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# Performance of a tetracarbonylmolybdenum(0) pyrazolylpyridine (pre)catalyst in olefin epoxidation and epoxide alcoholysis



Lucie S. Nogueira, Patrícia Neves, Ana C. Gomes, Anabela A. Valente<sup>\*</sup>, Martyn Pillinger, Isabel S. Gonçalves<sup>\*\*</sup>

Department of Chemistry, CICECO - Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

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# ABSTRACT

Tetracarbonylmolybdenum(0) complexes of the type *cis*-[Mo(CO)<sub>4</sub>(L)] are attractive synthetic precursors of high oxidation state oxomolybdenum catalysts since the byproducts (CO/CO<sub>2</sub>) readily separate from the reaction mixture, facilitating separation/purification procedures (e.g. avoiding contamination/acidification of the medium for halide (X)-containing precursors such as [Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl(CO)<sub>2</sub>(L)]). In this work, the conversion of the tetracarbonyl complex *cis*-[Mo(CO)<sub>4</sub>(ppp)] (ppp = 2-(1-pentyl-3-pyrazolyl) pyridine) to oxomolybdenum compounds has been studied. The molybdenum compounds prepared were explored for liquid phase oxidation and acid catalysis, specifically the epoxidation of *cis*-cyclooctene with hydroperoxide oxidants, and the alcoholysis of styrene oxide. The routes for the conversion of the *cis*-[Mo(CO)<sub>4</sub>(ppp)] precursor to oxomolybdenum compounds, during either the synthesis (*ex situ*) or catalytic (*in situ*) processes (involving isolation/characterisation of metal species after the catalytic runs), were studied for the different catalytic systems, which helped establish relationships between the type of metal species formed and the catalytic performance. Catalyst recyclability was investigated using a homogeneous catalytic ionic liquid-standing approach.

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#### 1. Introduction

The oxidative decarbonylation (OD) of molybdenum carbonyl complexes is a rewarding approach for the preparation of compounds containing Mo centres in high oxidation states [1-3]. For example, the oxidation of  $[Cp'Mo(CO)_3X]$  [Cp' = unsubstituted orsubstituted cyclopentadienyl, X = halide, alkyl, alkyl ester, ansabridged alkyl or cycloalkyl group, etc.] with tert-butylhydroperoxide (TBHP) gives molybdenum(VI) complexes of the type  $[Cp'MoO(O_2)X],$  $[(Cp'MoO_2)_2(\mu-O)]$ [Cp'MoO<sub>2</sub>X]. and [(Cp'MoO(O<sub>2</sub>))<sub>2</sub>( $\mu$ -O)] [1–10], the oxidation of [CpMo(CO)<sub>2</sub>(NHC)  $(CH_3CN)](BF_4)$  with TBHP gives  $[CpMoO_2(NHC)]BF_4$  (NHC = Nheterocyclic carbene) [11], the oxidation of [Mo(CO)<sub>3</sub>(HC(3,5-Me<sub>2</sub>pz)<sub>3</sub>)] with nitric acid yields [(HC(3,5-Me<sub>2</sub>pz)<sub>3</sub>)MoO<sub>3</sub>]  $(HC(3,5-Me_2pz)_3 = tris(3,5-dimethyl-1-pyrazolyl)methane)$  [12], and the reaction of Li[Mo(CO)<sub>3</sub>(tpms)] with AgBF<sub>4</sub> in air gives dinuclear  $[(MoO_2(tpms))_2(\mu-O)]$  (tpms = tris(1-pyrazolyl) methanesulfonate) [13]. These oxomolybdenum complexes have assumed an increasing level of attention in recent years because of their frequently impressive performance as catalysts for organic reactions such as the oxidation of sulfides [14,15], alcohols [16,17] and amines [18], and the epoxidation of olefins [19–21].

The OD synthetic chemistry is not limited to the formation of mononuclear and dinuclear complexes. Some of the more complex species formed include tetranuclear  $[Mo_4O_{12}(pypz)_4]$  from *cis*- $[Mo(CO)_4(pypz)]$  (pypz = 2-[3(5)-pyrazolyl]pyridine) [22], octanuclear  $[Mo_8O_{24}(di-tBu-bipy)_4]$  from *cis*- $[Mo(CO)_4(di-tBu-bipy)]$  (di-tBu-bipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) [23], and the one-dimensional (1D) molybdenum oxide/bipyridine polymer  $[MoO_3(2,2'-bipy)]$  from *cis*- $[Mo(CO)_4(2,2'-bipy)]$  (2,2'-bipy = 2,2'-bipyridine) [23]. The latter reaction is remarkable since it can be performed at ambient temperature with excess TBHP as the oxidant and within a few hours leads to a quantitative yield of the 1D polymer which had only previously been obtained by the hydro-thermal treatment of a mixture of  $MoO_3$ , 2,2'-bipy and H<sub>2</sub>O at 160 °C for at least 5 days [24,25].

Herein we report on the synthesis of the tetracarbonyl complex cis-[Mo(CO)<sub>4</sub>(ppp)] (ppp = 2-(1-pentyl-3-pyrazolyl)pyridine) and its oxidative decarbonylation to give oxomolybdenum species. The



<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: atav@ua.pt (A.A. Valente), igoncalves@ua.pt (I.S. Gonçalves).

tetracarbonyl complex and oxidised compounds have been studied as catalysts or catalyst precursors for the epoxidation of *cis*-cyclooctene and the ethanolysis of styrene oxide. Particular attention has been paid to the characterisation of solids recovered after catalytic runs.

