



Catalytic olefin epoxidation with a carboxylic acid-functionalized cyclopentadienyl molybdenum tricarbonyl complex



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ABSTRACT

The complex $\text{CpMo}(\text{CO})_3\text{CH}_2\text{COOH}$ (**1**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) has been examined as a precatalyst for the epoxidation of *cis*-cyclooctene and α -pinene using *tert*-butylhydroperoxide (TBHP) as oxidant. A high turnover frequency of ca. $600 \text{ mol mol}_{\text{Mo}}^{-1} \text{ h}^{-1}$ was achieved in the epoxidation of cyclooctene, giving the epoxide as the only reaction product. With α -pinene as substrate, the added-value products α -pinene oxide and campholenic aldehyde were obtained. Two different approaches to facilitate catalyst recovery and reuse were explored: (1) use of an ionic liquid (IL) as solvent, and (2) intercalation of **1** in a Zn,Al layered double hydroxide (LDH) by a direct synthesis (coprecipitation) route. Characterization of the LDH by powder X-ray diffraction, thermogravimetric analysis, FT-IR and ^{13}C CP MAS NMR spectroscopies showed that the $\text{CpMo}(\text{CO})_3\text{CH}_2\text{COO}^-$ anions intercalate in a bilayer arrangement, resulting in an interlayer spacing of 20.7 Å. In the epoxidation of cyclooctene, catalytic activity in the first batch run was very high for the catalyst/IL mixture and moderate for the LDH. Characterization of the LDH after catalysis indicated that nearly complete oxidative decarbonylation of supported complexes had occurred (by reaction with TBHP), resulting in the presence of immobilized oxomolybdenum species. However, catalytic activities for both the recovered LDH and catalyst/IL decreased in consecutive runs, due in part to progressive removal of active species during either the catalytic reaction (for the LDH) or the solvent extraction/work-up (for the catalyst/IL mixture).

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1. Introduction

The epoxidation of olefins catalyzed by molecular transition metal compounds continues to be a topic of considerable academic and industrial interest [1–3]. Molybdenum-based catalysts have been widely used in this reaction. The well known industrial example is the Arco-Lyondell process for the epoxidation of propene using $\text{Mo}(\text{CO})_6$ as a precursor, which is oxidized *in situ* by the oxidant *tert*-butylhydroperoxide (TBHP) to give the active molybdenum(VI) catalyst [4–6]. During the last decade there has been increasing interest in the use of cyclopentadienyl molybdenum carbonyls of the type $\text{Cp}'\text{Mo}(\text{CO})_3\text{X}$ ($\text{Cp}' = \eta^5\text{-C}_5\text{R}_5$ ($\text{R} = \text{H}$, alkyl, *ansa*-bridge); $\text{X} = \text{halide}$, alkyl, *ansa*-bridge) as precatalysts for olefin epoxidation [7,8]. Great variability by ligand modification (both on the Cp-ring and directly at the metal center) is possible, opening the way to immobilization [9,10] and chirality introduction

[11,12]. Based on catalytic activities obtained for the epoxidation of *cis*-cyclooctene (used as a benchmark substrate), standout precatalysts include $(\eta^5\text{-C}_5\text{Bz}_5)\text{Mo}(\text{CO})_3\text{Cl}$ ($\text{Bz} = \text{benzyl}$) [13], the *ansa*-complex $[\text{Mo}(\eta^5\text{-C}_5\text{H}_4(\text{CH}(\text{CH}_2)_3)\text{-}\eta^1\text{-CH})(\text{CO})_3]$ (with a room temperature ionic liquid (RTIL) as a solvent) [14], and the fluorinated complex $\text{CpMo}(\text{CO})_3\text{CF}_3$ (with hexafluoroisopropanol as a solvent; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) [15]. These tricarbonyl complexes undergo oxidative decarbonylation *in situ* by reaction with TBHP, forming catalytically active Mo-oxo, $\text{Cp}'\text{MoO}_2\text{X}$, and Mo-oxo-peroxo, $\text{Cp}'\text{MoO}(\eta^2\text{-O}_2)\text{X}$, species. More complex species may also be formed as in the analogous oxidation of $(\text{CpBz})\text{Mo}(\text{CO})_3\text{Me}$ that gives $[(\text{CpBz})\text{MoO}_2]_2(\mu\text{-O})$ [16]. Computational studies support a mechanism in which active intermediates of the type $\text{Cp}'\text{MoO}(\text{OH})(\text{OO}^t\text{Bu})\text{X}$ and $\text{Cp}'\text{Mo}(\eta^2\text{-O}_2)(\text{OH})(\text{OO}^t\text{Bu})\text{X}$ are formed by reaction of the respective Mo-oxo and Mo-oxo-peroxo complexes with excess TBHP [17,18].

In the present study the complex $\text{CpMo}(\text{CO})_3\text{CH}_2\text{COOH}$ (**1**) has been prepared, characterized, and examined as a precatalyst for the epoxidation of *cis*-cyclooctene and α -pinene. The recovery and reuse of the homogeneous catalyst was explored using an ionic

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liquid as a solvent. Additionally, a new approach for the immobilization of cyclopentadienyl molybdenum tricarbonyl complexes is reported, based on the intercalation of **1** in a layered double hydroxide.

