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The complex CpMo(CO)₃(CH₂-pC₆H₄-CO₂CH₃) and its inclusion complexes with heptakis(2,6-di-*O*-methyl)- β -cyclodextrin (CD) and heptakis(2,3,6-tri-*O*-methyl)- β -CD were prepared and characterized, and investigated as catalyst precursors for the epoxidation of *cis*cyclooctene at 55 °C. Different types of oxidants (*tert*-butylhydroperoxide or H₂O₂) and biphasic liquid-liquid solvent systems were used with the aim of facilitating catalyst recycling. Revised manuscript for J. Organomet. Chem.

Synthesis and Characterization of $CpMo(CO)_3(CH_2-pC_6H_4-CO_2CH_3)$ and its Inclusion Compounds with Methylated Cyclodextrins. Applications in Olefin Epoxidation Catalysis

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Dedicated to the memory of Professor F. Gordon A. Stone in recognition of his outstanding contributions to the development of organometallic chemistry

The cyclopentadienyl molybdenum tricarbonyl complex $CpMo(CO)_3(CH_2-pC_6H_4-CO_2CH_3)$ (1) ($Cp = \eta^5-C_5H_5$) and its 1:1 inclusion complexes with heptakis(2,6-di-*O*-methyl)- β -cyclodextrin (1@DIMEB) and heptakis(2,3,6-tri-*O*-methyl)- β -cyclodextrin (1@TRIMEB)

were prepared and characterized by elemental and thermogravimetric analyses, powder X-ray diffraction, NMR, FT-IR and Raman spectroscopy. All three compounds were investigated as catalyst precursors for olefin epoxidation using *cis*-cyclooctene (Cy) as a model substrate, a reaction temperature of 55 °C, and different types of oxidants (*tert*-butylhydroperoxide in decane (TBHPdec) or in water (TBHPaq), and aqueous hydrogen peroxide). With the aim of facilitating recycling of the homogeneous catalytic systems, different solvent mixtures were tested: biphasic liquid-liquid solvent systems [(water, glycerol, ionic liquid)-(n-hexane, α,α -trifluorotoluene (TFT), iso-butyl methyl ketone)], and in some cases no cosolvent was added. Excellent epoxide selectivity (100%) was observed for all tested catalytic systems. An example of an interesting catalytic system is that of **1@TRIMEB/TBHPaq/TFT/H**₂O since the catalyst can be easily separated in the form of an aqueous solution, by decantation, from the organic phase containing the reaction products and recycled.

Keywords: Molybdenum; Cyclopentadienyl complexes; Carbonyl ligands; Methylated cyclodextrins; Olefin epoxidation

1. Introduction

During the last decade cyclopentadienyl oxomolybdenum(VI) complexes have received much interest as catalysts of oxygen transfer reactions [1]. Although the ability of organometallic (η^5 -C₅R₅)MoO₂X derivatives to act as catalysts for the epoxidation of olefins by alkyl hydroperoxides was first reported by Trost and Bergman in 1991 (for the complex with X = Cl and R = Me) [2], the study of these complexes in olefin epoxidation only gained momentum with the discovery of a general and straightforward one-step synthesis involving reaction of the corresponding and readily available (η^5 -C₅R₅)Mo(CO)₃Cl precursors (R = H,

CH₃, CH₂Ph) with *tert*-butylhydroperoxide (TBHP) [1a]. In fact, the parent tricarbonyls can be used directly as catalyst precursors since they are transformed into (η^5 -C₅R₅)MoO₂Cl under the operating catalytic conditions. A number of half-sandwich molybdenum dicarbonyl and tricarbonyl complexes have since been investigated as catalyst precursors for the epoxidation of olefins [3], the *cis*-dehydroxylation of olefins [4], and the oxidation of amines [5], alcohols [6] and sulfides [7]. Apart from dioxomolybdenum(VI) derivatives of the type Cp'MoO₂X (Cp' = η^5 -C₅H₅ (Cp), η^5 -C₅H₄R, η^5 -C₅R₅), the species formed upon oxidative decarbonylation of these precursors include Cp'MoO(O₂)X [1e], [Cp'MoO₂]₂(μ -O) and [Cp'MoO(O₂)]₂(μ -O) [1d] from Cp'Mo(CO)₃X, [CpMoO₂(NHC)]⁺ from [CpMo(CO)₂(NHC)(NCMe)]⁺ (NHC = N-heterocyclic carbene) [3j], and [Cp^{ox}MoO₂]⁺ from [Cp^{ox}Mo(CO)₂(NCMe)]⁺ (Cp^{ox} = cyclopentadienyl functionalized with oxazoline bridging unit) [3k].