# 2. Experimental

## 2.1. Materials and methods

Hydrazine (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, hydrate solution, 80%), sodium hydride (60% dispersion in mineral oil), 1-iodopentane (98%), 1-butyl-3methylimidazolium (bmim) chloride (98%, Solchemar), 1-butyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide (99%, Iolitec), 1-butyl-3-methylimidazolium hexafluorophosphate (99%, Iolitec), molybdenum hexacarbonyl, molybdenum trioxide (99.5%, Analar), ammonium heptamolybdate tetrahydrate (Merck), 37% hydrochloric acid, 30 wt% hydrogen peroxide, 5-6 M tert-butylhydroperoxide in decane, cis-cyclooctene (95%, Alfa Aesar), cyclooctene oxide (99%), styrene oxide (98%), tetrahydrofuran (99.9%), dichloromethane (puriss), 1,2-dichloroethane (99%), anhydrous acetonitrile (99.8%), chloroform (99.8%), hexane (99%), pentane (>95%, Carlo-Erba), acetone (99.5%), diethyl ether (99.8%) and anhydrous absolute ethanol (≥99.9%, Carlo-Erba) were acquired from Sigma-Aldrich unless otherwise indicated, and used as received. 2-[3(5)-Pyrazolyl]pyridine and 2-(1-pentyl-3-pyrazolyl) pyridine (ppp) were prepared as described previously [26,27]. The hybrid material with the composition  $[Mo_2O_6(ppp)]$  (3) was obtained by the reaction of the complex [MoO<sub>2</sub>Cl<sub>2</sub>(ppp)] with water [27]. Instead of performing the reaction in a Teflon-lined digestion bomb [27], the reaction was carried out with water under reflux conditions. The octamolybdate salt  $[bmim]_4[\beta-Mo_8O_{26}]$  (5) was prepared by addition of [bmim]Cl to an acidified solution of ammonium heptamolybdate [28].

Microanalyses for C, H and N were carried out at the Department of Chemistry, University of Aveiro, with a Truspec Micro CHNS 630-200-200 elemental analyser. Powder X-ray diffraction (PXRD) data were collected at ambient temperature using a PANalytical Empyrean instrument equipped with a PIXcel 1D detector set at 240 mm from the sample. Cu-K<sub> $\alpha$ 1,2</sub> X-radiation ( $\lambda_1 = 1.540598$  Å;  $\lambda_2 = 1.544426$  Å) filtered with a nickel foil was used along with a standard transmission sample holder. Working operating conditions for the X-ray tube: 45 kV and 40 mA. Intensity data were collected in continuous mode in the ca.  $3.5 < 2\theta < 70^{\circ}$  range. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 system at a heating rate of 5 °C min<sup>-1</sup> under air. FT-IR spectra were recorded on a Mattson 7000 FT-IR spectrometer using KBr pellets. Attenuated total reflectance (ATR) FT-IR spectra were measured using a Specac Golden Gate Mk II ATR accessory having a diamond top plate and KRS-5 focusing lenses. FT-Raman spectra were recorded on an RFS-100 Bruker FT-Spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm. <sup>1</sup>H and <sup>13</sup>C solution NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers. Chemical shifts are quoted in ppm from TMS.

#### 2.2. Synthesis

#### 2.2.1. [*Mo*(*CO*)<sub>4</sub>(2-(1-pentyl-3-pyrazolyl)pyridine)] (**1**)

In a Schlenk tube,  $Mo(CO)_6$  (0.50 g, 1.89 mmol) and ppp (0.41 g, 1.90 mmol) were added to toluene (30 mL) and the mixture was refluxed under N<sub>2</sub> for 45 min. After concentrating the resultant solution, hexane (15 mL) and pentane (5 mL) were added, and the mixture was left undisturbed overnight. The resultant yellowish green precipitate was washed with pentane (2 × 15 mL) and finally

vacuum-dried. Yield: 0.45 g, 56%. Anal. Calcd for  $C_{17}H_{17}MoN_3O_4$  (423.27): C, 48.24; H, 4.05; N, 9.93. Found: C, 48.18; H, 4.20; N, 9.79%. Selected FT-IR (KBr, cm<sup>-1</sup>): 361 (s), 405 (w), 467 (w), 478 (w), 557 (m), 584 (m), 602 (m), 627 (w), 648 (m), 760 (vs), 791 (w), 883 (w), 958 (w), 1030 (w), 1157 (w), 1234 (m), 1336 (w), 1361 (m), 1439 (s), 1460 (w), 1498 (w), 1523 (w), 1606 (m), 1824 (vs), 1861 (vs), 2013 (vs), 2864 (m), 2933 (m), 2960 (w). <sup>1</sup>H NMR (300.1 MHz, 295 K, CDCl<sub>3</sub>):  $\delta$  = 9.04 (qd, 1H, H-11), 7.83 (dt, 1H, H-9), 7.73 (td, 1H, H-8), 7.60 (d, 1H, H-5), 7.26 (H-10, overlap with solvent peak), 6.81 (d, 1H, H-4), 4.44 (t, 2H, N-CH<sub>2</sub>), 2.02 (m, 2H, CH<sub>2</sub>), 1.40 (m, 4H, CH<sub>2</sub>), 0.93 (t, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, 295 K, CD<sub>3</sub>CN):  $\delta$  = 223.13 (CO *cis*), 222.62 (CO *cis*), 204.74 (CO *trans*), 153.62 (C-7), 152.38 (C-11), 151.77 (C-3), 139.37 (C-9), 135.58 (C-5), 124.91 (C-8), 122.50 (C-10), 105.53 (C-4), 54.21 (N-CH<sub>2</sub>), 31.12 (CH<sub>2</sub>), 29.15 (CH<sub>2</sub>), 22.88 (CH<sub>2</sub>), 14.08 (CH<sub>3</sub>) ppm.

