Epoxidation of cyclooctene using soluble or MCM-41-supported molybdenum tetracarbonyl−pyridylimine complexes as catalyst precursors

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ABSTRACT

The ligand *N*-(n-propyl)-2-pyridylmethanimine (pyim) and an immobilised analogue of this ligand (MCM-41-pyim) were prepared by the condensation reaction of 2-pyridinecarboxaldehyde with either propylamine or aminopropyl groups covalently attached to the ordered mesoporous silica MCM-41. Free and immobilised tetracarbonyl complexes of the type *cis*-[Mo(CO)$_4$(L)] (L = pyim (**1**), MCM-41-pyim) were then prepared by microwave-assisted heating of a mixture of Mo(CO)$_6$ and the organic ligand or ligand-silica in toluene at 110 °C for 30–45 min. The products were characterised by NMR spectroscopy (^{1}H, ^{13}C and ^{29}Si, in solution and in the solid state), elemental analysis, N$_2$ adsorption, and FT-IR spectroscopy. When used as catalyst precursors for the epoxidation of *cis*-cyclooctene by *tert*-butylhydroperoxide at 55 °C (1 mol% catalyst (Mo), no additional co-solvent), 1,2-epoxy-cyclooctane was obtained as the only reaction product in quantitative yield after 5 h for **1** and 36% yield after 24 h for the supported complex. The use of the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate as co-solvent led to lower catalytic activities (epoxide selectivity was always 100%) but allowed the catalyst/IL mixtures (homogeneous mixture for IL+**1** and a biphasic solid + IL system for IL+MCM-41-pyim/Mo) to be easily recovered and reused in subsequent runs without loss of catalytic performance.

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1. Introduction

Transition metal carbonyl complexes play an important role in organometallic chemistry and are widely used as catalysts or catalyst precursors. During the last decade there has been growing interest in the use of molybdenum carbonyl complexes as precursors to Mo^{VI} catalysts for oxidation reactions, with most of the research being focussed on dicarbonyl [1] and tricarbonyl [2] complexes. We have recently turned our attention to tetracarbonyl complexes of the type *cis*-[Mo(CO)$_4$L] (L = bidentate diimine ligand) [3,4], which are readily available from Mo(CO)$_6$ by, for example, thermal [5], photochemical [6] or microwave-assisted synthesis (MAS) [7] methods. When used as catalyst precursors for the epoxidation of olefins by *tert*-butylhydroperoxide (TBHP), the complexes undergo in situ oxidative decarbonylation to give a tetrameric complex [Mo$_4$O$_{12}$L$_4$] for L = 2-[3(5)-pyrazolyl]pyridine

[4], an octameric complex [Mo$_8$O$_{24}$L$_4$] for L = 4,4′-di-*tert*-butyl-2,2′-bipyridine [3] and ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate [4], and a one-dimensional organic-inorganic polymer [MoO$_3$L] for L = 2,2′-bipyridine [3]. These molybdenum oxide/diimine compounds are moderately active, highly selective and stable catalysts for the epoxidation of olefins, and can be used as either homogeneous or heterogeneous catalysts depending on the nature of the organic ligand.

Among the numerous chelating α-diimine ligands known to form stable group 6 tetracarbonyls of the type *cis*-[M(CO)$_4$L], pyridylimines are attractive due to their ease of synthesis (from the condensation of 2-pyridinecarboxaldehyde with a primary amine) and the fact that their electronic properties are intermediate between those of the more classical ligands such as bipyridine and phenanthroline, and the more flexible diazabutadienes [8]. The steric, electronic and physicochemical properties can be customised by changing the nature of the primary amine used. In one of the main research lines on this topic, group 6 tetracarbonyl complexes bearing functionalised pyridylimines have been prepared with the intention of attaching them to biological molecules for labelling or therapeutic applications [9]. As part of our ongoing efforts to explore the catalytic

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potential of molybdenum carbonyl complexes for oxidation reactions, we now wish to report on the synthesis of a tetra-carbonyl complex containing a pyridylimine ligand and its use as a catalyst precursor for the epoxidation of cis-cyclooctene. With the intention of preparing a heterogenised version of this complex for easier catalyst separation and recycling, the ordered mesoporous silica MCM-41 has been functionalised with pyr-idylimine groups and complexed with molybdenum by reaction with $Mo(CO)_6$.