The above-mentioned catalytic systems are homogeneous in nature. Although the active catalysts can sometimes be recovered from the reaction mixtures and reused, the catalytic activities are prone to decrease with successive recycling runs, and catalyst losses are inevitable. Some of the approaches investigated to overcome these drawbacks include the heterogenization of either the parent carbonyls or the organometallic oxides on porous inorganic supports [8], immobilization in room temperature ionic liquids (RTILs) [3d,3e,9], and encapsulation in cyclodextrins (CDs) [10]. We found that CD inclusion complexes containing CpMo(CO)₃X precatalysts (X = Cl, CH₂CONH₂) could be used in solid-liquid, homogeneous or liquid-liquid (aqueous/organic) biphasic systems for the epoxidation of cyclooctene with TBHP or H₂O₂ [10]. Of particular note was the observation that the introduction of native β -CD or permethylated β -CD (TRIMEB) to the system with CpMo(CO)₃Cl and H₂O₂ was able to instill some catalytic epoxidation activity under certain reaction conditions. Due to their protective effects on encapsulated guests, the use of CDs in

organometallic oxidation catalysis may be particularly useful in cases where the free catalyst is initially highly active but loses activity during the reaction due to decomposition. Immobilization in a CD may help to stabilize the catalyst and also facilitate subsequent recycling. Furthermore, CDs are excellent organic supports to work in aqueous solutions, allowing more "environmentally friendly" oxidants to be used such as hydrogen peroxide.

As part of our ongoing work on the applications of molybdenum carbonyl complexes and their cyclodextrin inclusion complexes in catalytic olefin epoxidation, we now wish to report on the encapsulation of the tricarbonyl complex $CpMo(CO)_3(CH_2-pC_6H_4-CO_2CH_3)$ in heptakis(2,6-di-*O*-methyl)- β -cyclodextrin (DIMEB) and heptakis-2,3,6-tri-*O*-methyl- β cyclodextrin (TRIMEB), and an investigation of the catalytic behavior of the inclusion compounds in the epoxidation of cyclooctene using TBHP or H₂O₂ as oxidant.

2. Experimental

2.1. Materials and methods

Microanalyses (CH) were obtained at the University of Aveiro (by M. Marques) and the Analysis Laboratory of the Instituto Superior Técnico, Technical University of Lisbon. ICP measurements for Mo were performed at the latter Analysis Laboratory. Powder X-ray diffraction (XRD) data were collected on a Philips X'pert MPD diffractometer equipped with an X'Celerator detector, a graphite monochromator (Cu-K α X-radiation filtered by Ni (λ = 1.5418 Å)) and a flat-plate sample holder, in a Bragg-Brentano para-focusing optics configuration (45 kV, 50 mA). Samples were step-scanned in 0.02° 2 θ steps with a counting time of 50 s per step. Thermogravimetric analysis (TGA) studies were performed using a Shimadzu TGA-50 system at a heating rate of 5 °C min⁻¹ under air.

Transmission FT-IR spectra were measured on a Mattson 7000 spectrometer. FT-Raman spectra were recorded on a RFS-100 Bruker FT-Spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm. Solution NMR spectra were recorded on a Bruker Avance II+ 400 MHz (UltraShieldTM Magnet) spectrometer at ambient temperature. Chemical shifts are given in ppm relative to TMS (¹H, ¹³C{¹H}, ¹³C, ¹H-HSQC) or 1 M Na₂MoO₄ in D₂O (⁹⁵Mo). Solid-state magic-angle-spinning (MAS) NMR spectra were recorded 125.76 MHz for ¹³C on a Bruker Avance 500 spectrometer. ¹³C CP MAS NMR spectra were recorded with 3.5 ms ¹H 90° pulses, 2 ms contact time, spinning rates of 7 and 11 kHz, and 4 s recycle delays.

THF, *n*-pentane and diethyl ether were dried by standard procedures, distilled under nitrogen, and kept over 3 Å molecular sieves; CH_2Cl_2 was used as received. Mo(CO)₆ (Fluka, tech.), methyl 4-(bromomethyl)benzoate (BrCH₂PhCO₂CH₃, Sigma-Aldrich, 98%), Na (Fluka, pure), dicyclopentadiene (Fluka, >95%), heptakis(2,6-di-*O*-methyl)- β -cyclodextrin (DIMEB, Sigma-Aldrich), and heptakis(2,3,6-tri-*O*-methyl)- β -cyclodextrin (TRIMEB, Sigma-Aldrich) were purchased from commercial sources and used as received.