#### 2.2.2. $[Mo_8O_{24}(2-(1-pentyl-3-pyrazolyl)pyridine)_4]$ (2)

In a Schlenk tube, 5–6 M TBHP in decane (1.3 mL, ca. 7.1 mmol) was added to a mixture comprising complex 1 (0.30 g, 0.71 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (30 mL), and stirring was continued for 4 h under N<sub>2</sub> at room temperature. The resultant off-white solid was recovered by filtration, washed with diethyl ether (2  $\times$  30 mL), and finally vacuum-dried. Yield: 0.08 g, 45%. Anal. Calcd for C<sub>52</sub>H<sub>68</sub>Mo<sub>8</sub>N<sub>12</sub>O<sub>24</sub> (2012.68): C, 31.03; H, 3.41; N, 8.35. Found: C, 30.91; H, 3.57; N, 8.48%. TGA revealed a residual mass of 57.5% at 600 °C (calcd, for MoO<sub>3</sub>: 57.2%). Selected FT-IR (KBr, cm<sup>-1</sup>): 357 (w), 374 (w), 405 (w), 426 (w), 524 (w), 559 (w), 667 (vs), 702 (s), 775 (s), 804 (s), 843 (w), 910 (s), 942 (s), 1024 (w), 1055 (w), 1080 (w), 1099 (m), 1161 (w), 1192 (w), 1236 (m), 1371 (m), 1442 (s), 1466 (m), 1504 (m), 1543 (w), 1570 (w), 1612 (s), 1630 (m), 1741 (w), 2865 (m), 2927 (m), 2956 (m), 3116 (m). Selected FT-Raman (cm<sup>-1</sup>): 203 (m), 220 (sh), 933 (vs), 962 (m), 985 (w), 1021 (m), 1235 (w), 1369 (m), 1419 (m), 1438 (w), 1502 (m), 1534 (s), 1569 (s), 1609 (s).

#### 2.2.3. $[MoO(O_2)_2(2-(1-pentyl-3-pyrazolyl)pyridine)]$ (4)

A mixture of MoO<sub>3</sub> (0.25 g, 1.73 mmol) and 30% H<sub>2</sub>O<sub>2</sub> (2.50 mL, 24.5 mmol) was stirred for 3 h at 60 °C under N<sub>2</sub>. The resultant yellow solution was cooled in an ice-bath and then added slowly to a Schlenk tube containing ppp (0.37 g, 1.73 mmol). A yellow solution and paste were obtained at this stage. After the addition of H<sub>2</sub>O (4 mL), the mixture was stirred until a yellow solid was obtained, which was recovered by filtration, washed with  $H_2O(2 \times 5 \text{ mL})$  and pentane (2  $\times$  4 mL), and finally vacuum-dried. Yield: 0.41 g, 60%. Anal. Calcd for C<sub>13</sub>H<sub>17</sub>MoN<sub>3</sub>O<sub>5</sub> (391.23): C, 39.91; H, 4.38; N, 10.74. Found: C, 40.15; H, 4.45; N, 10.65%. Selected FT-IR (KBr, cm<sup>-1</sup>): 320 (w), 407 (w), 432 (w), 534 (m), 546 (m), 585 (m), 627 (w), 642 (w), 660 (m), 737 (w), 779 (s), 800 (w), 863 (s), 881 (m), 948 (s), 1022 (w), 1053 (w), 1093 (m), 1103 (m), 1151 (w), 1163 (w), 1198 (w), 1234 (m), 1263 (w), 1300 (w), 1332 (w), 1361 (m), 1442 (m), 1468 (m), 1504 (m), 1531 (w), 1574 (w), 1610 (m), 2866 (m), 2935 (m). 2951 (m), 3142 (w), 3136 (w). Selected FT-Raman (cm<sup>-1</sup>): 221 (w), 252 (m), 281 (m), 301 (m), 318 (w), 406 (w), 471 (w), 502 (w), 532 (m), 550 (w), 584 (w), 642 (w), 661 (w), 702 (w), 798 (w), 866 (w), 882 (m), 953 (s), 1022 (m), 1053 (w), 1093 (w), 1102 (w), 1119 (w), 1163 (w), 1331 (m), 1362 (m), 1421 (m), 1441 (m), 1504 (m), 1535 (s), 1572 (m), 1608 (m), 2730 (w), 2861 (m), 2906 (m), 2997 (w), 3065 (m), 3088 (w), 3134 (m).

#### 2.3. Epoxidation tests

The typical epoxidation experiments were carried out in 10 mL borosilicate batch reactors, equipped with an appropriate PTFE-coated magnetic stirring bar (1000 rpm) and a valve for sampling. The heating source was a thermostatically controlled oil bath (55 °C). The reactors were charged with the (pre)catalyst (amount

equivalent to 16  $\mu$ mol Mo), 1.8 mmol of *cis*-cyclooctene (Cy), and a cosolvent [1 mL of 1,2-dichloroethane (DCE) or 0.3 mL of an ionic liquid]. The reactor containing the catalyst, olefin and cosolvent was preheated for 10 min at the reaction temperature. In a separate flask, the oxidant TBHP (5–6 M in decane) was preheated in a similar fashion, and subsequently added to the reactor to give a Mo:Cy:oxidant molar ratio of 1:113:172; this instant was taken as time zero.

Catalytic tests using 30 wt% aq.  $H_2O_2$  as oxidant were carried out using tubular borosilicate batch reactors with pear-shaped bottoms (ca. 12 mL capacity), equipped with an appropriate PTFE-coated magnetic stirring bar (1000 rpm) and a valve for (un)charging of the reactor. Catalyst (16 µmol Mo), Cy (1.8 mmol), CH<sub>3</sub>CN (1 mL) and  $H_2O_2$  (Mo:Cy:oxidant molar ratio of 1:113:172) were added to the reactor, which was subsequently immersed in a thermostatically controlled oil bath (55 °C). Separate catalytic experiments were carried out for each reaction time.

lodometric titrations were carried out in order to quantify the non-productive decomposition of the oxidant (TBHP or  $H_2O_2$ ). The reactors containing the (pre)catalyst, solvent and oxidant, without substrate, were heated at 55 °C for 24 h (stirring rate of 1000 rpm). After cooling the reactors to ambient temperature, liquid samples were withdrawn for titration.

