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Synthesis and characterization of the inclusion compound of a methyltrioxorhenium(VII) adduct of 4-ferrocenylpyridine with β-cyclodextrin

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Abstract

An organometallic Lewis base adduct of methyltrioxorhenium(VII) (MTO), comprising the ligand 4-ferrocenylpyridine, has been isolated and characterized. The binuclear complex and also the precursor free ligand have been immobilized in β-cyclodextrin (CD) to give inclusion complexes with a one-to-one stoichiometry. Powder X-ray diffraction (XRD) indicates that the microcrystalline powders obtained are true homogeneous inclusion complexes. This is corroborated by thermogravimetric analysis (TGA), which indicates that the ferrocenylpyridine ligand gains an additional thermal stability upon encapsulation. FTIR and ^{13}C- solid-state CP MAS NMR spectroscopy confirm that the Re–N ligation is intact for the included binuclear complex. The NMR results also support the conclusion that the monosubstituted ferrocene derivatives adhere to an inclusion model in which the ferrocene penetrates deeply into the CD cavity in axial mode while the substituent protrudes out. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyclodextrins; Inclusion compounds; Lewis base adducts; Methyltrioxorhenium; Ferrocene derivatives

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven or eight (1→4)-linked α-D-glucopyranose units (α-, β- and γ-CD, respectively) [1–3]. They form inclusion complexes with smaller molecules that fit into their 5–8 Å cavity [3–5]. 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 [5,6]. With these ligands, the weaker categories of non-covalent bonding, e.g. van der Waals and charge transfer interactions, assume considerable importance. Encapsulated metallo-organic complexes often exhibit markedly different physical and chemical properties compared with the bulk material, for example, in their nonlinear optical properties [7,8], and ligand substitution/insertion reactions [9,10]. CD are known to bind ferrocene and its derivatives [11–17], titanocene and molybdenocene dihalides [18,19], aromatic ruthenium complexes [20], mixed sandwich complexes such as $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)](PF_6)$ [21], and half-sandwich complexes such as $CpFe(CO)_2X$ (X = Cl, Me) [9,10,22], $[CpFe(CO)_2NH_3](PF_6)$ [23], $CpMn(CO)_3$ [24], $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ [25], $Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2$ [26], $Cp'Mo(\eta^3\text{-}C_6H_7)(CO)_2$ and $[Cp'Mo(\eta^4\text{-}C_6H_8)(CO)_2](BF_4)$ (Cp′ = Cp, Ind) [27]. Ferrocene itself forms a 2:1 (host-to-guest) adduct with α-CD, and 1:1 adducts with β and γ-CD [11–14]. On the other hand, the interaction of CD with binuclear organometallic compounds has scarcely been studied [28]. In the present work, 4-ferrocenylpyridine and its 1:1 adduct with methyltrioxorhenium(VII) (MTO) have been immobilized in β-CD and the resulting novel inclusion compounds characterized by a range of solid-state physicochemical techniques.

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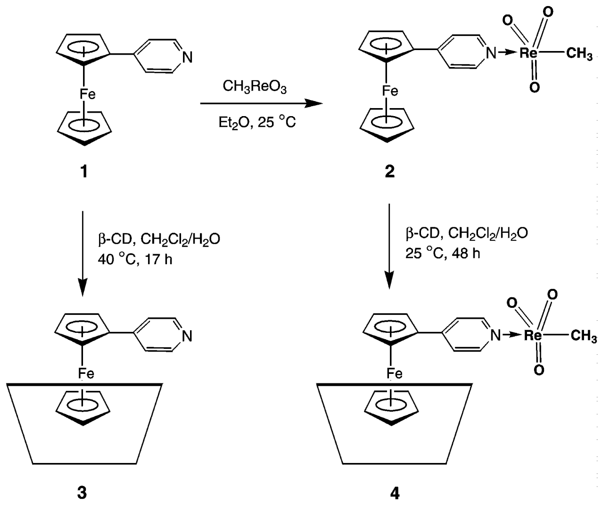
2. Results and discussion