2.2. $CpMo(CO)_3(CH_2-pC_6H_4-CO_2CH_3)$ (1)

NaCp was synthesized using a modified literature procedure [11]. Accordingly, freshly cut sodium (0.390 g, 16.96 mmol) was added to dicyclopentadiene (20 mL, 149.2 mmol) under nitrogen, and the mixture was refluxed overnight at 160 °C. The resultant dark brown suspension with white solid particles was filtered, and the residue washed with *n*-pentane (3 × 2.5 mL) and vacuum-dried. The resultant light pink powder of NaCp was refluxed overnight in THF (30 mL) with Mo(CO)₆ (2.35 g, 8.90 mmol). The reaction mixture was then cooled to room temperature and BrCH₂-*p*C₆H₄-CO₂Me (2.04 g, 8.90 mmol) in THF (30 mL) was added,

and the mixture stirred for 2 h. A yellowish brown solution with a white precipitate was obtained. The suspension was evaporated to dryness and the resultant residue washed with warm water (complex **1** is stable in water). The collected yellow solid was vacuum-dried and recrystallized from diethyl ether (2.49 g, 71%). Anal. Calcd for $C_{17}H_{14}MOO_5$ (394.23); C, 51.79; H, 3.58. Found: C, 51.98; H, 3.65%. Selected FT-IR (KBr, cm⁻¹): $\nu = 2004$ (vs, ν_{CO}), 1936 (vs, ν_{CO}), 1906 (vs, ν_{CO}), 1705 (vs, ν_{CO}), 1598 (vs), 1282 (s). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): $\delta = 7.79$ (d, J = 6.2 Hz, 2H, pC_6H_4), 7.22 (d, J = 6.2 Hz, 2H, pC_6H_4), 5.26 (s, 5H, Cp), 3.84 (s, 3H, O-CH₃), 2.88 (s, 2H, CH_2 - pC_6H_4) ppm. ¹³C {¹H} (126 MHz, CD₂Cl₂, 298 K): $\delta = 240.1$ (CO trans to CH₂- pC_6H_4 -CO₂CH₃), 28.9 (2 CO cis to CH₂- pC_6H_4 -CO₂CH₃), 167.4 (C⁸), 158.5 (C²), 129.5 (C^{4.6/3.7}), 127.6 (C^{4.6/3.7}), 125.5 (C⁵), 94.4 (Cp), 51.9 (C^{4.6/3.7}H), 129.5/7.22 (C^{4.6/3.7}H), 94.4/5.26 (Cp), 51.9/3.84 (C⁹H₃), 4.1/2.88 (C¹H₂- pC_6H_4) ppm. ⁹⁵Mo (26 MHz, CD₂Cl₂, 298 K): $\delta = -1546$ ppm. ¹³C CP MAS NMR: $\delta = 240.7$ (CO), 229.0 (CO), 166.5 (C⁸), 157.9 (C²), 130.1 (C^{4.6/3.7}), 126.8 (C^{4.6/3.7}), 122.9 (C⁵), 94.4 (Cp), 51.9 (C⁹), 4.6 (C¹) ppm.

2.3. 1@DIMEB

A solution of **1** (0.15 g, 0.38 mmol) in CH₂Cl₂ (6 mL) was added slowly to a solution of DIMEB (0.50 g, 0.38 mmol) in CH₂Cl₂ (10 mL) under air. The mixture was stirred for 2 h at 40 °C and then evaporated to dryness, yielding a yellow solid. Anal. Calcd for C₅₆H₉₈O₃₅· C₁₇H₁₄MoO₅·2H₂O (1761.6): C, 49.77; H, 6.64. Found: C, 49.67; H, 6.47. Selected FTIR (KBr, cm⁻¹): $\nu = 2017$ (vs, ν_{CO}), 1932 (vs, ν_{CO}), 1716 (m, ν_{CO}), 1600 (m), 1282 (m). ¹³C CP MAS NMR: $\delta = 165.8$ (guest COOCH₃), 130.5 (guest C^{4,6/3,7}), 127.0 (guest C^{4,6/3,7}), 124.2 (guest C⁵), 101.1 (DIMEB C¹), 93.7 (guest Cp), 82.3 (DIMEB C^{2,4}), 69.6 (DIMEB C^{3,5,6}),

58.8 (DIMEB OCH₃), 50.5 (guest C⁹).

2.4. 1@TRIMEB

A solution of **1** (0.14 g, 0.35 mmol) in CH₂Cl₂ (6 mL) was added slowly to a solution of TRIMEB (0.50 g, 0.35 mmol) in CH₂Cl₂ (10 mL) under air. The mixture was stirred for 2 h at 40 °C and then evaporated to dryness, yielding a yellow solid. Anal. Calcd for C₆₃H₁₁₂O₃₅· C₁₇H₁₄MoO₅· 3H₂O (1877.82): C, 51.17; H, 7.08. Found: C, 51.23; H, 6.80. Selected FTIR (KBr, cm⁻¹): $\nu = 2017$ (vs, ν_{CO}), 1930 (vs, ν_{CO}), 1718 (m, ν_{CO}), 1600 (m), 1282 (m). ¹³C CP MAS NMR: $\delta = 239.3$ (CO), 228.3 (CO), 165.8 (guest COOCH₃), 130.5 (guest C^{4,6/3,7}), 128.5 (guest C^{4,6/3,7}), 124.2 (guest C⁵), 99.25 (TRIMEB C¹), 93.7 (guest Cp), 81.6 (TRIMEB C^{2,4}), 70.4 (TRIMEB C^{3,5,6}), 58.8 (TRIMEB OCH₃), 49.8 (guest C⁹).