The reaction mixtures were analysed by using a Varian 3900 GC equipped DB-5 capillarv column with а (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu m$ ) and a FID detector, with H\_2 as the carrier gas. The concentrations of reactants/products were determined using the internal calibration method, i.e. based on calibration curves with undecane as internal standard. The FID response was linear in the ranges of concentrations used for the calibration curves and sample analysis. Using the internal calibration method, the determined concentrations of Cy and CyO are reliable (experimental range of error of ca. 6%), i.e. the conversion values account for substrate consumption irrespective of the types of products formed being detected or not by GC. The reactant/ products were identified using GC-MS (Trace GC 2000 Series Thermo Quest CE Instruments GC; Thermo Scientific DSQ II), using He as the carrier gas.

Catalyst reuse was investigated for Cy/TBHP/**2** using an ionic liquid (IL), namely [bmim]PF<sub>6</sub>. After a catalytic batch run, the reactant/products were separated from the IL phase by adding *n*-hexane (immiscible with the IL) to the reaction mixture, followed by centrifugation, decantation and removal of the upper liquid phase from the (denser) IL phase; this procedure was repeated five times, allowing the complete removal of reactant/products from the IL phase, as confirmed by GC analysis. Prior to reuse, the IL mixture was heated at 40 °C under vacuum for 1 h. A second batch run was initiated by adding Cy (preheated at 55 °C) and TBHP to the reactor containing the IL mixture (preheated at 55 °C); the reactants were added in equal amounts to those used for the first batch.

#### 2.4. Alcoholysis tests

The catalytic alcoholysis of styrene oxide (StyOx) was carried out at 55 °C in a similar fashion to that described above for the system Cy/TBHP. The reactor was charged with the catalyst (amount equivalent to 20  $\mu$ mol Mo), 1 mL of ethanol (EtOH) and styrene oxide (0.4 mmol). The analytical equipment and methods used were similar to those for the system Cy/TBHP. For these systems, the catalytic contribution of the solubilised species was checked by carrying out contact tests (CT) as follows. After heating the mixture of (pre)catalyst and solvent (no substrate) at 55 °C for 24 h, the reactor was cooled to ambient temperature. The solidliquid phases were separated by filtration using a 200 nm membrane. The liquid phase was transferred to a separate reactor for a subsequent homogeneous catalytic test at 55 °C. The substrate StyOx was added to the recovered liquid phase in an amount calculated to give an initial substrate concentration equal to that used for a normal catalytic test. The homogeneous catalytic reaction of StyOx was monitored for 24 h at 55 °C, as described above for Cy epoxidation.

#### 2.5. Isolation of metal species after catalytic reactions

For reaction mixtures which were biphasic solid-liquid, the solid phase was separated from the catalytic reaction mixture (TBHP/ DCE or  $H_2O_2/CH_3CN$ ) by centrifugation (3500 rpm), washed with organic solvents (pentane, hexane, ethanol and/or acetone), dried overnight under atmospheric conditions, and subsequently under vacuum (ca. 4 mbar) for 1 h at 60 °C. These undissolved solids are denoted **i**-S-oxid where oxid is the oxidant (TBHP or  $H_2O_2$ ) and **i** is compound **1** or **2**. For epoxidation systems using ionic liquids, the recovered solids (when present) are denoted **i**-S-TBHP-IL {IL = [bmim]NTf<sub>2</sub>}, and for StyOx reactions the recovered solids are denoted as **i**-S-EtOH.

In some cases, metal species could be isolated from the liquid phases of the catalytic reactions by precipitation of solids after addition of an appropriate organic solvent. The precipitated solids were washed and dried as described above for the recovery of the undissolved solids. The precipitated solids are denoted as **i**-L-oxid for catalytic epoxidation of Cy and **i**-L-EtOH for alcoholysis of StyOx. The isolated solids were characterised by ATR FT-IR spectroscopy.

#### 3. Results and discussion

#### 3.1. Synthesis and characterisation

The ligand 2-(1-pentyl-3-pyrazolyl)pyridine (ppp) was prepared by deprotonation of 2-(3-pyrazolyl)pyridine followed by addition of 1-iodopentane and reflux for 24 h (Scheme 1). Characterisation data (FT-IR, <sup>1</sup>H and <sup>13</sup>C solution NMR) were in line with those reported previously for ppp and other related 2-(1-alkyl-3pyrazolyl)pyridine derivatives [27,29]. The molybdenum tetracarbonyl complex [Mo(CO)<sub>4</sub>(ppp)] (1) was obtained directly from  $Mo(CO)_6$  by refluxing a mixture of the hexacarbonyl and the organic ligand ppp in toluene (Scheme 1). Complex 1 displays longterm stability in the solid-state if stored under inert atmosphere. The FT-IR and Raman spectra contain bands for the pyrazolylpyridine and carbonyl ligands (Figs. 1 and 2). In the carbonyl stretching region (1800–2020  $\text{cm}^{-1}$ ) of the IR spectrum, complex **1** displays strong bands at 1824, 1861, ~1885 (sh) and 2013 cm<sup>-1</sup> (cf. sharp bands at 1819, 1875 and 2011  $\text{cm}^{-1}$  in the Raman spectrum). Overall the pattern of bands is consistent with complexes of the type *cis*- $[M(CO)_4(L)]$ . From 300 to 1700 cm<sup>-1</sup> the vibrational spectra of **1** exhibit numerous ligand (ppp) modes. Upon complexation the ligand undergoes structural changes which affect the 1550–1650 cm<sup>-1</sup> region [27,31]. In particular, ligand coordination results in a shift of the pyridyl C-N stretching mode from



Scheme 1. Preparation of the ligand ppp and complex 1.



