

A chiral menthyl cyclopentadienyl molybdenum tricarbonyl chloro complex: Synthesis, heterogenization on MCM-41/MCM-48 and application in olefin epoxidation catalysis

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Abstract

The complex $[(-)\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{Cl}$ (**1**) was synthesized by the reaction of $\text{Mo}(\text{CO})_3(\text{EtCN})_3$ with $[(-)\text{-menthylCpH}]$ to produce the hydride $[(-)\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{H}$. The latter compound was then reacted with CCl_4 to form $[(-)\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{Cl}$ (**1**). Compound **1** was tested as catalyst for the epoxidation of *cis*-cyclooctene, styrene and *trans*- β -methylstyrene in the presence of *tert*-butyl hydroperoxide (TBHP) at 55 °C using chloroform as solvent. Results under homogeneous conditions prompted the authors to immobilize complex **1** on mesoporous MCM-41 and MCM-48 surfaces leading to the grafted materials AM-41CpMoChi and AM-48CpMoChi. The presence of the organometallic complexes in the materials was confirmed by powder X-ray diffraction, N_2 adsorption/desorption isotherms, TEM, EA, FT-IR, ^1H MAS NMR and TG-MS. AM-41CpMoChi and AM-48CpMoChi were also tested as epoxidation catalysts. The catalytic examinations also included leaching experiments, and the reusing of the grafted materials for several runs.

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1. Introduction

Enantiopure epoxides are highly valuable chiral molecules, useful for the synthesis of various biologically active molecules [1,2]. For the preparation of chiral epoxides, transition metal-catalyzed enantioselective epoxidation of different organic substrates is of high importance and has been widely studied over the past decades [3–10]. The generally good catalytic activities of several molybdenum(VI)-oxo complexes in oxidation reactions [11–18] make this type of complexes – in principle – promising candidates for asymmetric catalysis by using chiral ligands. 2'-Pyridyl

alcohols and phosphinoalcohols [19–21] have been reported to induce enantiomeric excesses of 20–40% for functionalized olefins when coordinated to dioxo or peroxy molybdenum(VI) fragments. In this context, we and others have reported on the synthesis of a variety of *cis*- MoO_2^{2+} epoxidation catalysts bearing chiral ligands, such as bis-oxazoline, *cis*-diol, *cis*-8-phenylthiomenthyl and sugar derived chiral Schiff base ligands of general formula $\text{MoO}_2(\text{L})(\text{Solv})$ [22–29].

Recently cyclopentadienyl molybdenum complexes of general formula $\text{Cp}'\text{MoO}_2\text{Cl}$ ($\text{Cp}' = \text{C}_5\text{R}_5$; $\text{R} = \text{H}, \text{CH}_3, \text{Bz}$) were found to be efficient homogeneous catalysts for the epoxidation of alkenes with *tert*-butyl hydroperoxide (TBHP) as the oxidant [30–33]. Furthermore, it became clear that the direct application of their carbonyl precursor compounds of general formula $\text{Cp}'\text{Mo}(\text{CO})_3\text{R}$ ($\text{R} = \text{Cl}, \text{alkyl}$) leads to efficient catalysts, since the carbonyl

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complexes are in situ oxidized – also by TBHP – to their oxo and peroxy congeners [30–35]. The carbonyl precursor compounds can be stored for long times without changes, while the oxides are somewhat more sensitive [30–35]. Thus, introduction of chirality in these molybdenum carbonyl compounds such as $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Cl}$ seems an interesting target both due their synthetic availability and their good catalytic activity.

A menthyl moiety attached to the cyclopentadienyl ring of metallocenes is a powerful tool for the amplification of chiral information [36–45]. Chiral menthyl-derived cyclopentadienyl and indenyl complexes of various transition metals are being widely exploited in different stoichiometric and catalytic asymmetric reactions and with respect to asymmetric structural effects [36–45]. In the case of molybdenum, the complexes $(-)-[(2\text{-menthylindenyl})\text{Mo}(\text{CO})_3\text{I}]$, allyl(2-menthylindenyl)- $\text{Mo}(\text{CO})_2$ and $(-)-[(2\text{-menthylindenyl})\text{Mo}(\text{CO})_3]\text{Li}(\text{THF})$ have been synthesized [38,39]. However, to the best of our knowledge there are no reports on the synthesis of molybdenum complexes with menthyl-derived cyclopentadienyl ligands and no reports on catalytic applications of molybdenum complexes with menthyl-derived cyclopentadienyl or indenyl ligands.