2.5. Cyclooctene epoxidation catalysis

The catalytic reactions were carried out under air (autogeneous pressure) and stirred magnetically (1000 rpm) in a closed borosilicate micro reactor (10 mL capacity) equipped with a valve for sampling, and immersed in an oil bath thermostated at 55 °C. Typically, the micro reactor was loaded with 18 µmol of molybdenum complex, 1.8 mmol of *cis*-cycloctene (Cy) and 2.75 mmol of oxidant, without cosolvent, or using a biphasic liquid-liquid solvent mixture. The biphasic liquid-liquid solvent mixtures consisted of (A) a polar solvent (H₂O, glycerol (Gly, Aldrich, ≥99%) or the ionic liquid (IL) 1-butyl-3-methylimidazolium chloride (Aldrich, 98%)) and (B) an immiscible cosolvent (*n*-hexane (Hex, Sigma-Aldrich, PA), α , α , α trifluorotoluene (TFT, Aldrich, >99%) or iso-butyl methyl ketone (IBMK, Merck, PA)). The total volume of solvent mixture (A+B) was 2 mL with an A:B ratio of 1:3 (v/v), except for the

IL:hexane mixture for which the total volume was 1.65 mL and the A:B ratio was 1:10 (v/v).

The oxidants used were *tert*-butylhydroperoxide dissolved in water (TBHPaq, Sigma-Aldrich, 70 wt% aq.) or in decane (TBHPdec, Sigma-Aldrich, 5-6 M in decane, <4% water), or aqueous hydrogen peroxide (H₂O₂, Sigma-Aldrich, 30% w/v aq.). Prior to use, TBHPdec was pre-dried using activated molecular sieves (4 Å), while the IL was pre-dried under vacuum for 2 h, at 100 °C.

The olefin, oxidant and cosolvents were pre-heated in separate vessels (10 min at the desired reaction temperature) and then the corresponding desired amounts were transferred to the micro reactor (with pre-heated walls) containing the catalyst. Zero time (initial instant of the reaction of Cy) was taken as the instant the oxidant was added to the reactor. After each 24 h-batch run at 55 °C, the reaction mixtures were cooled to ambient temperature, centrifuged, and their features (color and type of physical states) noted. The course of the reactions was monitored using a Varian 3800 GC equipped with a BR-5 (Bruker) capillary column (30 m × 0.25 mm; 0.25 μ m) and a flame ionization detector, using H₂ as the carrier gas and undecane as internal standard.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the complex $CpMo(CO)_3(CH_2-pC_6H_4-CO_2CH_3)$ (1) (Chart 1) was adapted from literature procedures for analogous compounds [12]. Complex 1 presents three strong terminal carbonyl absorptions at 2004, 1936 and 1906 cm⁻¹ in the FT-IR spectrum (KBr disc), in agreement with that reported for other complexes of the type $Cp'Mo(CO)_3X$ [1a,8c,10a]. A strong band at 1705 cm⁻¹ is assigned to the carbonyl absorption of the ester

group. The successful synthesis of **1** was confirmed by elemental analysis, ¹H and ¹³C NMR spectroscopy. Of particular note is the appearance of two resonances for the carbonyl ligands at 228.9 and 240.1 ppm, which are attributed to the CO groups that are cis (×2) and trans (×1) to the CH_2 - pC_6H_4 - CO_2CH_3 group, respectively. Inclusion of molybdenum complex **1** in DIMEB and TRIMEB was performed by mixing solutions of the host and guest in dichloromethane, followed by vacuum-drying of the resultant solution to isolate **1**@DIMEB and **2**@TRIMEB as yellow solids. This technique works particularly well for the methylated cyclodextrins due to their high solubility in some organic solvents.

((Chart 1 here))

1@DIMEB and 2@TRIMEB were characterized in the solid state by elemental analysis, powder XRD, TGA, FT-IR, FT-Raman, and ¹³C CP MAS NMR spectroscopy. Unlike the previously reported inclusion compounds CpMo(CO)₃CH₂CONH₂@TRIMEB [10a] and CpMo(CO)₃Cl@TRIMEB [10b,13], which were prepared in the same way, 1@DIMEB and 2@TRIMEB form amorphous phases, showing only two or three very broad reflections in their powder XRD patterns (Fig. 1). Although no structural information can be extracted from these data, the absence of reflections due either to non-included 1 or the pure methylated CD shows that no separation of the two components occurred, which is an early indication of the stability of the respective inclusion compounds.