2.1. Synthesis and characterization of guest species

Lewis base adducts of MTO, particularly pyridine derivatives, are interesting to study because the addition of Lewis bases to MTO-catalyzed olefin epoxidations significantly reduces the formation of diols [29]. Recently, it was shown that MTO forms trigonal-bipyramidal adducts with 1,1′-bis(4-pyridylethynyl)ferrocene and ferrocenyl-4-pyridylacetylene [30]. These were the first stable and fully characterized organometallic Lewis base adducts of MTO to be reported. We have now prepared another organometallic Lewis base adduct of MTO, containing the ligand 4-ferrocenylpyridine (**1**). The ligand **1** was prepared by nickel-catalyzed coupling of the Grignard reagent from bromoferrocene with 4-bromopyridine [31]. Treatment of MTO with one equivalent of **1** in diethyl ether at room temperature immediately leads to the formation of complex **2** (Scheme 1), which can be isolated from the orange suspension as a light orange solid in good yield. The pyridyl ring stretching vibration of **2** appears at 1606 cm^{-1}, the corresponding band of **1** at 1598 cm^{-1}. A similar shift in the frequency of this vibration was observed upon coordination of ferrocenyl-4-pyridylacetylene to MTO [30]. The Re=O stretching vibrations are shifted from 958 (asym.) and 1005 cm^{-1} (sym.) for MTO to 930 and 942 cm^{-1} for **2**, reflecting the donor capacity of ligand **1**. The ^{17}O-NMR shift for **2** (δ 865) is significantly down-field shifted compared with free MTO (δ 829), indicating that less electron density is withdrawn from the terminal oxygen ligands. The pyridyl protons of **2** [$\delta(H_\alpha)$ 8.11, $\delta(H_\beta)$ 7.40] differ in their chemical shift from those of **1** [$\delta(H_\alpha)$ 8.44, $\delta(H_\beta)$ 7.30]. On the other hand, the ferrocene proton resonances are comparable with those of the 'free' ligand, because they are far apart from the Re^{VII}. The proton NMR signal corresponding to the methyl group of **2** appears at δ 1.88 which is shifted notably upfield compared with the un-coordinated MTO (δ 2.67) as a result of the electron density donated by the N-donor ligand to the Lewis acidic Re^{VII}. The 1:1 adduct of pyridine with MTO gave a similar chemical shift for this resonance (δ 1.90) [32].



Scheme 1.

2.2. Synthesis and characterization of β-CD inclusion compounds

Mixing of an aqueous solution of β-CD with a solution of **1** or **2** in dichloromethane results in the formation of an orange precipitate at the interface between the two solutions. The products **3** and **4** were isolated by filtration, rinsed with water and dichloromethane, and dried in vacuo at ambient temperature (Scheme 1). Elemental analysis supports the formation of stoichiometric 1:1 (host-to-guest) inclusion compounds. The washing steps did not liberate the guests from the host cavities. The products were further characterized in the solid-state by thermogravimetric analysis (TGA), powder X-ray diffraction (XRD), FTIR and ^{13}C- CP MAS NMR spectroscopy.

2.2.1. Powder XRD and TGA

The β-CD adducts **3** and **4** were obtained as microcrystalline powders and examined by powder XRD (Fig. 1). Also shown are the diffraction patterns of plain β-CD hydrate, 4-ferrocenylpyridine (**1**) and (4-ferrocenylpyridine)methyltrioxorhenium (**2**). Clearly, **3** and **4** do not contain measurable amounts of non-included crystalline **1** and **2**, respectively. The patterns for **3** and **4** are quite different from that of β-CD hydrate, suggesting that true inclusion complexes exist in the solid state [4]. Powder XRD can sometimes be used to quickly identify the type of crystal packing that exists in cyclodextrin inclusion compounds. For example, it was possible to show that channel-type inclusion compounds are formed after reacting β-CD with the half-sandwich molybdenum complexes $CpMo(\eta^3\text{-}C_3H_5)(CO)_2$, $IndMo(\eta^3\text{-}C_3H_5)(CO)_2$ [26], $CpMo(\eta^3\text{-}C_6H_7)(CO)_2$ and $[CpMo(\eta^4\text{-}C_6H_8)(CO)_2](BF_4)$ ($Cp = \eta^5\text{-}C_5H_5$, $Ind = C_9H_7$) [27]. However, in the cases of **3** and **4**, no clear conclusions can be drawn from the powder XRD data about the type of crystal packing.

