

Catalytic olefin epoxidation with cyclopentadienyl–molybdenum complexes in room temperature ionic liquids

Fritz E. Kühn,^{a,*} Jin Zhao,^a Marta Abrantes,^{a,b} Wei Sun,^a Carlos A. M. Afonso,^c Luis C. Branco,^{c,d} Isabel S. Gonçalves,^e Martyn Pillinger^e and Carlos C. Romão^{b,*}

^aAnorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany

^bInstituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa, Quinta do Marquês, EAN, Apt. 127, 2781-901 Oeiras, Portugal

^cCQFM, Department of Chemical Engineering, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

^dRequimte/CQFB, Department of Chemistry, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Monte da Caparica, 2829-516 Caparica, Portugal

^eDepartment of Chemistry, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

Received 8 October 2004; revised 4 November 2004; accepted 5 November 2004

Available online 23 November 2004

Abstract—Complexes of the type $(\eta^5\text{-C}_5\text{R}_5)\text{Mo}(\text{CO})_3\text{X}$ ($\text{X} = \text{Me}, \text{Cl}$; $\text{R} = \text{H}, \text{Me}$), being efficient homogeneous catalysts for the epoxidation of olefins, have been examined for their catalytic performance at 55 °C in systems containing room temperature ionic liquids (RTILs) of composition [BMIM]NTf₂, [BMIM]PF₆, [C₈MIM]PF₆ and [BMIM]BF₄. The catalytic performance for cyclooctene epoxidation depends strongly on the water content of the system, the catalyst solubility in the RTIL, and the reaction behaviour of the RTIL under the applied reaction conditions. The catalysts can be recycled without significant loss of activity when a reaction system containing [BMIM]NTf₂ and [BMIM]PF₆ in a 4:1 relationship is used. High proportions of [BMIM]PF₆ lead to a ring opening reaction (diol formation), due to HF formation and the presence of residual water.

© 2004 Elsevier Ltd. All rights reserved.

1. Introduction

Molybdenum(VI) complexes are versatile catalysts for the oxidation of organic substrates.¹ It has been shown that compounds of the type Cp'Mo(CO)₃Cl can be used as olefin epoxidation catalyst precursors being oxidized in situ to the Mo(VI) catalyst thereby presenting over the use of application of previously isolated but more sensitive Mo(VI) species of formula Cp'MoO₂Cl. The more stable carbonyl compounds can be stored easily for long periods of time.^{2a} Furthermore, Cp'Mo(CO)₃R (R = alkyl, or *ansa*-alkyl) complexes have also been described as homogeneous epoxidation catalyst precursors, showing a comparable catalytic activity to their chloro-analogues.^{2b} This type of complexes is highly selective towards epoxide formation and surpasses most other

Mo(VI)-dioxo complexes (e.g., of the composition MoX₂O₂L₂ (X = Cl, Br, Me; L = Lewis base)) significantly in catalytic activity and rivals even the highly active and well examined Re(VII) epoxidation catalyst methyltrioxorhenium (MTO).^{3a–c} The by-product of the oxidation of olefins with TBHP (*tert*-butyl hydroperoxide) in the presence of Mo(VI) dioxo complexes, *t*-BuOH, however, hampers the catalytic reaction with increasing concentration.^{3d–f} Heterogenization of the catalyst, or two-phase homogeneous catalysis, are therefore recommendable ways to avoid high amounts of *t*-BuOH in the same phase as the catalyst after several catalytic runs.^{2c} Another even more important advantage of the application of heterogeneous catalysts is the easy catalyst/product separation, which causes considerable catalyst losses in purely homogeneous systems.

In the last decade room temperature ionic liquids (RTILs) have been attracting considerable attention as possible replacements for conventional molecular solvents due to their unique physical properties such as

Keywords: Catalysis; Cyclopentadienyl; Ionic liquids; Molybdenum; Olefin epoxidation.

* Corresponding authors. Tel.: +49 (0)89 289 13108; fax: +49 (0)89 289 13473; e-mail: fritz.kuehn@ch.tum.de