((Figure 1 here))

Fig. 2 compares the TGA curves of 1@DIMEB and 1@TRIMEB with those of DIMEB, TRIMEB, and nonincluded 1. DIMEB decomposes abruptly in the temperature range 230-370

°C with a mass loss of 76%, followed by a smoother loss of 24% up to 730 °C. TRIMEB starts to melt and decompose at 170 °C, and at 630 °C 100% mass loss is reached. Complex 1 decomposes in two main steps up to 550 °C (70% mass loss). The first step occurs between 100 and 230 °C (30%) and is attributed to disruption of the Mo-CO bonds and subsequent liberation of CO, as well as partial decomposition of the remaining organic ligands. A further mass loss of 33% between 400 and 550 °C comprises the decomposition/combustion of all residual organic matter. The TGA profiles for 1@DIMEB and 1@TRIMEB are quite similar. Decomposition takes place between 140 and 300 °C, followed by a more gradual loss up to 500 °C, leaving a residual mass of 8.7% for 1@DIMEB and 7.8% for 1@TRIMEB, which are close to the calculated values assuming the formation of MoO_3 (8.2% and 7.7%, respectively). Both 1@DIMEB and 1@TRIMEB reach a mass loss of 19% at a temperature that is about 70 °C lower than that required to reach the same loss with the corresponding pure methylated CD. On the other hand, the onset of decomposition for the organometallic guest seems to be delayed by 40-50 °C compared with that for the nonincluded complex. The early degradation of the organic macrocycle in the inclusion compounds may be due to a combination of factors, such as the lower crystallinity of the samples, the presence of different crystal packing arrangements, and the promoting effect of the decomposition of the organometallic guest on the decomposition of the host molecules.

((Figure 2 here))

The FT-IR spectra of 1@DIMEB and 1@TRIMEB showed several

absorption bands assigned to the guest species in addition to the characteristic bands of the hosts. In the CO (carbonyl ligand) stretching region (1900–2050 cm^{-1}), the spectra of both compounds contain a strong, sharp peak at 2017 cm^{-1} , and a strong, broader peak at 1931 cm^{-1}

¹ (Fig. 3). The former absorption band is red-shifted by 13 cm⁻¹ compared with the corresponding band for **1**, while the latter probably comprises overlapping absorptions equivalent to the bands found at 1906 and 1936 cm⁻¹ for **1**. Another notable difference between the spectra for the inclusion compounds and that for nonincluded **1** concerns the shift of the carbonyl absorption of the ester group from 1705 cm⁻¹ for **1** to 1717 cm⁻¹ for **1**@DIMEB and **1**@TRIMEB.

((Figure 3 here))

In the ¹³C CP MAS NMR spectra of **1**@DIMEB and **1**@TRIMEB (Fig. S1 in the supporting information), the signals for the cyclodextrin carbon atoms appear mainly as single broad peaks, and additional signals due to the organometallic guest are found at 50 (CH₃), 93.7 (Cp), 124-131 (phenyl-C), 165.8 (COOCH₃), 228.3 and 239.3 ppm (CO, only detectable for **1**@TRIMEB), which are essentially unshifted compared with the corresponding signals for the free complex **1**.

3.2. Catalytic studies

Complex **1** and the corresponding inclusion compounds were evaluated as pre-catalysts for the epoxidation of olefins by using *cis*-cyclooctene (Cy) as a model substrate and a reaction temperature of 55 °C. Different types of oxidants (TBHP in water or decane, and H_2O_2) and biphasic liquid-liquid solvent systems [(water, glycerol, ionic liquid)-(n-hexane, α,α,α -trifluorotoluene, iso-butyl methyl ketone)] were used; in some cases no cosolvent was added (nsolv). For all reaction systems tested, 1,2-cyclooctene oxide (CyO) was the only product of the reaction of Cy (CyO selectivity was always 100%).

The catalytic performances were initially investigated using the conditions TBHPdec/nsolv. The catalytic results for 1 and 1@TRIMEB are fairly comparable (100% conversion at 3 h reaction), and superior to those for 1@DIMEB (74% conversion at 3 h), Fig. 4. The similar catalytic results for the free and TRIMEB-included complex parallels that reported in the literature for CpMo(CO)₃CH₂CONH₂ [10a] and CpMo(CO)₃Cl [10b], and the corresponding TRIMEB inclusion compounds used as pre-catalysts in the same reaction under similar conditions; when compared with the literature data, the catalytic activities for 1 and 1@TRIMEB are higher. For 1, 1@DIMEB and 1@TRIMEB a pale yellow solid and a single pale yellow liquid phase were obtained after a 24-h batch run (Table 1). The type of CD, acting as a second sphere ligand for the molybdenum center, may influence the steric and electronic properties of the active species [10a]. The DIMEB host possesses hydroxyl groups which may participate in guest-host hydrogen bonding interactions, thereby influencing the formation of transition states.