 $\begin{array}{l} \mbox{Fig. 1.} FT-IR \ (KBr) \ spectra \ in the \ 280-2100 \ cm^{-1} \ range \ for \ (a) \ ligand \ ppp, \ (b) \ 1, \ (c) \ 2, \ (d) \ [Mo_8O_{24}(eppa)_4] \ (Ref. \ [22]), \ (e) \ [Mo_8O_{24}(di-tBu-bipy)_4] \ (Ref. \ [23] \ and \ [30]) \ and \ (f) \ 3. \end{array}$ 



Fig. 2. FT-Raman spectra in the range of 500–2100  $\rm cm^{-1}$  for (a) 1, (b) 2 and (c)  $[\rm Mo_8O_{24}(\rm di-tBu-bipy)_4]$  (Ref. [30]).

 $1590 \text{ cm}^{-1}$  for the free ligand to  $1605 \text{ cm}^{-1}$  for **1**.

Complex **1** is soluble in acetone, CH<sub>3</sub>CN, ethanol, diethyl ether, toluene, chloroform and dichloromethane, and insoluble in water. Solutions of the complex present limited stability and therefore NMR spectra had to be recorded immediately after dissolution in CDCl<sub>3</sub> or CD<sub>3</sub>CN. The <sup>1</sup>H NMR spectrum was fully consistent with the presence of the substituted pyrazolylpyridine ligand. In particular, the resonances for the pyrazolylpyridine protons are generally shifted to lower field upon complexation, similar to that reported previously for complexes of the type [MoO<sub>2</sub>Cl<sub>2</sub>(2-(1-alkyl-3-pyrazolyl)pyridine)] [27,32]. Of particular note is the observation that the H-8 and H-9 resonances switch their relative positions on going from ppp ( $\delta_{H-8} > \delta_{H-9}$ ) to **1** ( $\delta_{H-8} < \delta_{H-9}$ ).

Oxidative decarbonylation of 1 was carried out by the dropwise

addition of 5–6 M TBHP (10 equiv.) in *n*-decane to a suspension of the complex in CH<sub>2</sub>Cl<sub>2</sub>. After stirring at room temperature for 4 h, the resultant off-white solid (2) was filtered, washed with diethyl ether and vacuum-dried. CHN microanalyses for 2 were consistent with the empirical formula [Mo<sub>2</sub>O<sub>6</sub>(ppp)]. In support, TGA revealed a residual mass of 57.5% at 600 °C which is in excellent agreement with the calculated value of 57.2% assuming that the residue at this temperature is MoO<sub>3</sub> (Fig. 3). Previously reported molybdenum oxide-(bidentate)organonitrogen polynuclear or polymeric compounds that have the same empirical formula include the octanuclear complexes  $[Mo_8O_{24}(L)_4]$  [L = di-tBu-bipy and ethyl[3-(2-thermal-text)] = di-tBu-bipy and ethyl[3-(2-thermal-text)]pyridyl)-1-pyrazolyl]acetate (eppa)] [22,23], the 1D hybrid material [Mo<sub>2</sub>O<sub>6</sub>(2,2'-bipy)] [24], and a polymeric hybrid material with the composition  $[Mo_2O_6(ppp)]$  (3) [27]. Whereas the octanuclear complexes were prepared by the oxidative decarbonylation of *cis*- $[Mo(CO)_4(L)]$  in an identical fashion to that performed in the present work, material 3 was obtained upon the reaction of the complex [MoO<sub>2</sub>Cl<sub>2</sub>(ppp)] with water. To date, the structures of [Mo<sub>8</sub>O<sub>24</sub>(eppa)<sub>4</sub>] and **2** have not been unequivocally determined since the compounds precipitate as either amorphous or (poorly) microcrystalline solids (Fig. 4). The structural assignment for [Mo<sub>8</sub>O<sub>24</sub>(eppa)<sub>4</sub>] was based on the similarity of its FT-IR spectrum in the region of Mo–O stretching vibrations  $(650-950 \text{ cm}^{-1})$  with that found for [Mo<sub>8</sub>O<sub>24</sub>(di-tBu-bipy)<sub>4</sub>] (Fig. 1) [22], the structure of which had previously been determined by X-ray crystallography and found to consist of octanuclear windmill-type complexes containing a central cubane-type  $Mo_4(\mu_3-0)_4$  core [23]. As can be verified in Fig. 1, the infrared spectral profile for 2 in the region of 500–1000 cm<sup>-1</sup> is remarkably similar to that for  $[Mo_8O_{24}(eppa)_4]$ . suggesting that the two compounds have closely related structures. On the other hand, the spectral profile for  $\mathbf{3}$  in this region [Fig. 1(f)] exhibits some notable differences especially concerning the relative intensities of some bands. Whereas 2, [Mo<sub>8</sub>O<sub>24</sub>(eppa)<sub>4</sub>] and  $[Mo_8O_{24}(di-tBu-bipy)_4]$  display a weak band at 845 ± 2 cm<sup>-1</sup>, no such band is observed for 3. The existence of different structures for **2** and **3** is further supported by a comparison of the TGA data (Fig. 3). While the TGA curves are similar in terms of the weight loss steps and the residual mass at 600 °C, there are significant differences with respect to the onset temperatures for each step. Considering the Raman data (Fig. 2), the group of bands found between 885 and 1000 cm<sup>-1</sup> for **2** match well with those observed



Fig. 3. TGA curves for compounds  $1 (- \cdot - \cdot)$ , 2 (---) and 3 (---).