Thermal analysis methods can be used for the recognition of inclusion complexation [33]. Fig. 2 shows the results of TGA of 4-ferrocenylpyridine (**1**), 4-ferrocenylpyridine·β-CD (**3**), plain β-CD hydrate and a physical mixture of β-CD and **1** in a 1:1 molar ratio. TGA of β-CD shows loss of hydrated water up to 130 °C (14.4%, 10–11 water molecules per β-CD molecule), the maximum rate of mass loss occurring at 90 °C. There is no further change until 260 °C when

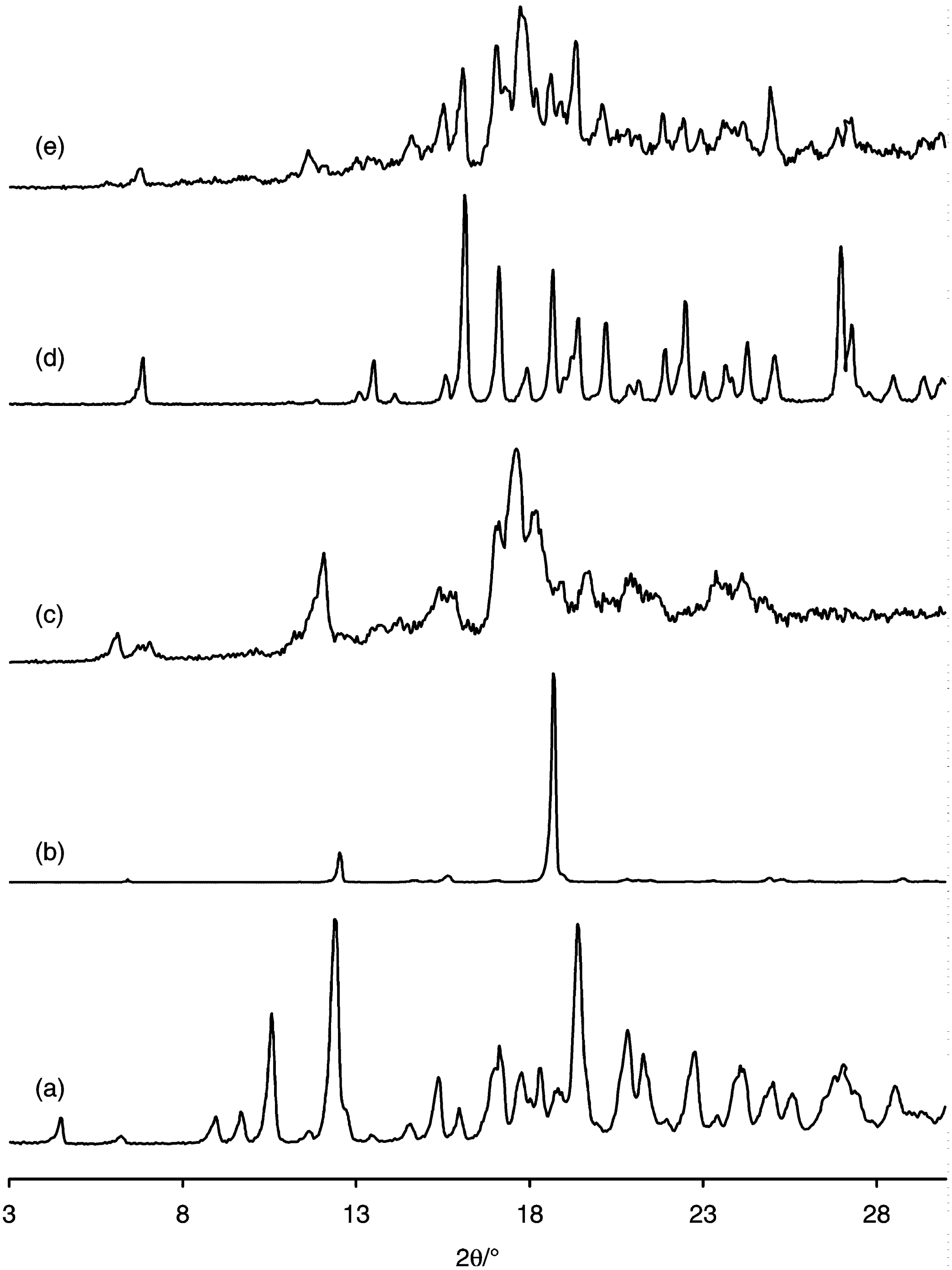


Fig. 1. Powder XRD patterns of (a) plain β-CD hydrate, (b) 4-ferrocenylpyridine (**1**), (c) 4-ferrocenylpyridine β-CD (**3**), (d) (4-ferrocenylpyridine)methyltrioxorhenium (**2**), and (e) (4-ferrocenylpyridine)methyltrioxorhenium·β-CD (**4**).