In terms of industrial applications, the heterogenization of homogeneous catalysts is of significant interest, in order to combine the advantages of heterogeneous catalysts such as easier product/catalyst separation with the advantages of homogeneous catalysts, e.g. higher selectivity [46–60]. Recently, we and several other groups have successfully heterogenized homogeneous Mo based catalysts and some mixed metal carbonylate salts on mesoporous solids (MCM-41 and MCM-48) by various methodologies and found that the resulting heterogeneous materials can be utilized as active and relatively stable catalysts [51–60]. Among the various supporting materials available, the mesoporous silicates, designated as MCM-41 and MCM-48 by Mobil scientist [61] with regular pore size, large surface areas, a large number of surface silanol groups and high chemical and thermal stability, are potential and promising candidates as both catalysts and catalyst supports [46–65].

In the present study, the chiral complex $[(-)\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{Cl}$ has been synthesized, characterized and grafted on H- AlMCM-41 and H- AlMCM-48 surfaces. Both the homogeneous and the heterogeneous catalyst were tested and compared for the epoxidation of *cis*-cyclohexene, styrene and of *trans*- β -methyl styrene.

2. Experimental

2.1. General considerations

All preparations and manipulations were executed utilizing standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone ketyl; CH_2Cl_2 and EtCN over CaH_2), distilled under nitrogen

and used immediately (THF) or kept over 4 Å molecular sieves.

Microanalyses were performed at the ITQB (C. Almeida) and at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). Mid-IR spectra were measured on a Mattson 7000 FT-IR spectrometer using KBr pellets. ^1H NMR spectra were recorded at 300 MHz on Bruker CXP 300. ^{95}Mo and ^{13}C NMR were obtained using a 400 MHz Bruker Avance DPX-400 spectrometer. Gas chromatographic studies were performed with a Thermo Quest Trace GC gas chromatograph, equipped with a split injector, a Cyclosilb J&W column and a FID detector. Atomic absorption spectroscopy (AAS; Varian SpectrAA-400 spectrometer) was used to determine the copper content. Powder XRD data were collected with a Philips X'pert diffractometer using $\text{Cu K}\alpha$ radiation filtered by Ni. Nitrogen adsorption/desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41/48 was degassed at 723 K overnight to a residual pressure of about 10–24 mbar. A lower degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume (VP) was estimated from the N_2 uptake at $p/p_0 = 0.95$, using the liquid nitrogen density of 0.8081 g cm^{-3} . The pore size distribution curves (PSD, differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron microscopy (TEM) was executed on a JEOL JEM2010 operated at 120 kV. Thermogravimetric mass spectra analysis (TG-MS) measurements were conducted with a Netzsch TG209 system; typically about 10 mg of sample was heated from 300 to 1473 K at 10 K min^{-1} under argon. ^1H MAS NMR spectra were recorded at 300 MHz using Bruker Avance 300 spectrometer with $3.0 \mu\text{s}^1 \text{H } 90^\circ$ pulses, with a spinning rate of 8 kHz. $[(-)\text{-MenthylCp}]\text{H}$ was prepared as described in the literature [36,37].

2.2. Preparation of $[(-)\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{Cl}$ (1)

3.0 g (9.6 mmol) $\text{Mo}(\text{CO})_6$ and 30 mL of propionitrile were refluxed overnight to yield $\text{Mo}(\text{CO})_3(\text{EtCN})_3$. Solvent was removed and $[(-)\text{-menthylCp}]\text{H}$ 1.96 g (9.6 mmol) in 75 mL of toluene were added to the residue. The obtained brown suspension was stirred for 2 h and then warmed to 323–333 K for 30 min. The solvent was evaporated and a brown oil was obtained. This oil was redissolved in CH_2Cl_2 . Addition of 10 mL of CCl_4 changes the colour of the solution to dark red. After 30 min of reaction the solvent was evaporated, an oily brown red residue is obtained. The residue was subjected to column chromatography

(silica/gel) under inert gas conditions. First CH₂Cl₂/hexane (1:4) ratio is used to elute a pink band of impurities. After this band is completely eluted, the eluent ratio is changed to CH₂Cl₂/hexane (1:2) and the desired product starts to elute as orange band. The maintenance of this ratio enables the separation of the desired product from the dark residue on the top of the column. Complete elution of the desired product is performed using a CH₂Cl₂/hexane (1:1) ratio. After evaporation of the solvents, an orange solid is obtained. Oily traces can be removed by washing the solid with cold hexane. Yield (based on Mo(CO)₆): 1.04 g, 26%. Elemental Analysis: Calc. for C₁₈H₂₃O₃ClMo (414.74): C, 51.63; H, 5.54. Found: C, 51.38; H, 5.45%. FTIR: ν/cm^{-1} = 3109 w, 2960 m, 2934 m, 2869 m, 2047 s, 1965 s, 1950 s, 1495 ms, 1459 w, 1385 w, 1369 w, 1346 w, 1128 w, 1084 w, 1025 w, 853 w, 567 m, 530 w, 469 w. $\delta_{\text{H}}/\text{ppm}$ [300 MHz, CDCl₃, 293 K, TMS]: 5.59 (2H, t), 5.44 (1H, d), 5.19 (1 H, d) (all from C₅H₄); 2.01–0.74 (19H, menthyl). $\delta_{\text{Mo}}/\text{ppm}$ [400 MHz, CDCl₃, 293 K, Na₂MoO₄]: –1001.