Fig. 4. Experimental PXRD patterns of (a)  $[Mo_8O_{24}(eppa)_4]$  (from Ref. [22]), (b) 3 and (c) 2.

for  $[Mo_8O_{24}(di-tBu-bipy)_4]$ . Hence, we propose that **2** may have a similar octanuclear-type structure based on a central cubane-type core (structure **A** in Scheme 2). Additional structural information cannot be garnered from the PXRD data for **2** since the material is (like **3** and  $[Mo_8O_{24}(eppa)_4]$ ) almost amorphous, only giving rise to two extremely broad features centred at 10 and  $24^\circ 2\theta$  (Fig. 4).

#### 3.2. Catalysis

# 3.2.1. Catalytic epoxidation

The reaction of cis-cyclooctene (Cy) using TBHP or H<sub>2</sub>O<sub>2</sub> as



Scheme 2. Representations of the proposed structures for  $Mo^{VI}$  compounds isolated in this work.

oxidant in the presence of compounds 1 or 2 led to 1,2epoxycyclooctane (CyO) with 100% selectivity. These results suggest that CyO is a relatively stable epoxide (even in the presence of excess water added together with H<sub>2</sub>O<sub>2</sub>). This was ascertained by using CyO as substrate instead of Cy, using a very large excess of H<sub>2</sub>O<sub>2</sub> (initial molar ratio of ca. 1CyO:15H<sub>2</sub>O<sub>2</sub>), in the presence of **2**; no reaction of CvO occurred within 24 h reaction, at 55 °C. CvO vields reached 93% for 1 and 99% for 2 at 6 h/55 °C with TBHP as oxidant (Fig. 5, Table 1). In the absence of oxidant and/or molybdenum species the conversions were negligible. Iodometric titrations performed for 2 in the absence of substrate showed that the undesirable (non-productive) decomposition of TBHP (into molecular oxygen and tert-butanol) was not considerable (23% TBHP conversion at 24 h). Hence, the high epoxidation activity of **2** is accompanied by efficient TBHP consumption for the epoxide product formation.

The systems (1 or 2)/TBHP were biphasic solid-liquid mixtures. The ATR FT-IR spectra of the recovered solids 1-S-TBHP and 2-S-TBHP were practically identical and only slightly different from that for 2 (Fig. 6). The differences essentially concern the relative intensities of bands between 750 and 1000 cm<sup>-1</sup>. Similarly, the Raman spectrum of 2-S-TBHP was almost unchanged from that for 2 except for slight changes in the relative intensities of bands between 850 and 1050 cm<sup>-1</sup> (not shown here). These results suggest that compound **2** may be formed from **1** under the catalytic reaction conditions and that the solid **2** is relatively stable. Nevertheless, the minor spectral differences noted above were found to be reproducible, suggesting that the recovered solids may not be entirely pure (2) and/or some structural alteration had occurred. In support, a solid was precipitated from the liquid phase of the 2/ TBHP reaction system (2-L-TBHP) and found to display an ATR FT-IR spectrum that was significantly different from that for 2, especially concerning bands in the 740-1000 cm<sup>-1</sup> interval (Fig. 6). While **2** exhibits a strong band centred at 910 cm<sup>-1</sup>, a slightly weaker one at 942 cm<sup>-1</sup>, and a weak band at 843 cm<sup>-1</sup>, in the spectrum of **2**-L-TBHP a band at 910 cm<sup>-1</sup> is still observed but the strongest band in this region  $(830-1000 \text{ cm}^{-1})$  is at 952 cm<sup>-1</sup> and no band is observed at ca. 843 cm<sup>-1</sup>. Comparison of the spectra for **2** and **2**-L-TBHP with those for 1-S-TBHP and 2-S-TBHP suggests that the latter two solids



**Fig. 5.** *cis*-Cyclooctene epoxidation with TBHP in the presence of 1 ( $\Delta$ ) and 2 ( $\bigcirc$ ) at 55 °C (DCE as cosolvent). The dashed lines are visual guides.

 Table 1
 cis-Cyclooctene epoxidation at 55 °C in the presence of compounds 1 and 2.°

Compound	Oxidant	Cosolvent	Epoxide yield at 1 h/6 h/24 h (%) <sup>b</sup>
1	TBHP TBHP	DCE [bmim]NTf <sub>2</sub>	18/93/100 21/55/88 21/02
1 1 2	TBHP H <sub>2</sub> O <sub>2</sub> TBHP	CH <sub>3</sub> CN DCF	21/64/83 -/-/41 80/99/-
2 2 2 2	TBHP TBHP H <sub>2</sub> O <sub>2</sub>	[bmim]NTf <sub>2</sub> [bmim]PF <sub>6</sub> CH <sub>3</sub> CN	21/67/95 23/56/93 -/-/55

 $^a$  Initial Mo:olefin:oxidant molar ratio = 1:113:172, initial olefin concentration = 1.0 M for TBHP/DCE, 1.2 M for H\_2O\_2/CH\_3CN and 1.7 M for the system TBHP/IL.

<sup>b</sup> Cyclooctene epoxide (CyO) yield (%); selectivity was always 100%.

could be mixtures of **2** and **2**-L-TBHP. Furthermore, the IR spectrum of **2**-L-TBHP in the range of  $350-1650 \text{ cm}^{-1}$  is very close to that for the polymeric hybrid material **3** formulated as [Mo<sub>2</sub>O<sub>6</sub>(ppp)] (Fig. 1). These structural transformations are summarised in Scheme 3. The nature of the Mo-containing active species in solution for the **2**/TBHP system cannot be inferred from these results but they may be mono/polynuclear oxo(peroxo)molybdenum(VI) species derived from **2** (see further discussion below) which may precipitate out as material **3** during the course of the catalytic



**Fig. 6.** ATR FT-IR spectra in the range of 350–2000 cm<sup>-1</sup> for (a) **1** and (b) **2**, and the recovered solids (c) **1**-S-TBHP, (d) **2**-S-TBHP, (e) **2**-L-TBHP, (f) **2**-L-H<sub>2</sub>O<sub>2</sub>, (h) **1**-S-TBHP-[bmim]NTf<sub>2</sub> and (i) **2**-S-TBHP-[bmim]NTf<sub>2</sub>. For comparison, the FT-IR (KBr) spectra of compounds **4** (g) and **5** (j) are shown.

reaction or upon addition of organic solvents to the liquid phase.