((Figure 4 and Table 1 here))

Using TBHPaq instead of TBHPdec would be preferable since decane is more expensive than water, and the final reaction mixture using TBHPdec is more demanding with respect to product separation/purification (b.p. of decane is 174 °C). The reaction of Cy in the presence of **1** or **1**@TRIMEB was slower using TBHPaq (64-73% conversion at 3 h reaction) instead of TBHPdec (Fig. 4). These results somewhat parallel those reported in the literature for the free and TRIMEB-included complex CpMo(CO)₃Cl used as pre-catalysts in the same reaction under similar conditions [10b]. The reaction mixtures using **1**, **1**@DIMEB and **1**@TRIMEB, and TBHPaq, are triphasic liquid-liquid-solid (L-L-S), and mass transfer limitations may at least partly explain the lower overall reaction rate in comparison to the

TBHPdec-based systems (Table 1). Nevertheless, in the case of 1@DIMEB the catalytic results using TBHPaq or TBHPdec are similar (96% conversion at 24 h). Based on the different features of the reaction mixture for 1@DIMEB in relation to those for 1 and 1@TRIMEB, the DIMEB host seems to enhance the solubility of the catalyst in the aqueous phase in comparison to TRIMEB (somewhat more evident and in parallel with these observations are those when comparing the three compounds using the biphasic H₂O/Hex solvent system as discussed below, Table 1). Notably, the presence of water (in TBHPaq) does not seem to have a detrimental effect on the catalytic reaction. According to the literature, water molecules can participate in the formation (and stabilization) of transition states through hydrogen bonding [1h].

The performances of **1**, **1**@DIMEB and **1**@TRIMEB with TBHPaq were further investigated using the biphasic solvent mixtures H_2O/Hex (Hex = hexane) and Gly/Hex (Gly = glycerol); under these conditions, no solid phases were obtained, i.e., the metal species were always completely dissolved. Preliminary solubility tests for the pre-catalysts showed that **1**@DIMEB was the most soluble in water, and the opposite was the case with Gly. Although these differences may not necessarily be maintained for the corresponding active species under the reaction conditions, it motivated us to explore the possibility of using a polar medium containing the catalyst combined with an immiscible organic cosolvent for the *in situ* extraction of the reaction products, and facilitated catalyst recycling. For each compound, the catalytic activity was considerably higher for the solvent system H₂O/Hex than for Gly/Hex (conversions at 24 h were 80-87% for H₂O/Hex and 7-18% for Gly/Hex, Table 1). The same applies for the IL/Hex solvent systems (less than 10% conversion at 24 h, 55 °C). The detrimental effects on the catalytic reaction associated with the use of Gly and IL may be partly due to major mass transfer limitations (Gly and IL possess relatively high viscosities in comparison to water).

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In the case of 1@TRIMEB/TBHPaq, the catalytic performance was further explored using different aqueous-organic solvent systems (H₂O/(Hex, IBMK, TFT); IBMK = iso-butyl methyl ketone, TFT = α, α, α -trifluorotoluene). The reaction rate (based on conversions at 6 h/24 h, Table 1) followed the order H₂O/IBMK \leq TFT/H₂O \cong H₂O/Hex. Of the three organic solvents tested, IBMK possesses the highest solubility in water (ca. 19 g L^{-1} compared to less than 1 g L^{-1} for the other two organic solvents, at 20 °C) and thus one would expect superior catalytic results for this solvent (enhanced water-organic solvent miscibility), which was not the case. It has been generally accepted that for these types of molybdenum complexes the olefin epoxidation reaction involves oxygen atom transfer from active oxidizing species (formed via reaction of the metal complex with the hydroperoxide oxidant) to the olefin [1e-1h,3d]. Accordingly, the negative effect of IBMK may be partly due to the fact that it can act as a Lewis base and coordinate to the metal center, inhibiting the formation of transition states in the catalytic epoxidation. Based on the BF₃ affinities (kJ mol⁻¹) of Lewis bases measured in dichloromethane (25 °C, 1 atm), the Lewis basicity of IBMK (BF₃ affinity of ca. 75.1 kJ mol⁻ ¹) is intermediate between those of N,N-dimethylformamide (DMF, ca. 110 kJ mol⁻¹) and tetrahydrofuran (THF, ca. 90.4 kJ mol⁻¹), and that of acetonitrile (ca. 60.4 kJ mol⁻¹); THF, DMF and CH₃CN are sufficiently strong to form solvent adducts of oxomolybdenum(VI) complexes [14].

The performances of **1**, **1**@DIMEB and **1**@TRIMEB as pre-catalysts in the reaction of Cy were further investigated using aqueous H_2O_2 as oxidant instead of TBHPaq, and the solvent system H_2O /Hex, at 55 °C (Table 1). For **1** and **1**@TRIMEB, a conversion of ca. 80% was reached at 24 h, which is far superior to that measured previously for free and CD-included CpMo(CO)₃Cl tested as (pre-)catalysts in the same reaction under similar conditions (5% and 16% Cy conversion, respectively) [10b]. For these two catalytic systems the organic phase was pale yellow in color while the aqueous one was colorless, suggesting that the active

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species are in the former phase where they are mixed with the reaction products (making catalyst separation and reuse somewhat troublesome). The catalytic results for $1@DIMEB/H_2O_2$ are considerably poorer (13% conversion at 24 h), which may be due to differences in the partition ratio of the catalyst between the two liquid phases and/or in the type of active species (no yellow colored phase was obtained for 1@DIMEB in contrast to that observed for 1 and 1@TRIMEB). All of the tested catalytic systems which were completely colorless were sluggish in contrast to those possessing at least one colored phase, suggesting that the yellow color is associated with the presence of active species (Table 1).