2.3. Preparation of AM-41CpMoChi and AM-48CpMoChi (heterogenization procedure)

Mesoporous AlMCM-41 and AlMCM-48 molecular sieves were synthesized following procedures described earlier [51–53] with molar gel compositions of 1 SiO₂ : 0.2 NaOH : 0.27 TMAOH : 0.27 CTABr : 60 H₂O : 0.005 Al₂O₃ for Al-MCM-41, and 5.0 SiO₂ : 2.5 NaOH : 0.87 CTABr : 0.13 Brij30 : 0.025 Al₂O₃ : 400 H₂O for Al-MCM-48 respectively. All the grafting procedures were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. The mesoporous molecular sieves H-AlMCM-41 and H-AlMCM-48 (1 g) were first pre-activated at 473 K under vacuum (10^{–3} mbar) for 6 h to remove physisorbed water. The activated samples (1 g) were treated with 0.5 mmol of complex **1** in 30 ml dry CH₂Cl₂ under an argon atmosphere. The mixtures were stirred at 313 K for 2 days. The resulting solutions were filtered off and the white solids were washed repeatedly with CH₂Cl₂ until all physisorbed complexes were removed from the surfaces. The washed samples were dried under vacuum at RT. The resulting materials prepared from H-AlMCM-41 and H-AlMCM-48 samples are designated as AM-41CpMoChi and AM-48CpMoChi, respectively.

2.4. Catalytic reactions

The catalytic oxidation of the different olefins was carried out at 328 K under N₂ atmosphere in a reaction vessel equipped with a magnetic stirrer and a condenser. The vessel was loaded with olefin (100%), internal standard, catalyst (1%), oxidant (200%) and 3 mL of solvent. Addition of the oxidant determines the initial time of the reaction. The course of the reaction was monitored by quantitative GC-analysis. Samples were taken every 30 min during the first hours of reaction, diluted with dichloromethane and chilled

in an ice bath. For the destruction of hydroperoxide a catalytic amount of manganese dioxide was added. The resulting slurry was filtered over a filter equipped Pasteur pipette and the filtrate injected in the GC column.

The conversion of the olefins as well as the formation of some of epoxides was quantified by gas chromatography from calibration curves recorded prior to the reaction course. The presence of other reaction by-products was determined by NMR spectroscopy, by comparison of the catalytic mixture with standard samples.

2.5. Epoxidation of *cis*-cyclooctene

cis-Cyclooctene (800 mg, 7.3 mmol), 800 mg dibutyl ether (internal standard), 1 mol% of catalyst, 2.64 mL TBHP (5.5 M in *n*-decane) and 3 mL of CHCl₃.

2.6. Epoxidation of styrene

Styrene (800 mg, 7.65 mmol), 200 mg mesitylene (internal standard), 1 mol% of catalyst, 2.78 mL TBHP (5.5 M in *n*-decane) and 3 mL of CHCl₃.

2.7. Epoxidation of *trans*- β -methylstyrene

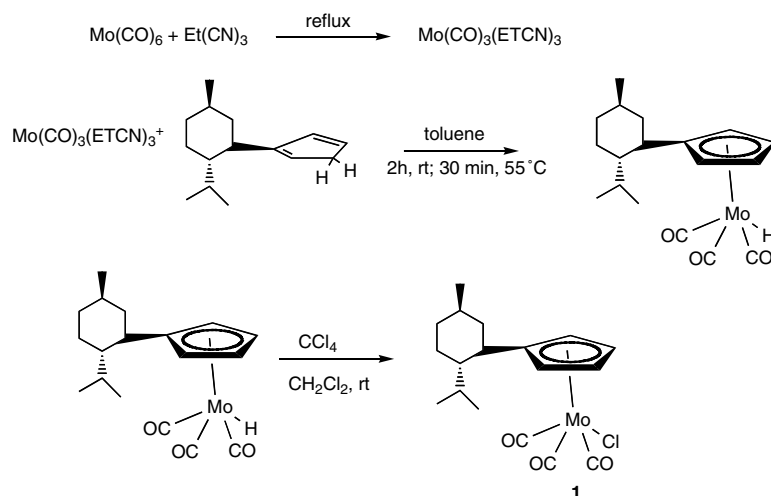
Trans- β -methylstyrene (200 mg, 1.7 mmol), 200 mg mesitylene (internal standard), 1 mol% of catalyst, 0.62 mL TBHP (5.5 M in *n*-decane) and 3 mL of CHCl₃.