2. Experimental

2.1. Materials and methods

Microanalyses for CHN and ICP-OES analysis for Mo were determined by C.A.C.T.I., University of Vigo. Powder X-Ray diffraction (XRD) data were collected at room temperature on an X'pert MPD Philips diffractometer with a curved graphite monochromator (Cu-K α radiation, $\lambda = 1.54060 \text{ \AA}$) and a flat-plate sample holder, in a Bragg–Brentano para-focusing optics configuration (45 kV, 50 mA). Samples were step-scanned in $0.02^\circ 2\theta$ steps with a counting time of 50 s per step. SEM with coupled EDS was carried out on a Hitachi SU-70 (S-4100) instrument using a 15 kV accelerating voltage. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 system at a heating rate of $5^\circ \text{C min}^{-1}$ under air. FT-IR spectra were obtained as KBr pellets using an FTIR Mattson-7000 spectrophotometer and recorded from 4000 to 350 cm^{-1} . Raman spectra were recorded on a Bruker RFS100/S FT instrument (Nd:YAG laser, 1064 nm excitation, InGaAs detector). Liquid-state ^1H and ^{13}C NMR spectra were measured with a Bruker Avance 300 instrument. Solid-state NMR spectra were recorded on a Bruker Avance 400 spectrometer. ^{13}C cross polarization (CP) magic-angle spinning (MAS) NMR spectra were recorded at 100.62 MHz with $3.3 \mu\text{s } ^1\text{H } 90^\circ$ pulses, a 2 ms contact time, a spinning rate of 12 kHz and 4 s recycle delays. Chemicals shifts are quoted in ppm relative to TMS. ^{27}Al MAS NMR spectra were recorded at 104.26 MHz using a $\pi/12$ pulse of 0.78 μs , a spinning rate of 14 kHz and 1 s recycle delays. Chemicals shifts are quoted in ppm relative to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

Where appropriate, preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. The chemicals sodium (Riedel-de-Haën), dicyclopentadiene (BDH), $\text{Mo}(\text{CO})_6$ (Fluka), 2-chloroacetamide ($\text{ClCH}_2\text{CONH}_2$, 98%, Sigma–Aldrich), anhydrous *n*-pentane (95%, Sigma–Aldrich), anhydrous tetrahydrofuran (THF, 99.9%, Sigma–Aldrich), anhydrous chloroform (99%, Sigma–Aldrich), acetone (99%, Sigma–Aldrich), hydrochloric acid (HCl, 37%, Fluka), zinc nitrate hexahydrate (99%, Fluka), aluminum nitrate nonahydrate (98.5%, Riedel-de-Haën), 50% aqueous sodium hydroxide (Fluka), Na_2CO_3 (J.M. Vaz Pereira), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim]NTf $_2$, 99%, io-lo-tec) were obtained from commercial sources and used as received. The solution of *tert*-butylhydroperoxide (TBHP) in decane (5–6 M, Sigma–Aldrich, <4% water) was dried over activated 4 Å molecular sieves prior to use. The Zn,Al- NO_3 LDH precursor was prepared by the standard method of coprecipitation of the Zn^{2+} and Al^{3+} hydroxides (initial $\text{Zn}^{2+}/\text{Al}^{3+}$ molar ratio in solution = 2) in the presence of nitrate ions at constant pH (7.5–8) under nitrogen, followed by aging at 80°C for 20 h [19]. After washing, the material was stored as an aqueous suspension in a closed container.

2.2. Synthesis

2.2.1. $\text{CpMo}(\text{CO})_3\text{CH}_2\text{COOH}$ (**1**)

$\text{CpMo}(\text{CO})_3\text{CH}_2\text{COOH}$ (**1**) was synthesized according to the general procedure described by Ariyaratne et al. [20]. A detailed description of the preparation is given here. Freshly cut sodium (0.78 g, 34.0 mmol) was added to 40 mL of dicyclopentadiene under inert atmosphere. The mixture was refluxed overnight at 160°C . The resultant suspension was filtered and the remaining pink solid

