Applied Catalysis A: General 398 (2011) 88–95

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Dioxomolybdenum(VI) complexes containing chiral oxazolines applied in alkenes epoxidation in ionic liquids: A highly diastereoselective catalyst

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ARTICLE INFO

Article history:
Received 7 January 2011
Received in revised form 10 March 2011
Accepted 11 March 2011
Available online 21 March 2011

Keywords:
Oxomolybdenum(VI) complexes
Oxazoline
Olefin epoxidation
Ionic liquids
Diastereoselectivity

ABSTRACT

New monometallic dioxomolybdenum complexes, **2** and **3**, containing the bis(oxazoline) **B** and the oxazolinyl-pyridine **C** respectively, have been prepared and fully characterized both in solution and solid state, including the single-crystal X-ray diffraction analysis for **2**, which represents the first structure of a Mo(VI) complex coordinated to a bis(oxazoline). These complexes, together with the bimetallic system **1**, were used as catalytic precursors for alkenes epoxidation (cyclooctene, (R)-limonene, trans-β-methylstyrene) in imidazolium- and pyrrolidinium-based ionic liquids, exhibiting a high chemoselectivity towards the epoxide formation, mainly for cyclooctene and (R)-limonene epoxidation, without formation of the corresponding diols. In [BMP][NTf_2] (BMP = butyl methyl pyrrolidinium; NTf_2 = bis(trifluoromethanesulfonyl)amide), complex **1** exclusively gave trans(R)-limonene 1,2-epoxide, while monometallic catalytic systems led to a low diastereoselectivity. ^{95}Mo NMR studies helped to understand the catalytic behaviour of **1** and **2** in ionic liquid medium.

1. Introduction

Epoxides represent useful intermediates for the synthesis of fine chemicals including drugs and fragrances [1]. High-valent oxo-metal complexes have found applications as efficient catalysts for oxidation processes under homogeneous as well as heterogeneous conditions [2]. In particular, molybdenum systems are commercially applied to the production of propylene oxide using alkyl hydroperoxides as oxidants [3]. With the aim to overcome the metal leaching using homogeneous catalysts, several methodologies have been developed in order to immobilize the catalyst and reuse the catalyst without loss of catalytic efficiency. One of these approaches consists in the use of biphasic systems to preserve the homogeneous advantages of the catalysts [4]. Ionic liquids (ILs), solvents exhibiting negligible vapour pressure, thermal stability and high polarity, being their physico-chemical properties easily tuneable depending on the nature of the ions involved, turn into a convenient substitute to volatile organic solvents and a suitable medium to immobilize the catalyst [5]. These features confer them a wide number of applications in organic synthesis, mainly in catalysis [6]. IL phase containing the active catalyst could be readily reused without significant loss of catalytic activity [7], fact particularly interesting for asymmetric catalysis, due to the high added value of the chiral catalysts [8]. The pioneering work in this field was published by Chauvin and co-workers in 1995, concerning the use of N,N′-dialkylimidazolium salts in biphasic catalysis for Rh-catalysed olefin hydroformylation, isomerisation and asymmetric hydrogenation, demonstrating the feasibility to recover the catalyst [9]. However, the first works using neat ILs appeared later, in 2000, when Song's team reported that N,N′-dialkylimidazolium derivatives could be appropriated solvents to perform enantioselective alkene epoxidations [10] and ring opening of epoxides [11]. Although many applications in metal-catalysed organic transformations have been reported in the last two decades as stated by the literature mentioned above, few reports have been published concerning the olefin epoxidation catalysed by oxomolybdenum complexes in ionic liquid medium, being imidazolium-based ionic liquids (Im-ILs) the solvents of choice for the most studies. The first article was published in 2004 by Valente and co-workers where cyclooctene epoxide was obtained in several imidazolium-based ionic liquids using dioxomolybdenum(VI) complexes as catalytic precursors, getting a better catalyst recycling for that containing a tridentated amine [12]. Kühn et al. evaluated the catalytic behaviour of cyclopentadienyl-molybdenum complexes for cyclooctene epoxidation in Im-ILs, demonstrating the importance of the anion nature in the subsequent ring opening giving the corresponding diol [13]. The catalytic activity could be improved and the selectivity tuned using cyclopentadienyl ansa-bridged molybdenum complexes in the appropriate Im-IL [14]. Under microwave-assisted heating in [BMI][BF_4], cyclopentadienyl molybdenum