3. Results and discussion

3.1. Synthesis and characterization of [(–)-menthylCp]Mo(CO)₃Cl (**1**)

The chiral complex [(–)-menthylCp]Mo(CO)₃Cl (**1**) was synthesized according to the method previously developed in our group for the synthesis of the analogue complexes Cp'Mo(CO)₃Cl ((Cp' = C₅R₅; R = H, CH₃, Bz)) [30]. In this method Mo(CO)₃(EtCN)₃ (readily obtained from Mo(CO)₆ and propionitrile) reacts with the corresponding Cp'H to produce the hydride Cp'Mo(CO)₃H, which can then be reacted with CCl₄ without isolation and purification to form Cp'Mo(CO)₃Cl (Scheme 1). The yield (based on Mo(CO)₆) is 26%. The reason for this relatively low yield is the incomplete reaction of Mo(CO)₆ and propionitrile to obtain the hydride. One way to solve this problem is to sublime all unreacted Mo(CO)₆ after the reaction with propionitrile comes to an end. In this way the unreacted Mo(CO)₆ can be recycled and reused. The complex [(–)-menthylCp]Mo(CO)₃Cl can be handled in air for brief periods of time but in case of prolonged storage it should be kept under nitrogen atmosphere and at low temperature. The complex is very soluble in polar solvents such as CHCl₃ and CH₂Cl₂, but less soluble in unpolar solvents, e.g. *n*-hexane.

As expected, the IR spectrum (KBr) of compound **1** shows three strong carbonyl absorptions at 2047, 1965



Scheme 1. Synthesis of complex 1.

and 1950 cm^{-1} . The related complexes, $\text{CpMo}(\text{CO})_3\text{Cl}$ and $(\text{C}_5\text{H}_4\text{COOMe})\text{Mo}(\text{CO})_3\text{Cl}$ exhibit bands at 2056 , 1986 and 1962 cm^{-1} [66], and at 2056 , 1990 and 1973 cm^{-1} [59], respectively. The ^1H NMR spectrum of compound **1** displays two distinctly different signal groups. The first is a complex mixture of signals between 2.01 and 0.74 ppm , which can be attributed to the protons of the menthyl group. The other group comprises three signals between 5.59 and 5.19 ppm , which can be attributed to the cyclopentadienyl protons. These chemical shifts are comparable to the chemical shift of the protons of $\text{CpMo}(\text{CO})_3\text{Cl}$ (5.29 ppm) [67]. The obtained type of signals (see Section 2) indicates that the cyclopentadienyl ring possesses two equivalent and two non-equivalent protons. The ^{95}Mo spectrum of complex **1** displays a signal in the expected chemical shift range, namely at -1001 ppm . The related complex $\text{CpMo}(\text{CO})_3\text{Cl}$ displays a signal at -836 ppm [68].

3.2. Catalytic behavior of $[(-)\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{Cl}$ (**1**)

Compound **1** was tested as catalyst at 328 K for the epoxidation of *cis*-cyclooctene, styrene and *trans*- β -methylstyrene with TBHP in order to compare its activity towards different olefins. Styrene and *trans*- β -methylstyrene were also used because they yield epoxide enantiomers and thus can be used to test the chiral induction ability of our catalyst. In the present study the substrate:oxidant:catalyst ratio is $100:200:1$. The details concerning the catalytic reaction are given in the experimental part. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst.

The olefins used lead to different kinetic profiles regarding substrate conversion (Fig. 1). In the case of *cis*-cyclooctene, there is a quick increase in conversion during the first hour of reaction and then a slowing down. As expected, for less activated olefins, i.e. *trans*- β -methylstyrene and styrene, the reaction is not equally fast. For cyclooctene the

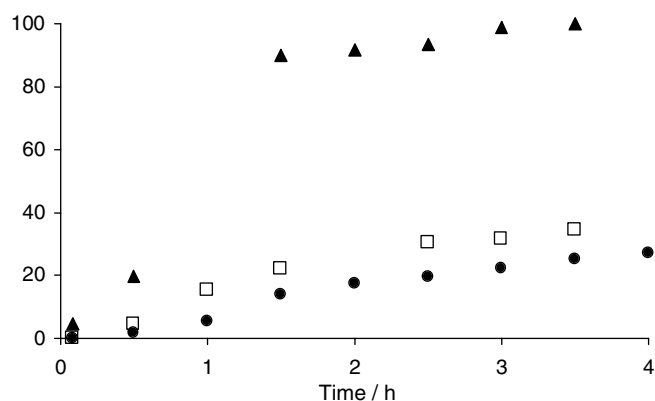


Fig. 1. Time dependent substrate conversion in the presence of compound **1** as catalyst, using TBHP as oxidant at 328 K , (catalyst:olefin:oxidant = $1:100:200$). Closed triangles: *cis*-cyclooctene, squares: *trans*- β -methylstyrene; closed circles: styrene.

only obtained product is the correspondent epoxide. After 3 h of reaction the conversion reaches 100% . This result surpasses the previously obtained result for the complexes $\text{CpMo}(\text{CO})_3\text{Cl}$ and $(\text{C}_5\text{Bz}_5)\text{Mo}(\text{CO})_3\text{Cl}$ under the same reaction conditions, in which 100% conversion of the olefin is obtained after 4 h reaction time [30].