Compounds 1 and 2 were less effective when using  $H_2O_2$  as oxidant instead of TBHP, giving 41% and 55% conversion, respectively, at 24 h (Table 1). The variable oxidant-dependent catalytic performance may be partly due to the formation of different types of intermediate oxidising species, leading to differences in activity for olefin epoxidation, since computational studies have indicated distinct reaction mechanisms for the two oxidants [33–35]. For H<sub>2</sub>O<sub>2</sub>, a hydroxide-hydroperoxo intermediate possessing the moiety {M(OH)( $O_{\alpha}O_{\beta}H$ )} may be formed via protonation of an oxo ligand (M=O). This step is not possible with TBHP as oxidant, which instead leads to the formation of an intermediate possessing the moiety {M(OH)( $O_{\alpha}O_{\beta}tBu$ )}. On the other hand, the original compounds may be converted to different types of metal species during the catalytic reaction. The systems  $(1 \text{ or } 2)/H_2O_2$  consisted of yellow transparent solutions. A yellow solid (2-L-H<sub>2</sub>O<sub>2</sub>) was isolated from the liquid phase of the system  $2/H_2O_2$ . Compound  $2-L-H_2O_2$  was identified by ATR FT-IR spectroscopy as the mononuclear oxodiperoxo complex  $[MoO(O_2)_2(ppp)]$  (4) (Schemes 2 and 3), which exhibits bands at 948 cm<sup>-1</sup> [ $\nu$ (Mo=O)], 863 cm<sup>-1</sup> [ $\nu$ (O–O)], 660, 585 and 534 cm<sup>-1</sup> ( $\nu$ [Mo(O<sub>2</sub>)<sub>2</sub>]) (Fig. 6) [27]. In order to check the catalytic contribution of these types of species, complex **4** was synthesised (separately) by the addition of the ligand ppp to a solution obtained by the dissolution of MoO<sub>3</sub> in a large excess of aq.  $H_2O_2$ . The Cy reaction with  $H_2O_2$  at 55 °C in the presence of **4** gave 39% conversion (100% CyO selectivity). This result is comparable with those obtained for the systems  $(1 \text{ or } 2)/H_2O_2$ , suggesting that species of the type  $[MoO(O_2)_2(ppp)]$  are responsible for the catalytic epoxidation.

A previous report showed that complex **4** possesses epoxidation activity with TBHP as oxidant (76%/97% conversion at 1 h/6 h, 55 °C), and may be formed *in situ* from the polymeric hybrid material [Mo<sub>2</sub>O<sub>6</sub>(ppp)] (**3**) [27]. The catalytic results with TBHP are superior to those found in this work with H<sub>2</sub>O<sub>2</sub>, suggesting that the complex is more effective with TBHP. Since the liquid phase for the biphasic system **2**/TBHP was pale yellow and, as discussed above, the solid recovered from this solution (**2**-L-TBHP) appears to be equivalent to [Mo<sub>2</sub>O<sub>6</sub>(ppp)] (**3**), one cannot rule out the possibility that complex **4** is formed in solution and contributes to the catalytic reaction (for **2**/TBHP and **4**/TBHP [27], conversion at 6 h/55 °C was 99% and 97%, respectively). Nevertheless, since we did not manage to isolate this species from the systems (**1** or **2**)/TBHP, its concentration (if formed) may be very low.

# 3.2.2. Acid catalysis

Compounds **1** and **2** were explored as Lewis acid catalysts for the ethanolysis of styrene oxide (StyOx) at 55 °C (Scheme 3). Compound **2** was very effective and led to the formation of the  $\beta$ alkoxyalcohol product, namely 2-ethoxy-2-phenylethanol (EPE), in 98% yield at 1 h (100% selectivity). For **1**, EPE was obtained in 66% yield at 24 h. Conversion was only 5% without catalyst.  $\beta$ -Alkoxyalcohols constitute an important class of organic compounds since this type of functionality is often present in naturally occurring compounds, and they can be employed as natural products, valuable organic solvents or intermediates in organic (to produce  $\beta$ alkoxy ketones,  $\beta$ -alkoxy acids and diols, for example) and inorganic syntheses [36–40].

Biphasic solid-liquid mixtures were formed for the ethanolysis of StyOx in the presence of **1** and **2**. Contact tests indicated that the StyOx reaction essentially occurred in homogeneous phase. Attempts to isolate metal species from the liquid phases of the reaction mixtures were only successful in the case of **1** (**1**-L-EtOH). Compound **1**-L-EtOH exhibited a very similar ATR FT-IR spectrum to **2** (Fig. 7). A comparison of the ATR FT-IR spectra of **1** and **2** with those for the undissolved metal species (**i**-S-EtOH) reveals that the



Scheme 3. Catalytic reactions studied in this work and summary of the transformations that are proposed to take place during either epoxidation of Cy with TBHP/H<sub>2</sub>O<sub>2</sub> or ethanolysis of styrene oxide. The blue reaction arrows indicate that the recovered undissolved solid is likely a mixture of 2 and 3. See Scheme 2 for structures A-C.

two compounds were transformed into different types of metal species (Fig. 7). The spectrum for **1**-S-EtOH is unfamiliar and no structural interpretation can be made. On the other hand, the infrared spectrum for **2**-S-EtOH strongly resembles that for the polymeric hybrid material  $[Mo_2O_6(ppp)]$  (**3**) [Fig. 1(f)]. The apparent conversion of **2** to **3** during the ethanolysis reaction somewhat parallels that observed in the epoxidation system **2**/TBHP.