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doi:10.1016/j.apcata.2011.03.024

complexes led to the exclusive formation of olefin epoxide [15]. Montilla et al. have recently studied olefins epoxidation catalysed by oxodiperoxo- and dioxoperoxo-molybdenum(VI) complexes in Im-ILs using urea-epoxide and hydrogen peroxide as oxidants [16]. Oxodiperoxomolybdenum(VI) complexes have also become active in the epoxidation of oleate derivatives using hydrogen peroxide as oxidant in Im-ILs, being reused up to five consecutive runs with slight loss of activity [17]. With the aim to improve the immobilization of the catalyst in the ionic liquid phase, Poli and coworkers have used Mo(VI) complexes containing Schiff base ligands tagged with sulfonated groups, but after the third recycling the activity considerably decreases [18]. Different molybdenum precursors have been recently applied in olefins epoxidation using Im-ILs and 1-butyl-4-methylpyridinium tetrafluoroborate, without observing remarkable differences between both kind of ILs [19]. To the best of our knowledge, only heterogenized oxomolybdenum complexes onto supports such as mesoporous silicates [20] have led to reasonable recycling although somewhat activity loss is observed comparing with the corresponding homogenous systems [21]. Concerning enantioselective epoxidation in ILs, only two contributions have been reported up to now (involving Im-ILs and pyridinium derivatives), using a dioxomolybdenum(VI) complex containing a chiral tetradentate bisoxazoline ligand [22] and an amino acid-pendant arm-cyclopentadienylmolybdenum(II) complex [23]; asymmetric induction could not be achieved in any case.

Based on our previous experience with oxomolybdenum complexes containing oxazoline ligands in epoxidation of olefins in organic solvents [24,25], we planned to study this kind of complexes in olefin epoxidation reactions in ionic liquid medium. Bimetallic complex **1** (Fig. 1) was previously described by us as an efficient catalyst for cyclooctene epoxidation and what is more interesting, leading to an important diastereomeric induction for the epoxidation of (R)-limonene [25]. Besides this system containing a bidentated oxazolinyl-pyridine ligand (**A**) (Fig. 1), we have synthesized and fully characterized two new dioxomolybdenum complexes containing a bis(oxazoline) (**B**) and a tridentate oxazolinyl-pyridine (**C**) ligands, complexes **2** and **3**, respectively (Fig. 1). In addition to Im-ILs, we have used for the first time in these processes pyrrolidinium-based ILs as solvents in order to study the influence of the nature of the ionic liquid in the catalytic process.

2. Experimental

2.1. General

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. The ionic liquids [BMI][PF_6] 99.5%, [BMI][NTf_2] 99% and [BMP][NTf_2] 99% were purchased from Solvionic and heated at 70 °C under vacuum overnight before use. Tert-butylhydroperoxide (TBHP) was purchased from Aldrich as ca. 5.5 M solution in n-decane over molecular sieves. [MoO_2Cl_2], cyclooctene and trans-stylbene were purchased from Aldrich; (R)-limonene from Sigma–Aldrich and trans-β-methylstyrene from Acros Organic. H_2O_2 (aq) (30%) was purchased from VWR Prolabo. Ligands **A** [26], **B** [27] and complex **1** [25a] were obtained following the procedure previously described. ^{1}H, ^{13}C{^{1}H} and ^{95}Mo NMR spectra were recorded on Bruker Avance 300 and Bruker Avance 400 at 293 K. Chemical shifts were reported downfield from standards. IR spectra were carried out on pellets of dispersed samples of the corresponding compounds in KBr and were obtained on an IR Varian 640-IR FTIR spectrometer. GC routine analyses were carried out using a Perkin Elmer Clarus 500 gas chromatograph (25 m × 0.32 mm methyl siloxane with 5% de phenyl siloxane (BPX5) column) with a FID detector and Perkin Elmer Clarus 5605 mass spectrometer.