In the case of styrene, less than 5% epoxide is obtained after 4 and 24 h . However, after 4 and 24 h the conversion of styrene reaches 27% and 68% , respectively. NMR analysis of the catalytic reaction mixture after 24 h reaction time reveals phenylethane-1,2-diol as main reaction product. Despite the fact that the ring opening reactions are well known in the case of styrene being the substrate [69], ring opening does not occur when complexes of the type $\text{Cp}'\text{MoO}_2\text{Cl}$ (obtained from the oxidative decarbonylation of $\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$ with TBHP) are used as catalysts. In this later case, the reaction was selective for epoxide formation [30].

In the case of *trans*- β -methylstyrene conversion reaches 34% after 4 h and 84% after 24 h . NMR analysis of the cat-

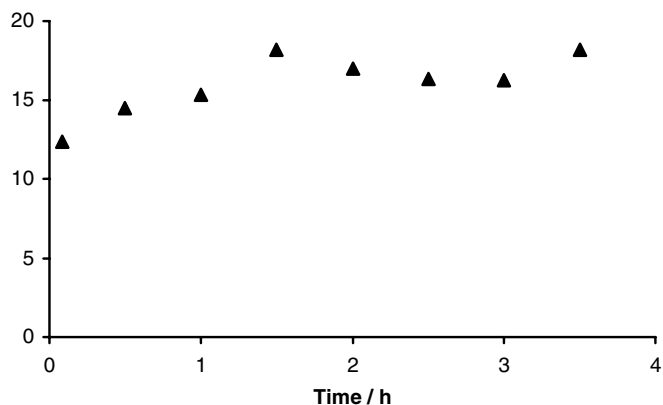


Fig. 2. Time dependent enantiomeric excess for the epoxidation of *trans*- β -methylstyrene in the presence of compound **1** as catalyst, using TBHP as oxidant at 328 K. (catalyst:olefin:oxidant = 1:100:200).

alytic mixture after 24 h of reaction time indicates that the corresponding epoxides are the only obtained products. After the first hour the catalytic system yields an enantiomeric excess ('ee') of 19%, which is maintained throughout the investigated reaction time (24 h), indicating that the catalyst maintains its integrity (Fig. 2). The chiral induction favors the *RR'* enantiomer. The stable but moderate enantiomeric excess is very likely due to the free rotation of the cyclopentadienyl ring, which enables the chiral group to move away from the substrate to a less hindered

Table 1

Catalytic epoxidation of olefins with TBHP at 328 K using compound **1** as catalyst (catalyst:olefin:oxidant = 1:100:200)

Olefin	Conv. (%) ^a		Epoxide yield (%)		ee ^d (%)
	After 4 h	After 24 h	After 4 h	After 24 h	
<i>cis</i> -Cyclooctene	100	100	100 ^a	100 ^a	–
<i>trans</i> - β -Methylstyrene	34	84	34 ^b	84 ^b	19
Styrene	27	68	<5 ^c	<5 ^c	–

^a Determined by GC analysis; Conv., conversion.

^b Determined by NMR.

