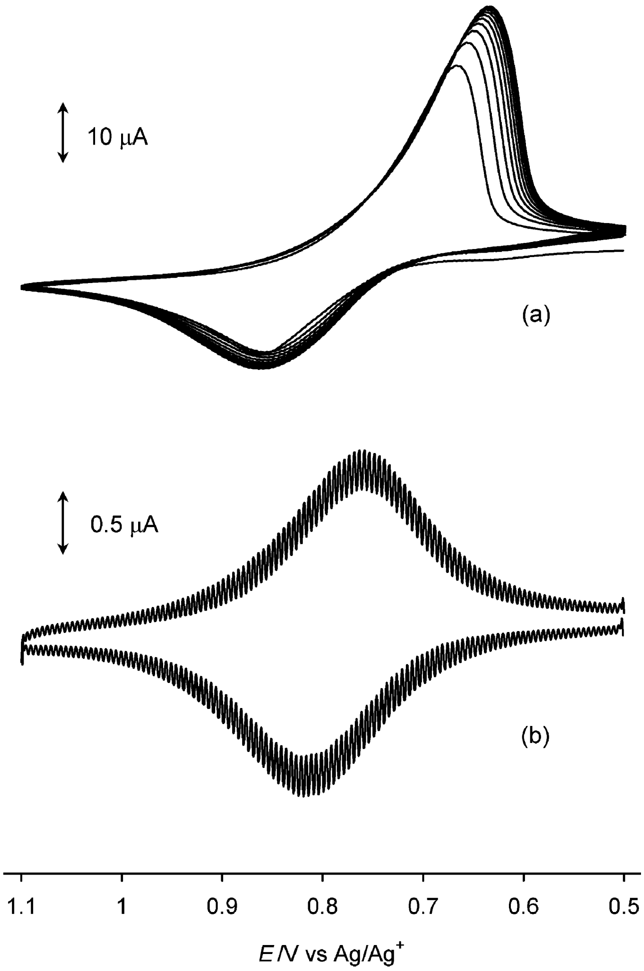


Fig. 5 (a) Series of sequential cyclic voltammograms of **2**. (b) CV of the modified electrode prepared in (a), in electrolyte solution free of **2**. Conditions: CH_2Cl_2 with 0.1 mol dm^{-3} NBu_4PF_6; potential range 0.5 to 1.1 V *vs.* Ag/AgCl (1 mol dm^{-3} NaCl); scan rate 0.25 V s^{-1}.

corresponding (likely) two-electron process occurs at more positive potentials, $E_{1/2} = 0.44$ V, in agreement with the better π-acceptor capability of the Fc-DAB ligand compared with FcNN. At more positive potentials, there is one anodic peak at $E_{pa} = 0.87$ that has its counterpart at $E_{pc} = 0.64$ V in the reverse scan. No splitting of the two Fc oxidation processes was observed after coordination to the $Cr(CO)_4$ fragment, in contrast to that observed for the (Fc-DAB)$Cr(CO)_4$ analogue.[26] The NMR data for **2** showed the exclusive presence of the *trans*,*trans* isomer **A**, in which the two ferrocenyl units are geometrically equivalent. The presence of only one ferrocenyl redox wave for **2** is therefore not unexpected (if there is minimal electrochemical communication between the Fe centres).

Because of the occurrence of electrode adsorption phenomena, multiscan voltammetry was carried out in the potential region 0.5 to 1.1 V. In the subsequent cycles (maximum 20), there was an increase in the current intensity of the anodic and cathodic peaks, indicating deposition of an insoluble electroactive film at the electrode surface [Fig. 5(a)].[31] In order to confirm the film formation and its electroactivity, the solution in the electrochemical cell was replaced by a new one, free of **2**, and the cyclic voltammograms were run under the same experimental conditions [Fig. 5(b)]. The modified electrode shows one reversible oxidation process with $E_{1/2} = 0.78$ V and $\Delta E_p = 0.04$ V. These results confirm that oxidation of (FcNN)$Cr(CO)_4$ (**2**) is accompanied by deposition of a monolayer type film at the surface of the working electrode. No further characterisation of the deposited film was carried out.