Due to the high solubility of the metal species in the L-L biphasic reaction media, for these systems we did not succeed in isolating metal species for characterization. According to the literature, complexes of the type Cp'Mo(CO)₃R (R = alkyl) can be oxidized into the corresponding dioxo Cp'MoO₂R and oxoperoxo Cp'MoO(O₂)R derivatives, using TBHP [1b,1e,1f,3a,3d] or H₂O₂ [15] as oxidants. For example, CpMoO₂Me can be oxidized with H₂O₂ into the oxoperoxo derivative CpMoO(O₂)Me (yellow-colored solids) [15]. The Cp'MoO₂R complexes are intermediates in the formation of Cp'MoO(O₂)R, and the two types may play a catalytic role [1e,1f,3a,16]. Attempts to identify the types of species were made for the system 1@TRIMEB/TBHPdec/nsolv. The ATR FT-IR spectrum of the recovered solid (not shown) did not exhibit the bands characteristic of the carbonyl ligands, which is consistent with oxidative decarbonylation of the pre-catalyst during the catalytic reaction. The unequivocal identification of bands assignable to metal-oxo or η^2 -peroxo groups was not possible due to overlap with bands attributed to the host.

As discussed above, the separation (by simple decantation) and reuse of the aqueous solution of the catalyst which is immiscible with the organic solvent containing the reaction products seems quite attractive. Based on the results of the catalytic tests (Table 1), the most interesting catalytic systems in terms of activity and recyclability seem to be

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1@TRIMEB/TBHPaq/TFT/H₂O and 1@DIMEB/TBHPaq/H₂O/Hex (in contrast to, for example, (1, 1@TRIMEB)/TBHPaq/H₂O/Hex in which the catalyst and products are apparently in the same liquid (organic) phase). The catalyst recyclability in the aqueousorganic biphasic reaction system was investigated for 1@TRIMEB/TBHPaq/TFT/H₂O. After a 24 h batch run the resultant aqueous and organic phases obtained were separated by decantation and transferred to separate reactors. ICP analysis of the TFT phase indicated negligible amount of molybdenum (< 0.05 wt% of the initial amount of molybdenum). The reagents Cy and TBHPaq were added to each reactor in similar amounts to those used in the first batch, and the reaction solutions were stirred for 24 h at 55 °C. Whereas the colorless organic phase had a negligible catalytic contribution, the pale yellow aqueous phase led to 63% conversion. These results are consistent with the above discussion relating the yellow color of the phases to the catalyst, and suggest that the catalyst can be easily separated in the form of an aqueous solution, by decantation, from the organic phase containing the reaction products and recycled. A third run of the water-catalyst system gave similar results to those of the second run (conversion was 0.91 of that in the first run and epoxide selectivity was always 100%). A recycling test was carried out for the system $1@DIMEB/TBHPaq/H_2O/Hex$ in a similar fashion to that for 1@TRIMEB/TBHPaq/TFT/H₂O: the recycled organic phase accounted for 33% conversion (100% epoxide selectivity). Hence, it seems that TFT allows a better partitioning of the metal species in the aqueous phase relative to the organic one, when compared with Hex as cosolvent.

4. Conclusions

For the three compounds prepared in this work, the catalytic epoxidation activity was investigated using *cis*-cyclooctene as a model substrate and different types of hydroperoxide

oxidants at 55 °C. The type of CD host can have a determinant effect on the catalytic reaction, possibly due to an interplay of different factors such as catalyst solubility and stability, electronic and steric effects on the formation of transition states. For example, the influence of the type of oxidant on the catalytic reaction is different depending on the type of CD host: while 1@TRIMEB was effective with aqueous TBHP or H_2O_2 under similar reaction conditions, 1@DIMEB was only effective with TBHP. On the other hand, the inclusion compounds may present advantages in relation to the corresponding free complex in terms of homogeneous catalyst recycling. Optimized compromises between catalytic activity and facilitated catalyst reuse may be achieved by using different types of solvent mixtures, depending on the type of CD host. An interesting catalytic system is, for example, that of 1@TRIMEB/TBHPaq/TFT/H₂O where the catalyst is in the aqueous phase immiscible with the organic extracting solvent (TFT) containing the reaction products: the catalyst can be separated in the form of an aqueous solution, by decantation, from the organic phase containing the reaction products and recycled.