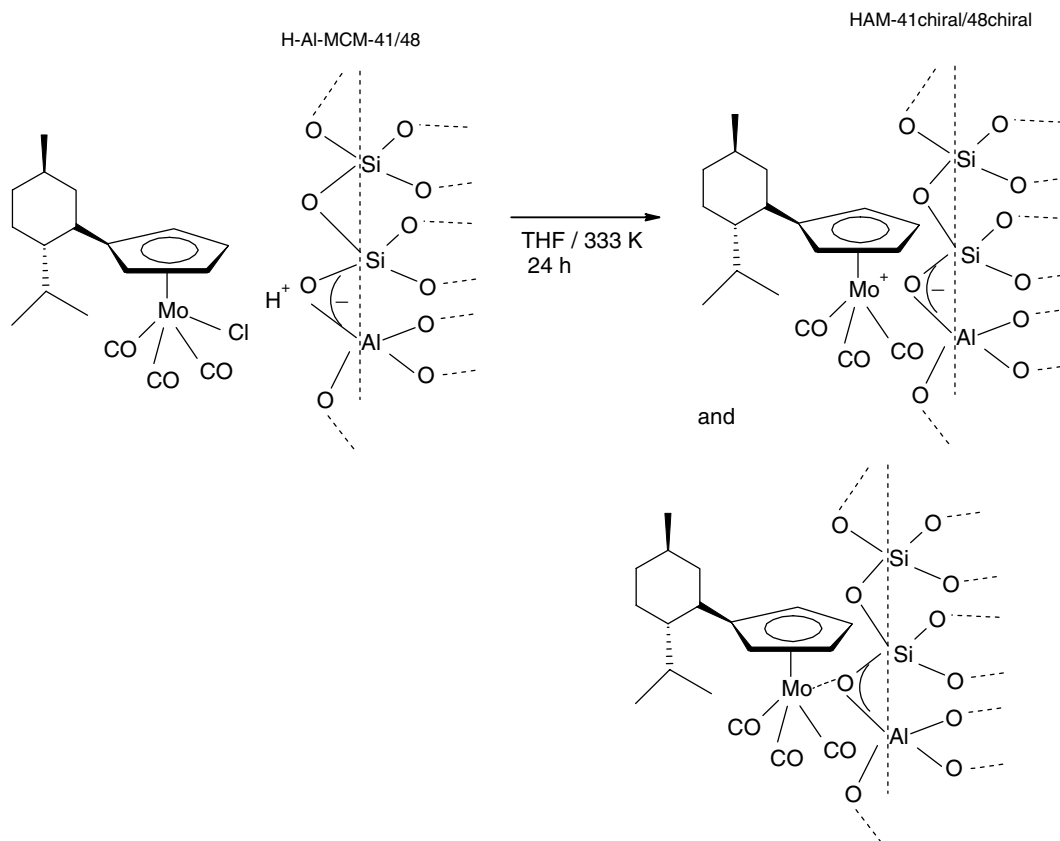
^c Styrene suffers a ring opening reaction being converted into phenylethane-1,2-diol.

^d Epoxide ee of the *RR'* isomer. Determined by GC analysis.

situation, thus reducing its chiral induction ability. A statistical orientation of the Cp-menthyl moiety would lead (in first approximation) to 20% ee for such a case. The observed value is surprisingly close to the expectations based on such a very simplistic approach (see Table 1).

3.3. Heterogenization of complex **1** on MCM-41/MCM-48

Heterogenization of the chiral menthyl complex **1** on H-AlMCM-41 and H-AlMCM-48 was carried out through ionic interactions as described previously [51–53] (Scheme 2). The XRD patterns of the grafted samples are depicted in Fig. 3. All four reflections for AM-41CpMoChi



Scheme 2. Immobilization of complex **1**.

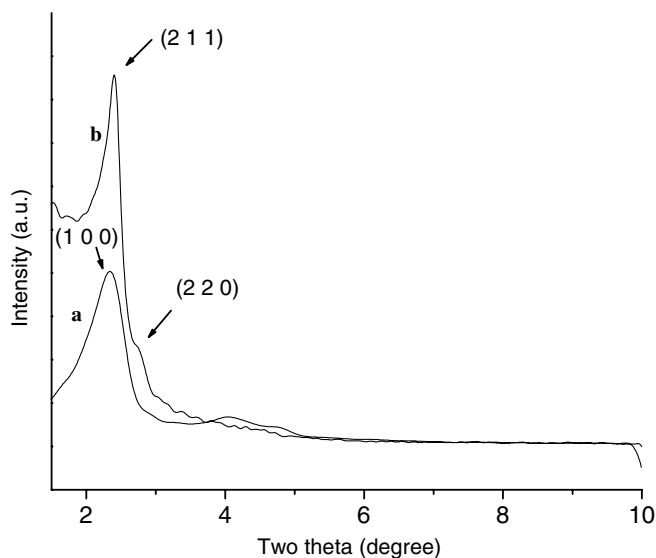


Fig. 3. Powder XRD pattern of: (a) AM-41CpMoChi; and (b) AM-48CpMoChi.

(Fig. 3a) are observed in the 2θ range of 2–8°, with an indexing corresponding to a hexagonal MCM-41 structure showing the (100), (110), (200) and (210) planes. Fig. 3b shows the XRD pattern of AM-48CpMoChi, which exhibits a main reflection corresponding to the (211) plane along with a shoulder peak derived from the (220) plane, typical for a cubic MCM-48 structure. Compared to parent MCM-41 and MCM-48, the grafted samples show (Table 2) a decrease in the relative intensities of the XRD reflections and there is a clear shift to higher 2θ values [51–57]. These changes originate from a contraction of the unit cells of the grafted samples, because of the immobilization of the bulky organometallic groups inside the channels of MCM-41 and MCM-48 [51–63]. The low temperature N_2 adsorption/desorption isotherm of parent MCM-41 and MCM-48 are of type IV according to the IUPAC [70] and characteristic for mesoporous solids. The calculated textural parameters using XRD and adsorption/desorption isotherms are summarized in Table 2. The parent MCM-41 and MCM-48 samples exhibit narrow pore size distributions with average pore diameters of 2.7 and 2.44 nm, respectively. The grafted materials exhibit a broader pore size distribution and display also a decrease in surface area and unit cell volume. The decrease of the unit cell values and the broad distribution of pore sizes evidence that the

