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Bis(pyrazolyl)methanetetracarbonyl-molybdenum(0) as precursor to a molybdenum(VI) catalyst for olefin epoxidation

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ABSTRACT

Bis(pyrazolyl)methanetetracarbonyl-molybdenum(0), *cis*-[Mo(CO)₄(BPM)] (1), was prepared from Mo(CO)₆ and the ligand bis(pyrazolyl)methane (BPM), and examined as a catalyst precursor for the epoxidation of olefins using *tert*-butylhydroperoxide (TBHP) as oxidant. Catalytic activities followed the sequence 1-octene < *trans*-2-octene < α -pinene < (*R*)-(+)-limonene < *cis*-cyclooctene, and, with the exception of α -pinene and limonene, the corresponding epoxide was always the only reaction product. Turnover frequencies for the epoxidation of cyclooctene were 580 mol mol_{M0}⁻¹ h⁻¹ at 55 °C and 1175 mol mol_{M0}⁻¹ h⁻¹ at 75 °C, which compare favourably with those found for other molybdenum carbonyl complexes used as catalyst precursors for the same reaction under similar conditions. Catalytic activities were lower in the presence of organic co-solvents, decreasing in the sequence 1,2-dichloroethane > nitromethane > ethanol > hexane > acetonitrile. It is proposed that the oxodiperoxo complex [MoO(O₂)₂(BPM)] (2) may be the active catalyst formed *in situ* by oxidative decarbonylation of 1, since crystals of 2 suitable for structure determination by X-ray diffraction were obtained from the reaction solution recovered after a catalytic run at 55 °C with *cis*-cyclooctene as substrate. In support of this hypothesis, the catalytic performance of **2** for the epoxidation of cyclooctene at 55 °C is very similar to that for **1**.

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1. Introduction

During the last decade, a wide range of molybdenum carbonyl complexes have been examined as precursors to molybdenum(VI) catalysts for the epoxidation of olefins [1], the *cis*-dehydroxylation of olefins [2], and the oxidation of amines [3], alcohols [4] and sulfides [5]. Catalyst generation can be carried out *in situ* since the complexes undergo oxidative decarbonylation by reaction with the oxidant, which is usually *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide. In our recent investigations of molybdenum tetracarbonyl complexes of the type *cis*-[Mo(CO)₄(L)] as catalyst precursors for olefin epoxidation using TBHP as oxidant [1t-1v], we found that the resultant systems were capable of high epoxide selectivities, moderate to high activities, and good stability, functioning as either homogeneous or heterogeneous catalysts depending on the type of ligand (L). A surprisingly diverse range of molybdenum species are formed upon oxidative decarbonylation,

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such as tetranuclear $[Mo_4O_{12}L_4]$ for L = 2-[3(5)-pyrazolyl]pyridine [1u], octanuclear $[Mo_8O_{24}L_4]$ for L = 4,4'-di-*tert*-butyl-2,2'-bipyridine [1t] and ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate [1u], and the one-dimensional molybdenum oxide/bipyridine polymer $[MoO_3L]$ for L = 2,2'-bipyridine [1t].

One family of ligands that have led to effective molecular catalysts of the type $[MoO_2X_2(L)]$ and $[MoO_2X(L)]X(X = Cl, Br)$ for olefin epoxidation are poly(azol-1-yl)alkanes such as bis(pyrazolyl) methanes, tris(pyrazolyl)methanes and tris(benzimidazolyl) methane [6]. As part of our ongoing exploration of molybdenum tetracarbonyl complexes, we have prepared a complex containing the bidentate ligand bis(pyrazol-1-yl)methane, and examined its performance for the epoxidation of olefins.