the compound starts to melt and decompose, characterized by an intense, sharp peak in the differential thermogravimetric (DTG) profile at 287 °C. At 500 °C, 100% mass loss is complete. The organometallic Lewis base ligand **1** starts to melt at 135 °C and then decomposes in a single stage, losing 83.5% mass up to 240 °C ($\mathrm{DTG_{max}} = 230$ °C). At 360 °C the residual mass is 7%. In the case of the physical mixture each component behaves independently. Steps are visible in the TG profile corresponding to the stages where dehydration of β-CD takes place, the organometallic ligand melts and decomposes, and β-CD melts and decomposes. The inclusion compound **3** is stable under N_2 up to 250 °C except for loss of water in the temperature range 25–175 °C (10%, nine to ten water molecules per β-CD molecule). Unlike the physical mixture, no clear step is observed corresponding to decomposition of the 'free' ligand **1**. Instead, the liberation of the organometallic ligand and degradation of the β-CD structure occur in the same temperature

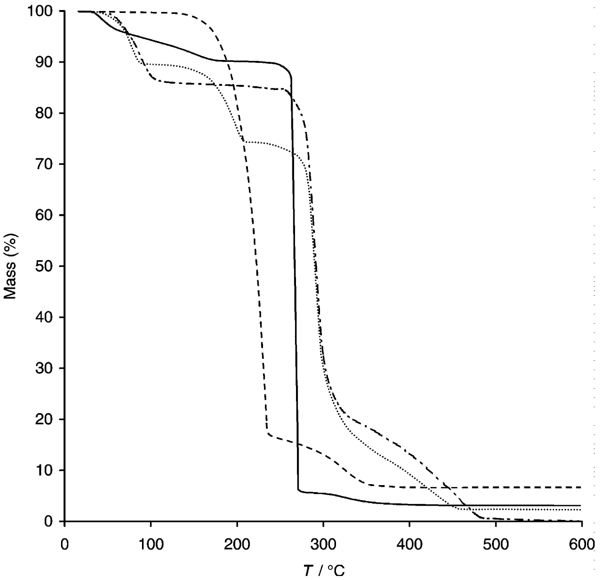


Fig. 2. TGA of 4-ferrocenylpyridine·β-CD (**3**) (—), 4-ferrocenylpyridine (**1**) (– – – –), free β-CD hydrate (—-—-), and a physical mixture of β-CD and **1** in a 1:1 molar ratio (·········).

range and are impossible to distinguish. A very rapid mass loss of 84% occurs in the temperature range 250–280 °C ($DTG_{max} = 267$ °C). These results indicate that the ferrocene derivative gains an additional thermal stability after inclusion complexation into the β-CD cavity.

Three main stages are observed in the thermal decomposition of the adduct (4-ferrocenylpyridine)methyltrioxorhenium (**2**) (Fig. 3), characterized by DTG maximums at 135, 375 and 500 °C. The first stage, which begins at 105 °C, must correspond to rupture of the Re–N bond and sublimation of the now un-coordinated MTO. Pure MTO sublimes below 100 °C under TG conditions [34]. Coordination of MTO to **1** obviously improves its thermal stability to a certain degree. In the case of the physical mixture of β-CD and **2**, two steps are observed below 150 °C corresponding to loss of hydrated water from β-CD and the first stage in the decomposition of 'free' **2**. As observed for β-CD and **1**, decomposition of the physical mixture can be interpreted in terms of decomposition of the individual components. The inclusion compound **4** displays a TG profile similar to that observed for **3**. A mass loss of 13% is recorded in the temperature range 25–210 °C. There is a shallow step centred at about 133 °C, presumably due to fragmentation of the included complex and subsequent sublimation of MTO. Further heating reveals a very different decomposition behavior than that observed for the physical mixture. An abrupt mass loss of 62% occurs in the temperature range 210–250 °C ($DTG_{max} = 240$ °C). Further heating gives a residual mass of 6.0% at 800 °C.