residue (NaCp) washed with anhydrous *n*-pentane ($2 \times 15 \text{ mL}$) and vacuum-dried. NaCp was treated overnight with $\text{Mo}(\text{CO})_6$ (5.40 g, 20.4 mmol) in refluxing THF (60 mL). The resultant reaction mixture was cooled to room temperature and $\text{ClCH}_2\text{CONH}_2$ (1.91 g, 20.4 mmol) in THF (60 mL) added. After stirring at room temperature for 2 h, the brown suspension was vacuum-dried and the resultant residue extracted with chloroform. The chloroform fractions were combined and evaporated to dryness, giving $\text{CpMo}(\text{CO})_3\text{CH}_2\text{COONH}_2$, which was subsequently treated with water (34 mL) and HCl (37%, 12 mL, ca. 140 mmol) at 80°C for 1 h. $\text{CpMo}(\text{CO})_3\text{CH}_2\text{COOH}$ (**1**) precipitated as a yellow powder, which was filtered, washed with water, vacuum-dried, and recrystallized from chloroform (1.30 g, 21%, relative to $\text{Mo}(\text{CO})_6$). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{MoO}_5$ (304.11): C, 39.50; H, 2.65. Found: C, 39.2; H, 2.65. FT-IR (KBr, cm^{-1}): $\nu = 3438$ (br), 3120 (w), 2935 (w), 2784 (w), 2624 (w), 2524 (w), 2025 (vs, $\nu(\text{CO})$), 1949 (vs, $\nu(\text{CO})$), 1931 (vs, $\nu(\text{CO})$), 1908 (vs, $\nu(\text{CO})$), 1647 (vs, $\nu(\text{C}=\text{O})$), 1427 (m), 1416 (m), 1283 (vs, $\nu(\text{C}-\text{O})$), 1104 (m), 1043 (m), 1002 (w), 923 (w), 844 (m), 825 (m), 742 (w), 655 (m), 580 (m), 552 (s), 482 (s), 435 (m), 360 (w). FT-Raman (cm^{-1}) $\nu = 3129$ (m), 3109 (w), 3020 (w), 2959 (w), 2013 (s), 1957 (vs), 1935 (w), 1903 (s), 1110 (s), 1058 (w), 1043 (s), 465 (w), 440 (m), 417 (m), 394 (m), 362 (s), 341 (s), 156 (w), 140 (s), 124 (vs), 112 (vs). ^1H NMR (300 MHz, CDCl_3 , 298 K): $\delta = 5.43$ (s, 5H, Cp), 1.80 (s, 2H, CH_2COOH). ^{13}C NMR (126 MHz, CDCl_3 , 298 K): $\delta = 239.3$ (CO), 226.3 (CO), 188.0 (CH_2COOH), 93.8 (Cp), -4.5 (CH_2COOH).

2.2.2. Zn,Al-CpMo

A yellow solution of the sodium salt $[\text{CpMo}(\text{CO})_3\text{CH}_2\text{COO}]\text{Na}$ was prepared by addition of 1 equivalent of NaOH to an aqueous suspension (30 mL) of complex **1** (0.46 g, 1.50 mmol). A solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.59 g, 2.00 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.37 g, 1.00 mmol) in decarbonated deionized (DD) water (30 mL) was then added dropwise, and the pH of the mixture was continuously maintained between 7.5 and 8 using 0.2 M NaOH. After the addition was completed the reaction mixture was aged at 65°C for 19 h. The resultant yellow solid was filtered, washed extensively with DD water and acetone, and finally vacuum-dried. Anal. found: Mo, 12.7%. FT-IR (KBr, cm^{-1}): $\nu = 3448$ (br), 2017 (vs, $\nu(\text{CO})$), 1950 (vs, $\nu(\text{CO})$), 1909 (vs, $\nu(\text{CO})$), 1633 (m), 1579 (m), 1491 (m), 1429 (m), 1360 (s), 1350 (s), 1261 (vw), 1113 (w), 1060 (w), 1014 (w), 825 (m), 790 (w), 748 (w), 625 (bd), 580 (w), 553 (w), 484 (m), 428 (m). FT-Raman (cm^{-1}): $\nu = 3119$ (m), 2945 (w), 2022 (m), 1944 (m), 1110 (s), 1061 (w), 918 (w), 448 (w), 415 (w), 339 (s), 115 (s). ^{13}C CP MAS NMR: $\delta = 242.8$ (CO), 232.0 (CO), 227.0 (CO), 191.5 (CH_2CO_2^-), 177.0 (CO_3^{2-}), 94.0 (Cp), 1.3 (CH_2CO_2^-). ^{27}Al MAS NMR: $\delta = 13.5$.

2.3. Catalytic tests

The catalytic reactions were carried out under air (autogenous pressure) and stirred magnetically (1000 rpm) in a closed borosilicate reactor (10 mL capacity) equipped with a valve for sampling, and immersed in an oil bath thermostated at 55°C . Typically, the reactor was loaded with catalyst (18 μmol of molybdenum), olefin (1.8 mmol, *cis*-cyclooctene (Cy) or α -pinene (Pin)) and 5–6 M TBHP in decane (ca. 2.75 mmol). When stated, 150 μL of [bmim]NTf $_2$ was used as a cosolvent. The olefin, oxidant and (when used) IL were heated in separate vessels (10 min at the reaction temperature) prior to addition to the reactor (with preheated walls) containing the catalyst. Time zero (i.e., the initial instant of the reaction) was taken as the moment the oxidant was added to the reactor. The leaching tests were performed by separating the solid (at 55°C) from the reaction mixture after 2 h, using a 0.2 μm PTFE GVS membrane; the filtrate was stirred for a further 22 h at 55°C . The course of the reactions was monitored using a Varian 3800 GC

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