nonvolatility, nonflammability, thermal stability and high polarity. Additionally, they enable solubilization of inorganic complexes (catalysts), while being immiscible with most hydrocarbons. As such, they provide a nonaqueous alternative for two-phase catalysis, in which the catalyst is 'immobilized' in the ionic liquid and can be easily separated from the products and recycled.⁴ RTILs have been used in several types of reactions such as hydrogenation, hydroformylation, oxidation, oligomerization of alkenes and aldehyde olefination.⁴ With regard to epoxidation catalysis, however, the application of RTIL is just emerging. Song and Roh first reported a Mn(III) (salen) complex (Jacobsen's complex) catalyzing asymmetric epoxidation in an ionic liquid a few years ago.⁵ Since then, RTILs have been successfully applied in the olefin epoxidation with Fe(III) porphyrin, Mn(III) porphyrin, or MTO as catalyst.⁶ It was found that some ionic liquids show enhancement in reaction rates and selectivity. An investigation on the catalytic activity of $\text{MoX}_2\text{O}_2\text{L}_2$ ($\text{X} = \text{Cl, Me}$; $\text{L} = \text{Lewis base}$) complexes in RTIL was reported recently by Valente et al.,⁷ in which a series of RTILs were tested as solvents in the catalytic epoxidation of *cis*-cyclooctene, using TBHP as oxidant. It shows that the use of RTILs for the recycling of dioxomolybdenum(VI) complexes is promising if the right RTIL is chosen for a certain catalyst. Additionally, catalyst recycling by removal of the by-product *t*-BuOH may become much easier.

Among the large variety of RTILs available in the literature, in this study we chose RTILs of the imidazolium salt type with different anions as solvents or 'immobilizing agents', due to their high oxidation stability as well as their easy accessibility in terms of synthesis.⁸ The performance of cyclopentadienyl molybdenum carbonyl complexes of the general formula $\text{Cp}'\text{Mo}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl, Me}$; $\text{Cp} = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$) in the presence of RTILs is examined in this work.

2. Experimental part

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately (THF) or kept over 4 Å molecular sieves. Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets. ^1H , ^{13}C NMR spectra were obtained using a 400 MHz Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II. GC-MS spectra were obtained on a Hewlett-Packard 6890 Series GC System and Hewlett-Packard 5973 Series Mass Selective Detector.

2.1. Synthesis and characterization

The RTILs $[\text{BMIM}]\text{PF}_6$, $[\text{C}_8\text{MIM}]\text{PF}_6$, $[\text{BMIM}]\text{NTf}_2$ and $[\text{BMIM}]\text{BF}_4$ were prepared and purified as described in the literature.⁸ $\text{CpMo}(\text{CO})_3\text{Me}$ (**1**), $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}$ (**2**), $\text{CpMo}(\text{CO})_3\text{Cl}$ (**3**), $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Cl}$ (**4**) and CpMoO_2Cl (**5**) were prepared according to literature procedures.^{2,9} Their spectroscopic data are in accordance with the data reported previously.

2.2. Catalytic reactions with compounds 1–4 as catalysts

All catalytic reactions were performed either under air (if not indicated otherwise) or under dry nitrogen (to exclude moisture) in reaction vessels equipped with a thermostated water bath at 55 °C. The course of the reactions was monitored by quantitative GC analysis. Samples were taken every 30 min during the first 4 h reaction time, diluted with diethyl ether and treated with a catalytic amount of MgSO_4 and MnO_2 to remove residual water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of cyclooctene and the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

Cyclooctene epoxidation: in a typical procedure (first run), after stabilization of the temperature of the water bath, the reaction vessel was charged with the catalyst (73 μmol , 1 mol%) and RTIL (0.5 mL) and a clear yellow or orange red solution (in the case of compound **3**) formed. After that, TBHP (2.65 mL, 5.5 M in *n*-decane) was added and the mixture was stirred for 10 min until a colour change occurred, indicating the oxidation of the Mo(II) carbonyl complexes to the corresponding Mo(VI) compounds. With the addition of the substrate, *cis*-cyclooctene (800 mg, 7.3 mmol) and internal standard, mesitylene (1 g), the catalytic reaction was started.

After reacting for 24 h, magnetic stirring was stopped. If the two phases could be easily visually detected, the upper phase was removed from the reaction vessel. If not, 2 mL *n*-hexane were added and the mixture was stirred until two layers could be clearly seen (after allowing the mixture to settle). The upper phase was then removed from the reaction vessel. In both cases, the remaining phase was washed twice with 1 mL aliquots of *n*-hexane and dried at 55 °C. *t*-BuOH is more soluble in the organic phase and can therefore be removed. Additionally, oil pump vacuum allows alternatively the removal of *t*-BuOH from the RTIL phase.

For the second and third runs new charges of *cis*-cyclooctene (800 mg, 7.3 mmol), mesitylene (1 g, internal standard) and TBHP (2.65 mL, 5.5 M in *n*-decane) were added.

Ring opening reaction of cyclooctene epoxide: compounds **1–5** as catalysts (73 μmol , 1 mol%) and 0.5 mL $[\text{BMIM}]\text{PF}_6$ or $[\text{BMIM}]\text{BF}_4$ were added to the reaction vessel at 55 °C and TBHP (2.65 mL, 5.5 M in *n*-decane) was added. The mixture was stirred until a colour

Download English Version:

<https://daneshyari.com/en/article/9564939>

Download Persian Version:

<https://daneshyari.com/article/9564939>

[Daneshyari.com](https://daneshyari.com)