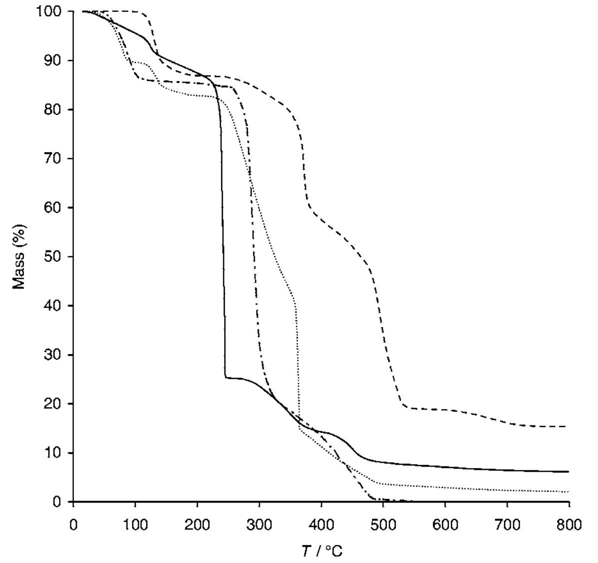


Fig. 3. TGA of (4-ferrocenylpyridine)methyltrioxorhenium·β-CD (**4**) (—), (4-ferrocenylpyridine)methyltrioxorhenium (**2**) (– – – –), free β-CD hydrate (—-—-), and a physical mixture of β-CD and **2** in a 1:1 molar ratio (·········).

2.2.2. *FTIR and solid-state ^{13}C- CP MAS NMR spectroscopy*

The KBr IR spectra of the inclusion compounds **3** and **4** show several new absorption bands on top of the characteristic vibrations of the host. These are assigned to vibrations of the guest molecules. In the case of **3**, the pyridyl ring stretching vibration appears at 1604 cm^{-1}, compared with 1598 cm^{-1} for the 'free' ligand **1**. This shift difference may be due to a number of factors, including the effect of placing the pyridyl ring in the constrained environment of the host. There may also be a hydrogen-bonding interaction with the hydroxyl groups of the host. Both **3** and **4** display at least one band in the range 800–850 cm^{-1} that can be assigned to out-of-plane C–H deformations of the cyclopentadienyl and/or pyridyl rings of the guest molecules. The pyridyl ring stretching vibration of **4** appears in the same position as that for the non-included adduct **2** (1606 cm^{-1}), which is an initial indication that the structural integrity of the binuclear complex is retained in the encapsulated state. This is confirmed by the presence of medium intensity bands for the Re=O stretching vibrations at 930 and 941 cm^{-1}, un-shifted compared with **2**.

The solid-state ^{13}C- CP MAS NMR spectra of β-CD hydrate, 4-ferrocenylpyridine (**1**) and 4-ferrocenylpyridine·β-CD (**3**) are shown in Fig. 4. The spectrum of β-CD hydrate is similar to that previously reported and exhibits multiple resonances for each type of carbon atom [35–37]. This has been mainly correlated with different torsion angles about the (1→4) linkages for C-1 and C-4 [35,36], and with torsion angles describing the orientation of the hydroxyl groups [37]. The different carbon resonances are assigned to C-1 (101–104 ppm), C-4 (78–84 ppm), C-2,3,5 (71–76 ppm)

