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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 [(−)-menthylCp]Mo(CO)$_3$Cl (**1**) was synthesized by the reaction of Mo(CO)$_3$(EtCN)$_3$ with [(−)-menthylCpH] to produce the hydride [(−)-menthylCp]Mo(CO)$_3$H. The latter compound was then reacted with CCl_4 to form [(−)-menthylCp]Mo(CO)$_3$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, ^{1}H 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.

Keywords: Epoxidation; Grafting; Molybdenum; Mesoporous materials; Organometallic complexes

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 peroxo 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 bisoxazoline, *cis*-diol, *cis*-8-phenylthiomenthol and sugar derived chiral Schiff base ligands of general formula $MoO_2(L)(Solv)$ [22–29].

Recently cyclopentadienyl molybdenum complexes of general formula Cp′MoO$_2$Cl (Cp′ = C$_5$R$_5$; R = H, CH$_3$, 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 Cp′Mo(CO)$_3$R (R = Cl, alkyl) leads to efficient catalysts, since the carbonyl

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complexes are in situ oxidized – also by TBHP – to their oxo and peroxo 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 $Cp'Mo(CO)_3Cl$ 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-menthylindenyl)$Mo(CO)_3I$], allyl(2-menthylindenyl)-$Mo(CO)_2$ and (−)-[(2-menthylindenyl)$Mo(CO)_3$]Li(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 [(−)-menthylCp]$Mo(CO)_3Cl$ 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*-cyclooctene, 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 Cu Kα 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 $3.0\ \mu s^1$ H 90° pulses, with a spinning rate of 8 kHz. [(−)-MenthylCp]H was prepared as described in the literature [36,37].

2.2. Preparation of [(−)menthylCp]$Mo(CO)_3Cl$ (**1**)

3.0 g (9.6 mmol) $Mo(CO)_6$ and 30 mL of proprionitrile were refluxed overnight to yield $Mo(CO)_3(EtCN)_3$. Solvent was removed and [(−)menthylCpH] 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