2.2. Synthesis of 2-(6-(4,5-dihydro-4-isopropyloxazol-2-yl)pyridin-2-yl)ethanol, *C*

m-CPBA (13.55 g, 70%, 55.0 mmol) was added to 2-(hydroxyethyl)pyridine (5.64 g, 45.8 mmol) in chloroform (150 mL) at 0 °C and stirred for 30 min. The suspension was then warmed at room temperature and stirred for 24 h. Residual m-CPBA was destroyed by the addition of paraformaldehyde (2.0 g, 66.6 mmol CH_2O). After stirring for 2 h, ammonia was bubbled through the reaction mixture for 10 min. The suspension was then dried with Na_2SO_4, filtered and the cake washed with dichloromethane (250 mL). Evaporation of the solvent gave 5.42 g (38.95 mmol, 85% yield) of 2-(hydroxyethyl)pyridine-N-oxide. To a solution of this N-oxide (0.47 g, 3.36 mmol) in CH_2Cl_2 (50 mL), N,N-dimethylcarbamoyl chloride (0.36 mL, 3.36 mmol) was drop wise added; after 2.5 h, trimethylsilyl cyanide (0.54 mL, 4.03 mmol) was also added. The mixture was stirred overnight at room temperature followed by 8 h at reflux and then cooled at room temperature; 1 equiv. each of N,N-dimethylcarbamoyl chloride and trimethylsilyl cyanide were again added. After an additional night of stirring at reflux, the reaction was quenched by addition of a saturated aqueous solution of Na_2CO_3 (25 mL). Both phases were separated, the aqueous layer was extracted with CH_2Cl_2 (2× 15 mL) and the combined organic extracts were dried over Na_2SO_4. Evaporation under reduced pressure gave a brown-red oil which was purified by flash chromatography on silica gel (15 cm × 4 cm column, ethyl acetate:hexane = 1:1, followed by ethyl acetate) to give the expected nitrile product like a white product (0.25 g, 1.60 mmol, 50%).

This nitrile (2.50 mg, 1.69 mmol) was mixed with (R)-2-amino-3-methylbutan-1-ol (2.62 mg, 2.54 mmol) and a pinch of $CuCl_2$ under dried conditions. The neat reaction mixture was stirred at 100 °C under reduced pressure overnight, and then dichloromethane (20 mL) was added and the organic phase was washed with water (3× 15 mL), dried (Na_2SO_4) and solvent eliminated under reduced pressure, to give the expected oxazoline **C** (3.76 mg, 1.60 mmol, 94%). $[\alpha]_D{}^{24} = -50$ (c 0.3, $CHCl_3$). HRMS (CI, CH_4) found *m*/*z*: 235.1445; $C_{13}H_{18}N_2O_2 + H$ requires: 235.1447. IR(KBr): 1660 cm^{-1} (st, C=N); 3374 cm^{-1} (st, C–OH). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 0.93 (3H, d, 6.7 Hz), 1.04 (3H, d, *J* = 6.7 Hz), 1.88 (1H, m), 3.08 (H_2, t, 5.6 Hz), 4.08 (2H, t, 5.6 Hz), 4.14 (1H, m), 4.19 (2H, pq), 4.47, 4.50 (2H, dd, 9.01 Hz; 9.01 Hz), 7.28 (1H, d, 7.91 Hz), 7.70 (1H, pt), 7.94 (1H, d, 7.7 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 18.5 (CH_3), 19.4 (CH_3), 33.1 (CH), 39.6 (CH_2), 62.1.9 (O–CH_2), 71.9 (O–CH_2), 73.2 (N–CH), 125.6 (CH), 137.4 (CH), 122.1 (CH), 146.9 (C), 160.8 (C=N), 162.9 (C).

2.3. Synthesis of [MoO_2Cl_2(κ^2-N,N-***B***)], **2**

The bis-oxazoline **B** (0.147 g, 1.15 mmol) dissolved in THF (5 mL) was added to a THF solution (15 mL) of [MoO_2Cl_2(DME)] [28] (0.100 g, 1.14 mmol) at −78 °C. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The solid obtained was successively washed with ether (3× 10 mL) and pentane (3× 10 mL). Recrystallization from CH_3CN afforded a light yellow solid. Yield: 0.130 g (60%). HRMS (ES) found *m*/*z*: 581.0885 [M−Cl]$^+$; $C_{25}H_{30}ClMoN_2O_6$ requires 581.0860. IR(KBr): 1655 cm^{-1} (st, C=N); 939 and 910 cm^{-1} (Mo=O) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 1.70 (s, 6H), 3.42 (s, 6H), 3.93 (dd, 2H, 10.24 and 3.05 Hz), 4.04 (dd, 2H, 10.29 and 4.61 Hz), 5.00 (m, 2H), 5.70 (d, 2H, 4.88 Hz), 7.41 (m, 10H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 24.2 (C–CH_3), 40.0 (C), 58.7 (O–CH_3), 72.2 (CH_2), 75.0 (N–CH), 83.9 (O–CH), 126.4