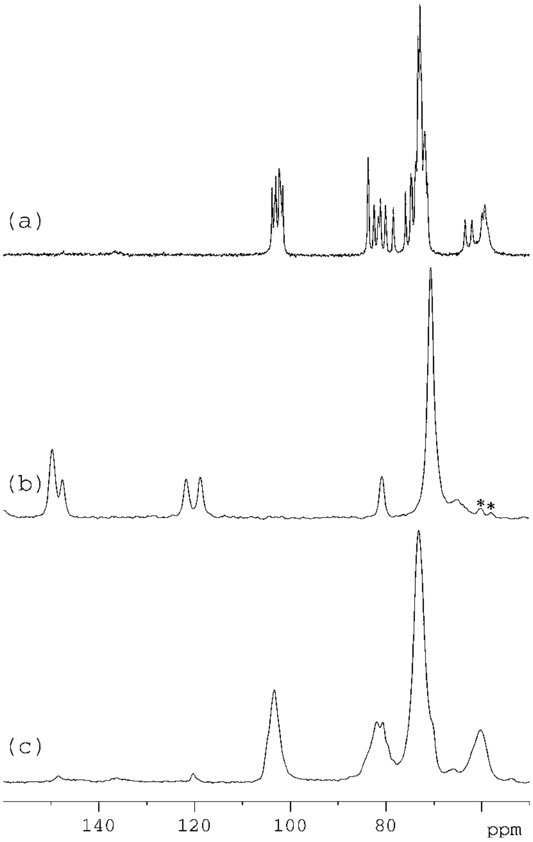


Fig. 4. Solid-state ^{13}C- CP MAS NMR spectra of (a) plain β-CD hydrate, (b) 4-ferrocenylpyridine (**1**), and (c) 4-ferrocenylpyridine·β-CD (**3**). Asterisks denote spinning sidebands.

and C-6 (57–65 ppm). Contrastingly, the β-CD carbons C-1, C-2,3,5 and C-6 for complex **3** are observed as single broad peaks at 103.3, 73.2 and 60.1 ppm, respectively. This is a clear indication that the ferrocenyl derivative is included in the cavities of β-CD, as it implies that β-CD adopts a more symmetrical conformation in the complex, with each glucose unit in a similar environment [38]. Additional peaks in the spectrum are readily assigned to the resonances of the carbon atoms of the guest molecule. The cyclopentadienyl and pyridyl rings give rise to peaks at 65.7 (C_5H_4), 70.2 (C_5H_5), 120.3 (C_5H_4N) and 148.5 ppm (C_5H_4N), largely un-shifted compared with the corresponding resonances for pure **1**. Comparable results were obtained for the inclusion complex **4** containing the binuclear adduct **2** (Fig. 5). The resonances for the Cp and methyl carbons of the guest molecule are observed at 70.8 and 30.0 ppm, respectively. These are un-shifted compared with the corresponding resonances for 'free' **2**.

The inclusion complex **4** was not effective as a catalyst for the heterogeneous epoxidation of cyclooctene by hydrogen peroxide (see Section 4 for details). After 24 h reacting, the conversion was 8.8% with selectivity to the epoxide of 27%.

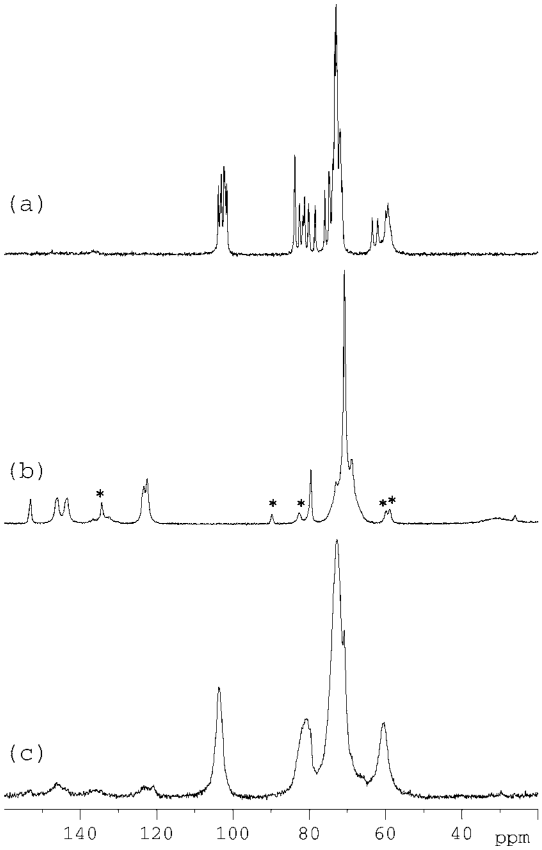


Fig. 5. Solid-state ^{13}C- CP MAS NMR spectra of (a) plain β-CD hydrate, (b) (4-ferrocenylpyridine)methyltrioxorhenium (**2**), and (c) (4-ferrocenylpyridine)methyltrioxorhenium·β-CD (**4**). Asterisks denote spinning sidebands.