2. Experimental

### 2.1. Chemicals and instrumentation

Microanalyses for CHN were performed at the University of Aveiro (M. Marques) and the Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa. The molybdenum loadings were determined by ICP-OES at the Central Laboratory for Analysis, University of Aveiro (L. Carvalho). Powder XRD data were collected on a Philips X'pert diffractometer with a curved graphite mono-chromator (Cu-Kα X-radiation, $\lambda = 1.5418$ Å) and a flate plate sample holder, in a Bragg-Brentano para-focussing optics configu-ration (40 kV, 50 mA). Samples were step-scanned in 0.02° 2θ steps with a counting time of 2 s per step. Nitrogen adsorp-tion–desorption isotherms were measured at −196 °C using a Gemini 2380 Micromeritics Instrument. Before analysis, pristine calcined MCM-41 was degassed at 250 °C and the modified mate-rials at 140 °C. Transmission FT-IR spectra (KBr pellets) were measured on a Mattson 7000 FT-IR spectrometer. Attenuated total reflectance (ATR) FT-IR spectra were measured on the same instrument equipped with a Specac Golden Gate Mk II ATR acces-sory having a diamond top-plate and KRS-5 focussing lenses with 4 cm^{-1} resolution. ^1H NMR spectra were measured in solution using a Bruker CXP 300 spectrometer. Solid-state NMR spectra were recorded at 79.49 MHz for ^{29}Si and 125.76 MHz for ^{13}C on Bruker Avance 400/500 spectrometers. ^{29}Si magic-angle-spinning (MAS) NMR spectra were recorded with 40° pulses, spinning rates of 5.0–5.5 kHz and 60 s recycle delays. ^{29}Si cross-polarisation (CP) MAS NMR spectra were recorded with 5.5 μs ^1H 90° pulses, 8 ms contact time with a spinning rate of 5 kHz and 4 s recycle delays. ^{13}C CP MAS NMR spectra were recorded with 3.5 μs ^1H 90° pulses and 2 ms contact time with a spinning rate of 10 kHz and 4 s recycle delays.

The microwave-assisted syntheses were carried out in a Discover S-Class (CEM Corporation, USA) microwave oven at 2.45 GHz under stirring and simultaneous cooling with compressed air (20 psi) to prevent bulk overheating. A vertical focused FT-IR sensor was used for temperature measurement. The reaction temperature of 110 °C was reached and maintained using a dynamic control mode in which the power (max. 150 W) was automatically adjusted.

Purely siliceous MCM-41 was synthesised as described previ-ously using $[CH_3(CH_2)_{13}N(CH_3)_3]Br$ as the templating agent [10]. Calcination was carried out at 540 °C for 6 h to remove the surfactant template. Powder XRD (2θ/°, hkl in parentheses): 2.51 (1 0 0), 4.32 (1 1 0), 4.98 (2 0 0), 6.57 (2 1 0); $a = 2d_{100}/\sqrt{3} = 40.6$ Å. Prior to the grafting experiment, physisorbed water was removed from calcined MCM-41 by heating at 180 °C under reduced pressure for 2 h. All other preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Anhydrous solvents (1,2-dichloromethane, toluene, n-hexane and diethyl ether), $Mo(CO)_6$, (3-aminopropyl)triethoxysilane (APTES), 2-pyridinecarboxaldehyde and propylamine were obtained from Aldrich and used as received.

2.2. N-(n-propyl)-2-pyridylmethanimine (pyim)

The following procedure was adapted from the one described by Haddleton et al. [11]. Propylamine (4.15 g, 0.070 mol) was added to a solution of 2-pyridinecarboxaldehyde (2.52 g, 0.024 mol) in toluene (50 mL), and the reaction mixture was stirred for 5 days under reflux. The toluene and excess amine were then removed in vacuo to give a brown oil. Yield: 3.40 g (96%). ATR FT-IR (cm^{-1}): $\nu = 3054$ (w), 3008 (w), 2960 (m), 2929 (m), 2875 (m), 2832 (w), 1648 (s) (C=N), 1587 (s), 1567 (s), 1467 (s), 1436 (s), 1378 (sh), 1361 (w), 1336 (m), 1292 (m), 1226 (w), 1137 (w), 1089 (w), 1045 (m), 991 (s), 970 (s), 885 (m), 852 (w), 769 (vs), 742 (s), 665 (w), 653 (w), 617 (s), 497 (s), 406 (s), 341 (w). ^1H NMR (300.1 MHz, CDCl_3, 25 °C, TMS): $\delta = 8.64$ (m, 1H, H_1), 8.38 (s, 1H, H_6), 7.98 (m, 1H, H_4), 7.71 (dt, 1H, H_3), 7.28 (m, 1H, H_2), 3.64 (t, 2H, H_7), 1.76 (m, 2H, H_8), 0.96 (t, 3H, H_9) (see Equation (1) for the atom numbering). ^{13}C NMR (75.5 MHz, CDCl_3, 25 °C, TMS): $\delta = 161.5$ (C_6), 154.3 (C_5), 149.1 (C_1), 136.3 (C_3), 124.4 (C_2), 121.0 (C_4), 63.0 (C_7), 23.6 (C_8), 11.6 (C_9).