A similar electrochemical response was observed for the Mo analogue **4** [Fig. 4(c)]. At less positive potentials ($E_{pa} = 0.56$ V) there is an oxidation process due to the $Mo(CO)_4$ fragment. At more positive potentials there are two partially overlapping anodic peaks at $E_{pa}(1) = 0.75$ V and $E_{pa}(2) = 0.85$ V. As discussed above, the NMR data for **4** show that isomer **C** is the dominant form. Hence it is possible that the two anodic peaks correspond to the oxidation of the two ferrocenyl moieties that become inequivalent after $Mo(CO)_4$ coordination, as observed for the Fc-DAB analogue.[26] On the other hand, it must be pointed out that for the tetracarbonyl adducts (Fc-DAB)M$(CO)_4$ (M = Cr, Mo, W) the ability of the metallacycle to favour an interaction between the two ferrocenyl donor units increases according to the sequence Cr < Mo < W, and thus the separation of the two sequential oxidations of the ferrocene groups after $M(CO)_4$ coordination also follows the same trend. For our compounds (FcNN)$M(CO)_4$, the same trend is partially observed, as no split of the two ferrocenyl oxidation processes was observed for the Cr analogue **2**, while two anodic peaks were observed for the Mo compound **4**. However, as was observed for (FcNN)$Cr(CO)_4$ (**2**), the anodic peak at more positive potential in the CV of complex **4** has its counterpart peak in the reverse scan at $E_{pc}(2) = 0.66$ V, with very high current intensity, and after several potential cycles there is also the deposition of a monolayer type electroactive film at the surface of the electrode. Consequently, no straightforward comparison can be made between these compounds and their homologous compounds derived from Fc-DAB due to the irreversible nature of the electrochemical process at more positive potentials.

Fig. 6 shows a series of cyclic voltammograms recorded at different times for a solution prepared by dissolving the inclusion compound 2TRIMEB·(FcNN)$Mo(CO)_4$ (**5**) in CH_2Cl_2. No increase in current intensity was observed during several consecutive cycles. The first CV, taken at 0.25 V s^{-1} as soon as possible after the preparation of the solution (t = 0 min), shows a shoulder at 0.58 V, with no cathodic counterpart (assigned to the Mo-centred oxidation), followed by two oxidations at 0.82 and 0.93 V, with the corresponding cathodic waves in the reverse sweep at 0.92 and 0.74 V. These two processes can be assigned to the two ferrocenyl oxidation processes, as film adsorption on the surface of the electrode is hindered by the redox site isolation induced by encapsulation of the two Fc groups in the CD moieties.

The cyclic voltammogram after 3 min is similar to the previous one, but after 6 min the waves at more positive potentials and the shoulder at 0.58 V start to decrease in intensity, and after 15 min they are no longer visible. On the other hand, the anodic wave at 0.82 V and the cathodic wave at 0.74 V retain their characteristics with minor potential shifts and are the only ones that can be seen after 15 min. This process must correspond to the oxidation of the two encapsulated ferrocenyl groups. The $E_{1/2}$ value is shifted 0.23 V to more positive potentials relative to that of free FcNN (**1**), as has been observed for inclusion compounds of ferrocene derivatives in β-CD.[32] The peak separation of 0.1 V matches that observed for the free ligand FcNN and confirms the presence of two isolated one-electron oxidation processes. Furthermore, no features due to the $Mo(CO)_4$ fragment could be detected in the last recorded cyclic voltammogram. Taken together, these results suggest that, upon encapsulation of (FcNN)$Mo(CO)_4$ in TRIMEB, strong interactions occur between the CD host and the Fc groups, leading to a decrease of the influence of the $M(CO)_4$ fragment on the overall Fc properties.

As no features due to the $Mo(CO)_4$ fragment could be detected, we checked the possibility of de-coordination of this fragment by preparing the inclusion compound of TRIMEB with FcNN (using the method applied for the synthesis of **5**) and recording its cyclic voltammogram under the same