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Appendix A. Supplementary material

Supplementary material (for **1**, **1**@DIMEB and **1**@TRIMEB: full listing of FT-IR and FT Raman bands, and ¹³C CP MAS NMR spectra) associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2013.XX.XXX.

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| Sample | Oxidant | Solvents | CyO yield | Features of the reaction mixtures ^c | | |
|----------|-------------------------------|-----------------------|------------------|--|-------------|----------|
| | | | (%) ^b | Lower layer | Upper layer | Solid |
| 1 | TBHPdec | nsolv | 100 ^d | single L phase, p-yellow | | p-yellow |
| | TBHPaq | nsolv | 80 / 95 | p-yellow | p-yellow | p-yellow |
| | | H ₂ O/Hex | 53 / 80 | cless | yellow | 7 |
| | | Gly/Hex | 3 / 10 | cless | cless | - |
| | | IL/Hex | 5 / 9 | p-yellow | cless | - |
| | H_2O_2 | H ₂ O/Hex | 8 / 78 | cless | yellow | - |
| 1@DIMEB | TBHPdec | nsolv | 89 / 96 | single L phase, p-yellow | | p-yellow |
| | TBHPaq | nsolv | 79 / 97 | p-yellow | cless | p-yellow |
| | | H ₂ O/Hex | 69 /87 | p-yellow | cless | - |
| | | Gly/Hex | 4 / 18 | cless | cless | - |
| | | IL/Hex | 8/9 | p-yellow | cless | - |
| | H_2O_2 | H ₂ O/Hex | 2 / 13 | cless | cless | - |
| 1@TRIMEB | TBHPdec | nsolv | 100 ^d | single L phase, p-yellow | | p-yellow |
| | TBHPaq | nsolv | 80 / 88 | p-yellow | p-yellow | p-yellow |
| | | H ₂ O/Hex | 49 /83 | cless | yellow | - |
| | | Gly/Hex | 2 / 7 | cless | cless | - |
| | | IL/Hex | 4 / 8 | p-yellow | cless | - |
| | | H ₂ O/IBMK | - / 20 | cless | cless | - |
| | | TFT/H ₂ O | 46 / 77 | cless | p-yellow | - |
| | H ₂ O ₂ | H ₂ O/Hex | 2 / 81 | cless | yellow | - |

Table 1. Cyclooctene conversions at 55 °C with different oxidants and solvents in the presence of complex 1 and the CD inclusion compounds, 1@DIMEB and 1@TRIMEB.^a

^a Reaction conditions: 1:100:150 molar ratios of Mo:Cy:Oxidant, 55 °C, 1000 rpm.

^b Yield of CyO at 6 h/24 h reaction (CyO selectivity was always 100%).

^c Color of the liquid (L) and solid phases after centrifugation of the reaction mixtures for a 24 h-batch; p-yellow = pale yellow; cless = colorless; for the biphasic liquid-liquid systems, the lower/upper layers match the order indicated in the solvents column.

^d At ca. 3 h reaction.

Figure captions

Chart 1. Guest (1) and hosts (DIMEB, TRIMEB) used in the present work.

Fig. 1. Powder XRD patterns of (a) DIMEB, (b) TRIMEB, (c) $CpMo(CO)_3(CH_2-pC_6H_4-CO_2CH_3)$ (1), (d) 1@DIMEB and (e) 1@TRIMEB.

 Fig. 2. TGA curves of (a) DIMEB (----), TRIMEB (----),

 CpMo(CO)₃(CH₂PhCO₂CH₃) (1) (-----), 1@DIMEB (----) and 1@TRIMEB (----).

Fig. 3. FT-IR spectra in the range $1000-2500 \text{ cm}^{-1}$ for (a) CpMo(CO)₃(CH₂-*p*C₆H₄-CO₂CH₃) (1), (b) 1@DIMEB and (c) 1@TRIMEB.

Fig. 4. Dependence of CyO yield (CyO selectivity was always 100%) on the reaction time of *cis*-cyclooctene in the presence of complex $1(+,\Box)$ and the related CD inclusion compounds, 1@DIMEB (\circ, \bullet) and 1@TRIMEB ($\triangle, \blacktriangle$), using TBHPaq ($+, \circ, \triangle$) or TBHPdec (\Box, \bullet, \bigstar), at 55 °C without additional cosolvent.

- 1. Synthesis and characterization of CpMo(CO)₃(CH₂-*p*C₆H₄-CO₂CH₃) (1).
- 2. Synthesis of 1:1 inclusion compounds between **1** and methylated cyclodextrins.
- 3. Complex 1 and its TRIMEB adduct are effective precatalysts for cyclooctene epoxidation.
- 4. Aqueous tert-butylhydroperoxide and hydrogen peroxide can be used as oxidants.
- 5. Biphasic liquid-liquid systems were studied, aiming to facilitate catalyst recycling.





DIMEB: $R = CH_3$, R' = HTRIMEB: $R = R' = CH_3$