3. Concluding remarks

An organometallic Lewis base adduct of MTO has been prepared and successfully immobilized in β-CD to give a true inclusion complex in a crystalline state. Spectroscopic evidence confirms that MTO remains coordinated to the organometallic ligand in the encapsulated guest species. The poor solubility of the inclusion complex in most solvents precludes its use in homogeneous catalysis, or liquid-phase biphasic catalysis. Use of a modified CD may improve this situation and is the focus of current research in our laboratories.

4. Experimental

4.1. General remarks

All air-sensitive operations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were dried by standard procedures, distilled under nitrogen or argon, and stored over 4 Å molecular sieves. Microanalyses were performed at the ITQB (Oeiras, Portugal) and the Mikroanalytisches

Labor of the TU München in Garching. TGA studies were performed using a Shimadzu TGA-50 system at a heating rate of 5 K min^{-1} under a nitrogen atmosphere. Powder XRD data were collected on a Philips X'pert diffractometer using Cu–K_α radiation filtered by Ni ($\lambda = 1.5418$ Å). Infrared spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker 270 spectrometer, and ^{17}O-NMR spectra on a Bruker Avance DPX-400 spectrometer. ^{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 9 kHz and 12 s recycle delays. Chemical shifts are quoted in parts per million from tetramethylsilane (TMS).

β-CD was obtained from Wacker Chemie and recrystallized before use. 4-Ferrocenylpyridine (**1**) was prepared as described in the literature [31]. ^{13}C- CP MAS NMR of **1**: δ 149.7, 147.6 (C_α of C_5H_4N), 121.7, 118.8 (C_β of C_5H_4N), 80.8 (C_5H_4), 70.7 (C_5H_5), 68.3 (C_5H_4).

4.2. (4-Ferrocenylpyridine)methyltrioxorhenium (*2*)

A solution of CH_3ReO_3 (0.30 g, 1.2 mmol) in diethyl ether (15 ml) was treated with 4-ferrocenylpyridine (0.32 g, 1.2 mmol). The color of the solution changed to orange and immediately a solid started to precipitate. After 60 min, the solution was evaporated to dryness and the product washed with *n*-hexane (20 ml). Yield: 0.59 g (96%). Found: C, 37.52; H, 2.82; N, 2.60; Fe, 10.84. $C_{16}H_{16}NO_3FeRe$ (512.35) requires C, 37.51; H, 3.15; N, 2.73; Fe, 10.90%—ν_{max} (cm^{-1}) 3101m, 1606vs, 1522m, 1433m, 1388m, 1383m, 1294m, 1225m, 1209m, 1107m, 1066m, 1040m, 1020s, 1011s, 942vs, 930vs, 892m, 862m, 839m, 830m, 820m, 688m, 644m, 562m, 529m, 517m, 496m, 479m, 436m (KBr)—δ_H (270 MHz, CD_2Cl_2, room temperature (r.t.)) 8.11 (d, 2 H, H_α of C_5H_4N), 7.40 (d, 2 H, H_β of C_5H_4N), 4.77 (t, 2 H, H_α of C_5H_4), 4.51 (t, 2 H, H_β of C_5H_4), 4.04 (s, 5 H, C_5H_5), 1.88 (s, 3 H, CH_3ReO_3). δ_C (CD_2Cl_2, r.t.) 153.25 (C_5H_4N), 147.05 (C_5H_4N), 121.97 (C_5H_4N), 79.41 (C_5H_4), 71.63 (C_5H_4), 70.62 (C_5H_5), 67.73 (C_5H_4), 24.88 (CH_3ReO_3)—^{13}C- CP MAS NMR: δ 153.1, 146.1, 143.5, 123.2, 122.5, 79.6, 70.7, 68.9, 29.9. δ_O (54.14 MHz, CD_2Cl_2, r.t.) 865.4.