There are few reports on the use of Mo-containing compounds for homogeneously catalysed styrene oxide alcoholysis. The com- $[(\eta^5 - C_5 H_4 R) Mo(CO)_2(\eta^3 - C_3 H_5)]$ plexes and  $[(\eta^{5}-C_{5}H_{5})]$  $Mo(CO)_3(CH_2R)$ ] (R = H, COOH) were previously tested for the same reaction, at 55 °C, using double the molar ratio of Mo:StyOx to that used in the present work [41]. The dicarbonyl compounds led to a faster alcoholysis reaction (100% conversion at 10 min) than the tricarbonyl complexes (100% conversion at 2 h for R = H, or at 90 min for R = COOH). In comparison to these compounds, the catalytic results for 2 (98% conversion at 1 h) are fairly good. In another study, the complexes  $[MoO_2Cl_2(di-tBu-bipy)]$ ,  $[Mo_2O_2(\mu_2 O_{2}Cl_{2}(di-tBu-bipy)_{2}$  and  $[Mo_{8}O_{24}(di-tBu-bipy)_{4}]$  led to 55%, 23% and 38% EPE yields at 1 h, 55 °C (EPE selectivity was always 100%), which are far inferior catalytic results to those obtained for 2 under similar reaction conditions [42]. In that work, characterisation data for the recovered metal species suggested that the mononuclear and dinuclear complexes were converted in situ to octanuclear  $[Mo_8O_{24}(di-tBu-bipy)_4]$  (structurally comparable to **2**).



Fig. 7. ATR FT-IR spectra in the range of 350–2000  $cm^{-1}$  of (a) 1, (b) 1-S-EtOH, (c) 1-L-EtOH, (d) 2 and (e) 2-S-EtOH.

### 3.2.3. Ionic liquid-supported metal species for olefin epoxidation

Compounds 1 and 2 were tested for Cy epoxidation with TBHP using an ionic liquid (IL) as cosolvent at 55 °C (Table 1). The ILs 1-butyl-3-methylimidazolium tested were bis(trifluoromethylsulfonyl)imide ([bmim]NTf<sub>2</sub>) and [bmim]PF<sub>6</sub>, partly due to the successful use of these types of ILs for recycling molybdenum compounds for catalytic epoxidation processes [43–48]. CyO was always the only reaction product observed and was obtained in yields of 83–88% for 1 and 93–95% for 2 (24 h). For each compound, the type of IL had no major influence on the catalytic reaction. The similar catalytic results may be related to the fact that the two ILs possess the same cation. To test for recyclability, the best-performing system 2/[bmim]NTf2 was reused in a second 24 h-batch run. Conversion decreased slightly from run 1 (95%) to run 2 (83%).

After 24 h-batch runs, the mixtures were liquid (IL)-liquid (organic phase)-solid for (1 or 2)/[bmim]NTf<sub>2</sub> and liquid (IL)-liquid (organic phase) for (1 or 2)/[bmim]PF<sub>6</sub>. Attempts to isolate soluble metal species from the IL media were unsuccessful. The undissolved solids recovered for the former systems (i-S-TBHP-[bmim] NTf<sub>2</sub>) display matching ATR FT-IR spectra (Fig. 6) which, on the basis of literature data [28], are attributed to the presence of the octamolybdate salt [bmim]<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (5). This was verified by synthesising 5 and comparing its infrared spectrum against those for the recovered solids (Fig. 6). Hence, the conversion of compounds 1 and 2 in the IL medium involves exchange of the pyrazolylpyridine type ligand for the cation of the IL.

# 4. Conclusions

A new tetracarbonylmolybdenum(0) complex containing a pentyl-functionalised pyrazolylpyridine ligand has been prepared and characterised. While complex 1 is stable in the solid-state under inert atmosphere, it is unstable in solution. These characteristics are consistent with the poor stability previously reported for tetracarbonylmolybdenum(0) pyridylpyrazole and associated with the coordination of hard bases such as pyridyl or pyrazole to a soft acid, in this case molybdenum(0) [49]. The tetracarbonyl complex readily undergoes oxidative decarbonylation in the presence of the oxidant TBHP to give compounds formulated generally as  $[Mo_nO_{3n}(ppp)_{n/2}]$ , which are proposed to include the octanuclear complex [Mo<sub>8</sub>O<sub>24</sub>(ppp)<sub>4</sub>] (**2**) and a polymeric hybrid material with the composition [Mo<sub>2</sub>O<sub>6</sub>(ppp)] (**3**). The formation of **2** from **1** even takes place in the ethanol/styrene oxide system. In this system compound **2** leads to a nearly quantitative yield of the  $\beta$ -alkoxyalcohol product within 1 h reaction. Good catalytic performance in olefin epoxidation is obtained with 1-3, which are sources of soluble active species such as the oxodiperoxo complex  $[MoO(O_2)_2(ppp)]$  (**4**). When ionic liquids of the type [bmim]X are used as cosolvents in the epoxidation reaction with TBHP, **1** and **2** are converted to the  $\beta$ -octamolybdate salt  $[bmim]_4[\beta-Mo_8O_{26}]$  (**5**). In conclusion, in this work considerable insight has been gained into the chemistry and catalytic performance of a tetracarbonylmolybdenum(0) pyrazolylpyridine complex, which should help guide future studies on the use of such complexes as (pre)catalysts and/or precursors to molybdenum oxide derivatives.

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