organometallic complexes in the grafted mesoporous samples are mainly located on internal surfaces of the mesoporous materials [51–63]. The TEM images (see Fig. 4) of the grafted materials provide strong evidence that the mesoporous structure of the support retains long range ordering [51–63] throughout the grafting process and that the channels remain accessible. The results clearly indicate that the structures of the mesoporous materials remain intact throughout the grafting procedure. Elemental analyses (EAs) of the grafted samples show Mo loadings of 1.33 and 0.7 wt.% for AM-41CpMoChi and AM-48CpMoChi, respectively.

FT-IR spectra of AM-41CpMoChi and AM-48CpMoChi show bands at 1214, 1060, 959, 806, and 471 cm^{-1} , which are attributable to asymmetric and symmetric stretching vibrations of the mesoporous silicate framework (Si–O–Si) [63–65]. New weak shoulder peak observed at ca. 3000 cm^{-1} and the two bands around 2961, 2857 cm^{-1} can be assigned to C–H stretching vibrations originating from the Cp ligand and menthyl groups [51–53]. The other new bands around 2060 and 1943 cm^{-1} are observed in the grafted samples. These bands can be assigned to terminal carbonyl (CO) group vibrations of the grafted compounds. However, after treatment of the heterogeneous catalyst with TBHP the bands around 2060 and 1943 cm^{-1} disappear and new bands around 914 and 964 cm^{-1} are formed, indicating the oxidative conversion of the $Mo(-CO)_3$ into a $Mo(=O)_2$ moiety [51–53]. The 1H MAS NMR spectra of grafted materials display broad peaks between 5.8 and 4.7 ppm and a peak at 2.12 ppm, which can be attributed to the cyclopentadienyl and menthyl protons. The TG-MS spectrum of AM-48CpMoChi shows a weight loss of about 7% up to 1000 °C, due to

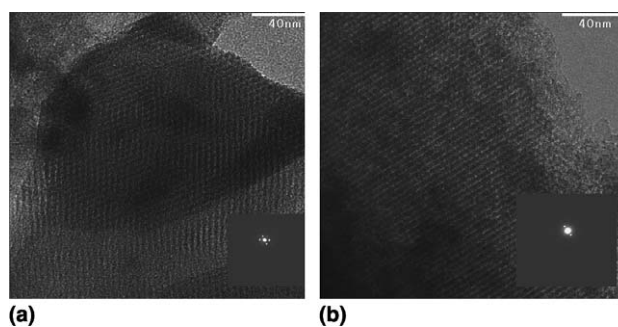


Fig. 4. TEM images of: (a) AM-41CpMoChi; and (b) AM-48CpMoChi.

Table 2
Textural properties of MCM-41/MCM-48 and AM-41CpMoChi/AM-48CpMoChi

Sample	Mo wt%	Interplane distance (nm) ^a	Unit cell parameter \bar{a} (nm) ^b	BET surface area ($m^2 g^{-1}$)	Pore diameter (nm)
MCM-41	–	3.75	4.39	899	2.69
AM-41CpMoChi	1.3	3.68	4.25	648	2.44
MCM-48	–	3.78	9.26	1043	2.41
AM-48CpMoChi	0.7	3.72	9.11	788	2.38

^a d_{100} for MCM-41 and d_{211} for MCM-48.

^b $\bar{a} = 2d_{100}/\sqrt{3}$ for MCM-41; $\bar{a} = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$ for MCM-48.

decomposition of the Mo-complexes present in the channels of the mesoporous molecular sieves. The observed mass values associated with $m/z^+ = 28$, 15 and 65 are corresponding to carbonyl, CH_3 , and Cp, again confirming the presence of the Mo-complex in the mesoporous channel.

3.4. Catalytic behavior of AM-41CpMoChi and AM-48CpMoChi

As in the case of complex **1**, AM-41CpMoChi and AM-48CpMoChi were tested as heterogeneous catalysts for the epoxidation of *cis*-cyclooctene, styrene and *trans*- β -methylstyrene with TBHP as the oxidizing agent (Tables 3 and 4). In the case of cyclooctene, the only major product is the correspondent epoxide, which is similar to the results obtained with the homogeneous catalyst **1** (Table 3). The initial activities (reflected by the TOFs) are somewhat higher for AM-48CpMoChi than for AM-41CpMoChi, owing probably to the three dimensional pore opening of the former compared to the one dimensional pore access of the later. The observed TOFs (360–420 mol(substr.)/(mol(Mo)*h)), are in the same range of than the TOFs of $\text{CpMo}(\text{CO})_3\text{Cl}$ directly grafted on a mesoporous surface (<400 mol(substr.)/(mol(Mo)*h)) [51]. Interestingly, they are higher than the TOFs obtained with the homogeneous catalyst (<100 mol(substr.)/(mol(Mo)*h)).