4.3. 4-Ferrocenylpyridine·β-CD (*3*)

A solution of β-CD (0.21 g, 0.18 mmol) in water (6 ml) was treated with a solution of 4-ferrocenylpyridine (0.05 g, 0.18 mmol) in dichloromethane (1.5 ml) and the mixture kept at 40 °C for 17 h. The suspension was filtered and the pale orange powder washed several times with water (10 ml), dichloromethane (3 ml), and vacuum dried. Yield: 0.19 g (68%). Found: C, 42.99; H, 6.46; N, 0.77; Fe, 3.32. $(C_{15}H_{13}NFe)\cdot(C_{42}H_{70}O_{35})\cdot 10H_2O$ (1578.25) requires C, 43.38; H, 6.56; N, 0.89; Fe, 3.54%—ν_{max} (cm^{-1}) 3381vs, 2925s, 1604m, 1413m, 1385m, 1368m, 1335m, 1302m, 1245m, 1202m, 1157vs, 1104s, 1080vs, 1055s, 1030vs, 1004m, 947m, 939m, 859m, 823m, 756m, 706s, 608m, 579s, 531s (KBr)—^{13}C-CP MAS NMR (see Fig. 6 for labeling): δ 148.5 (s, C_5H_4N), 120.3 (s, C_5H_4N), 103.3 (β-CD, C-1), 81.9, 80.7 (β-CD, C-4), 73.2 (β-CD, C-2,3,5), 70.2 (sh, C_5H_5), 65.7 (C_5H_4), 60.1 (β-CD, C-6).

4.4. (4-Ferrocenylpyridine)methyltrioxorhenium·β-CD (*4*)

A solution of β-CD (0.44 g, 0.39 mmol) in water (18 ml) was treated with a solution of **2** (0.20 g, 0.39 mmol) in dichloromethane (6 ml) and the mixture kept at r.t. for 48 h. The suspension was filtered and the pale orange powder washed several times with water (15 ml), dichloromethane (5 ml), and vacuum dried. Yield: 0.38 g (55%). Found: C, 39.08; H, 6.00; N, 0.68; Fe, 2.98. $(C_{16}H_{16}NO_3FeRe)\cdot(C_{42}H_{70}O_{35})\cdot 8H_2O$ (1791.46) requires C, 38.88; H, 5.74; N, 0.78; Fe, 3.11%—ν_{max} (cm^{-1}) 3374vs, 2926s, 1631m, 1607m, 1520m, 1433m, 1412m, 1384m, 1368m, 1334m, 1300m, 1225m, 1208m, 1157vs, 1106s, 1080vs, 1056s, 1030vs, 1006m, 941m, 930s, 892m, 862m, 840m, 821m, 758m, 705m, 688m, 668m, 609m, 579s, 529m, 497m, 479m, 412m (KBr)—^{13}C- CP MAS NMR: δ 146.2 (s, C_5H_4N), 120.7 (s, C_5H_4N), 103.7 (β-CD, C-1), 80.6 (β-CD, C-4), 72.7 (β-CD, C-2,3,5), 70.8 (sh, C_5H_5), 65.7 (C_5H_4), 60.4 (β-CD, C-6), 30.0 (CH_3ReO_3).

4.5. Catalytic epoxidation of cyclooctene

cis-Cyclooctene (400 mg, 3.65 mmol) and *n*-dibutylether (400 mg, internal standard), 1 mol% (36 μmol) **4** (as catalyst), appropriate amount of ligand and 2.5 ml of CH_2Cl_2–$CHCl_3$ were added to a thermostated reaction vessel. Hydrogen peroxide (0.8 ml, 35%, 9.3 mmol) was added to start the reaction. The two phase reaction system was stirred for 24 h. The course of the reaction was monitored by quantitative GC analysis; samples were taken from the organic phase, diluted with CH_2Cl_2, and treated with a catalytic amount of MnO_2 and $MgSO_4$ to destroy the hydrogen peroxide and remove water. The resulting slurry was filtered over a filter equipped with a Pasteur pipette, and the filtrate injected

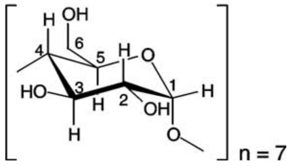


Fig. 6.

into a GC column. The conversion of *cis*-cyclooctene and the yield of cyclooctene epoxide were calculated from a calibration curve ($r^2 = 0.999$) recorded prior to the reaction course.

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