(1)
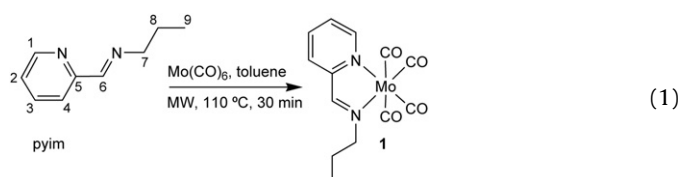
2.3. cis-[Mo(CO)_4(pyim)] (**1**)

A reactor with a capacity of 35 mL was loaded with $Mo(CO)_6$ (0.89 g, 3.41 mmol), pyim (0.50 g, 3.37 mmol) and toluene (20 mL), and the mixture was heated in the microwave oven at 110 °C for 30 min. After cooling to room temperature, the mixture was transferred to a Schlenk tube, the toluene filtered off, and the resultant solid washed with n-hexane and diethyl ether, and finally vacuum-dried to give a red solid. Yield: 0.83 g (69%). Anal. Calcd for $C_{13}H_{12}MoN_2O_4$ (356.2): C, 43.84; H, 3.39; N, 7.86. Found: C, 43.74; H, 3.68; N, 7.85. FT-IR (KBr, cm^{-1}): $\nu = 3438$ (br), 3057 (w), 2967 (w), 2939 (w), 2868 (w), 2008 (s), 1925 (vs), 1860 (vs), 1815 (s), 1616 (s, C=N), 1592 (w), 1554 (s), 1471 (s), 1443 (w), 1426 (w), 1381 (w), 1350 (w), 1303 (s), 1251 (w), 1238 (w), 1199 (w), 1157 (s), 1108 (w), 1052 (w), 1016 (w), 968 (w), 946 (w), 888 (w), 765 (s), 748 (s), 647 (s), 637 (s), 601 (w), 581 (s), 546 (w), 516 (w), 459 (w), 410 (w), 378 (s), 323 (w), 292 (w), 269 (w). ^1H NMR (300.1 MHz, 25 °C, CDCl_3): $\delta = 9.11$ (d, 1H, H_1), 8.42 (s, 1H, H_6), 7.91 (dt, 1H, H_4), 7.73 (m, 1H, H_3), 7.40 (m, 1H, H_2), 4.01 (t, 2H, H_7), 2.10 (m, 2H, H_8), 0.98 (t, 3H, H_9). ^{13}C NMR (75.5 MHz, CDCl_3, 25 °C, TMS): $\delta = 223.7$ (CO_{cis}), 222.7 (CO_{cis}), 203.0 (CO_{trans}), 161.1 (C_6), 153.8, 153.1 (C_5 and C_1), 136.8 (C_3), 126.87 (C_2), 125.8 (C_4), 67.7 (C_7), 24.5 (C_8), 11.1 (C_9).

2.4. MCM-41 grafted with aminopropylsilyl groups (MCM-41-APS)

A mixture of MCM-41 (7.0 g), APTES (7.53 g, 34.0 mmol) and toluene (60 mL) was stirred for 8 days under reflux. After filtering off the solution the colourless solid was washed several times with toluene and vacuum-dried at 100 °C. Elemental analysis found: C, 10.88; H, 2.84; N, 2.19%. FT-IR (KBr, cm^{-1}): $\nu = 3453$ (br), 2947 (w), 1638 (m), 1528 (w), 1472 (w), 1412 (w), 1386 (w), 1217 (sh), 1075 (br), 954 (w), 793 (s), 688 (w), 533 (w), 460 (vs). ^{13}C CP MAS NMR: $\delta = 57.5$ (CH_3CH_2O), 42.8 (CH_2NH_2), 22.1 ($CH_2CH_2CH_2$), 16.5 (CH_3CH_2O), 9.2 (CH_2Si). ^{29}Si MAS NMR: $\delta = -108.9$ (Q^4) ($Q^n = Si(OSi)_n(OH)_{4-n}$). ^{29}Si CP MAS NMR: $\delta = -56.8$ (T^2), −63.8 (T^3), −101.4 (Q^3), −108.9 (Q^4) ($T^m = RSi(OSi)_m(OEt)_{3-m}$).