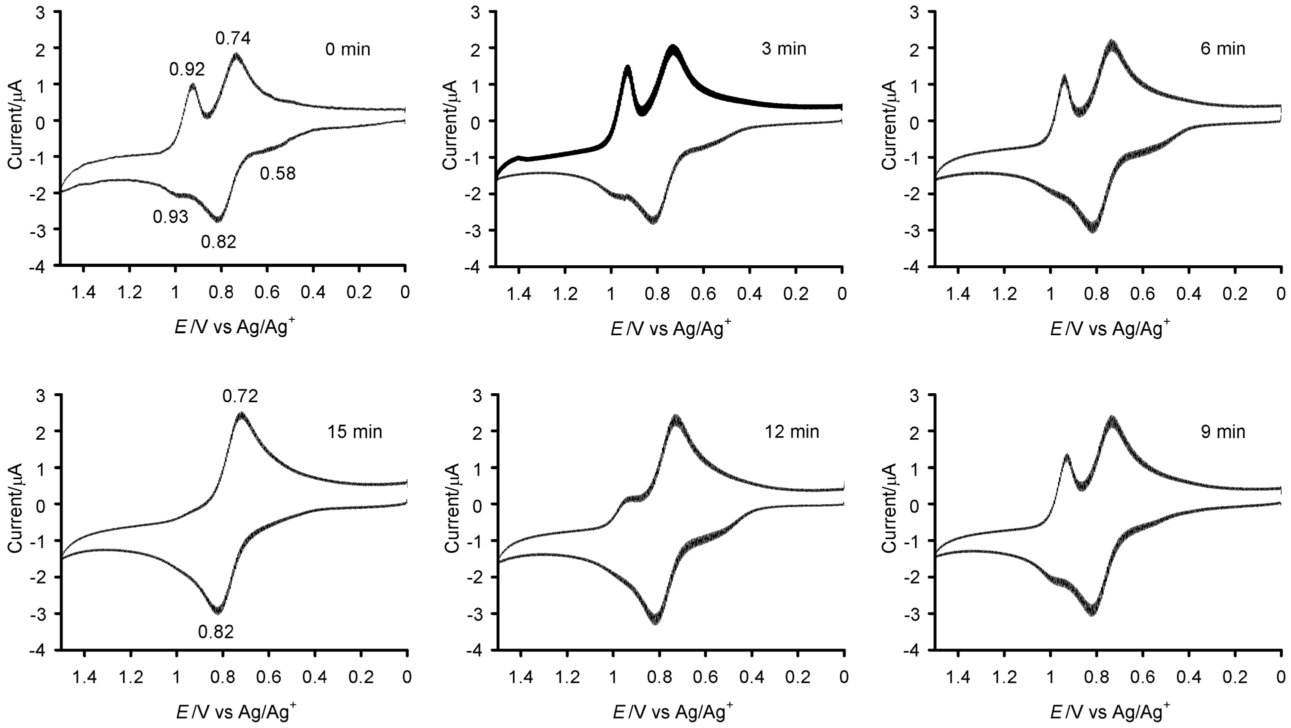


Fig. 6 Cyclic voltammograms of the inclusion compound **5** in CH_2Cl_2 at room temperature and 0.25 V s^{-1}, taken at 3 min intervals.

experimental conditions (not shown). After a stabilisation period, one reversible two-electron oxidation process was observed at $E_{1/2}$ = 0.83 V, with ΔE_p = 0.13 V. The strong influence of the CD moiety on the electrochemical properties of Fc groups is clearly seen in the high value of $E_{1/2}$ obtained, compared with the values for the free ligand ($E_{1/2}$ = 0.55) and the inclusion compound 2TRIMEB · (FcNN)Mo$(CO)_4$ ($E_{1/2}$ = 0.77 V). Furthermore, the difference between the latter value and that of the encapsulated ligand can be taken as evidence that no de-coordination of the Mo$(CO)_4$ fragment has occurred after encapsulation of (FcNN)Mo$(CO)_4$ in TRIMEB, as might be inferred by the disappearance of the Mo-based electrochemical response in the cyclic voltammogram.

Concluding remarks

Stable *cis*-$L_2M(CO)_4$ complexes have been prepared starting from the hexacarbonyl complexes and ferrocenyldiimine. The change from M = Cr to M = Mo is sufficient to induce isomerisation of the ligand. It has been shown that the molybdenum carbonyl complex (FcNN)Mo$(CO)_4$ can be immobilised in heptakis-2,3,6-tri-*O*-methyl-β-CD (TRIMEB) using a non-aqueous solvent. We assume that the guest species adhere to an inclusion model in which each ferrocenyl subunit penetrates deeply into the CD cavity in axial mode, giving rise to a 2 : 1 host : guest stoichiometry. This inclusion in **5** has a strong influence on the electrochemical properties of the ferrocenyl groups. Further studies aimed at understanding this phenomenon are under way in our laboratories. A comparison of the reactivity of free and encapsulated complexes, for example in oxidative decarbonylation, is also under investigation.

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