In order to test the stability and the catalytic reusability of the grafted materials, the catalyst was recycled for two additional runs, applying *cis*-cyclooctene as the substrate. After the first catalytic run, the heterogeneous catalyst was separated from the reaction solution, washed several times with dichloromethane to remove any physisorbed molecules, dried and reused in another catalytic cycle. The catalysts are found to be still active after the third catalytic run, without much change in the obtained conver-

sions (see Table 3). However, the selectivity to the cyclooctene epoxide decreases somewhat over the runs, showing more pronounced diol formation. Filtrate experiments demonstrate that in these systems, leaching does not seem to play an important role. An experiment to find out the extent of leaching was carried out by removing the heterogeneous catalyst (after 50% initial conversion) from the reaction medium by filtration. Then the filtrate solution was tested for catalytic activity for an additional 24 h reaction time. The filtrate solution showed no significant catalytic activity (ca. 5% additional conversion).

In the case of styrene, after 24 h of reaction time, the conversion reaches 75% and 99%, for AM-41CpMoChi and AM-48CpMoChi, respectively. However, and as previously noted for the homogeneous catalyst, the reaction presents low selectivity for the epoxide, being phenylethane-1,2-diol the other main product obtained.

In the case of *trans*- β -methylstyrene, conversion reaches 55% and 59% after 24 h for AM-41CpMoChi and AM-48CpMoChi catalysts, respectively. Contrary to the results obtained for the homogeneous catalyst, the reaction is not selective for the epoxide and additionally to the epoxide diol is formed. Further, the ee value for the reaction changes during the course of the reaction. After 5 minutes of reaction the ee value is 19.8 and 14.4 (for AM-41CpMoChi and AM-48CpMoChi) favouring the RR' enantiomer. However, after 24 h the ee changes into 25.7 and 25.0 favouring the SS' enantiomer. The observed change in the ee values and more importantly the product configuration during the course of the reaction is possibly due to available free protons on the mesoporous materials (H-AIMCM-41 and H-AIMCM-48), similar to observations made during the hydrolytic ring opening of epoxides on H-AIMCM-41 and H-AIMCM-48 materials [71].

Table 3

Catalytic *cis*-cyclooctene epoxidation with TBHP at 328 K using AM-41CpMoChi and AM-48CpMoChi as catalyst (catalyst:olefin:oxidant = 1:100:200)

Catalysts	1st run				2nd run		3rd run		TOF during 1st run [1/h]
	5 min		24 h		24 h		24 h		
	Conv. ^a	Sel. ^a	Conv. ^a	Sel. ^a	Conv. ^a	Sel. ^a	Conv. ^a	Sel. ^a	
AM-41CpMoChi	30	90	100	98	89	87	88	70	360
AM-48CpMoChi	35	85	100	92	100	98	96	84	420

^a Conv., conversion; Sel., cyclooctene epoxide selectivity.

Table 4

Catalytic epoxidation of olefins with TBHP at 328 K using AM-41CpMoChi and AM-48CpMoChi as catalyst (catalyst:olefin:oxidant = 1:100:200)

Olefin	AM-41CpMoChi			AM-48CpMoChi		
	Conv. ^a	Epoxide yield ^a	ee of epoxide ^a (%)	Conv. ^a	Epoxide yield ^a	ee of epoxide ^a (%)
<i>cis</i> -Cyclooctene	100	98	–	100	92	–
<i>trans</i> - β -Methylstyrene	55	–	26	59	–	25
Styrene	75 ^b	41	–	99 ^b	41	–

^a Determined by GC analysis; epoxide ee of the SS isomer.

^b Styrene suffers a ring opening reaction being converted into phenylethane-1,2-diol.

4. Conclusions

The complex $[(\text{-})\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{Cl}$ was successfully synthesized and immobilized on MCM-41 and MCM-48. Both the homogeneous and heterogeneous catalysts are applicable for *cis*-cyclooctene epoxidation. After a recycling procedure, the heterogeneous catalysts can be reused in subsequent catalytic cycles, however with some loss of selectivity. In the case of styrene, selectivity to the epoxide is generally low resulting in ring-opening of the epoxide ring under diol formation. For *trans*- β -methylstyrene both homogeneous and heterogeneous catalysts originate ees of around 20%. For the homogeneous catalyst this ee remains constant throughout the reaction time and favors the RR' enantiomer. However, for the heterogeneous catalyst the RR' enantiomer is originally favoured but over longer reaction time the SS' enantiomer predominates, possibly due to the acid sites present on the supporting materials.

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