2. Experimental

2.1. General considerations

Microanalyses for CHN were performed at the University of Aveiro. Transmission FT-IR spectra were measured on a Mattson 7000 spectrometer. Attenuated total reflectance (ATR) FT-IR spectra

⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2012.09.019

were measured on a Bruker optics Tensor 27 equipped with a Specac Golden Gate Mk II ATR accessory having a diamond top-plate and KRS-5 focussing lenses. FT-Raman spectra were recorded on a RFS-100 Bruker FT-Spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm. ¹H NMR spectra were measured with a Bruker CXP 300 instrument; chemical shifts are quoted in parts per million and referenced to tetramethylsilane.

All preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Where appropriate, solvents were dried by standard procedures, distilled under nitrogen, and kept over 4 Å molecular sieves. 1*H*-Pyrazole (98%, Sigma–Aldrich), KOH (\geq 99%, Sigma–Aldrich), DMSO (\geq 99%, Lab-Scan), MgSO₄ (José M. Vaz Pereira), chloroform (\geq 99%, Sigma–Aldrich), CH₂Br₂ (99%, Sigma–Aldrich), Mo(CO)₆ (Fluka), and diethyl ether (99.5%, Sigma–Aldrich) were purchased from commercial sources and used as received. The ligand bis(pyrazol-1-yl)methane (BPM) was prepared as described in the literature [7]. Satisfactory elemental analyses were obtained, and the spectroscopic data (¹H NMR and FT-IR) were in agreement with the published data.

2.2. cis-[Mo(CO)₄(BPM)] (1)

A mixture of Mo(CO)₆ (2.02 g, 7.65 mmol) and the ligand BPM (1.13 g, 7.65 mmol) was vacuum-dried for 15 min. Dry toluene (20 mL) was then added under a continuous flow of nitrogen. The mixture was heated at 110 °C with stirring for 4 h under a continuous flow of nitrogen. After cooling to room temperature, the mixture was filtered, and the resultant greenish-vellow precipitate was washed with diethyl ether (3 \times 20 mL), and finally vacuumdried. Yield: 2.45 g (90%). Anal. Calcd for C₁₁H₈MoN₄O₄: C, 37.10; H, 2.26; N, 15.73. Found: C, 36.73; H, 2.16; N, 15.74%. FT-IR (KBr, cm^{-1}): $\nu = 3150$ (w), 3139 (m), 3035 (w), 2956 (w), 2017 (s, $\nu(CO)$), 1927 (vs, v(CO)), 1871 (vs, v(CO)), 1804 (vs, v(CO)), 1515 (m), 1459 (m), 1428 (s), 1401 (s), 1330 (m), 1300 (w), 1283 (s), 1221 (m), 1096 (s), 1066 (m), 1054 (m), 980 (s), 916 (w), 892 (m), 850 (m), 762 (s), 734 (s), 730 (m), 647 (m), 607 (s), 581 (s), 560 (m), 494 (w), 463 (w), 418 (m), 392 (m), 368 (s). FT-Raman (cm⁻¹): $\nu = 3152$ (w), 3138 (w), 3036 (w), 2956 (w), 2017 (vs), 1911 (w), 1871 (vs), 1803 (s), 1519 (w), 1457 (w), 1427 (w), 1414 (w), 1401 (w), 1330 (w), 1280 (vs), 1240 (w), 1222 (w), 1153 (w), 1097 (w), 1066 (w), 1055 (w), 982 (m), 921 (w), 848 (w), 775 (w), 760 (w), 730 (w), 646 (w), 603 (w), 583 (w), 487 (s), 461 (m), 410 (m), 393 (w). ¹H NMR (300 MHz, 25 °C, DMSO d_6): $\delta = 8.18$ (d, 2H, 3-H pz), 7.92 (d, 2H, 5-H pz), 6.49 (t, 2H, 4-H pz), 6.39 (s, 2H, CH₂). 13 C NMR (75 MHz, 25 °C, DMSO- d_6): δ = 220.4 (CO), 146.2 (3-C pz), 133.9 (5-C pz), 107.3 (4-C pz), 62.6 (CH₂).

2.3. [MoO(O₂)₂(BPM)] (2)

After a catalytic run at 55 °C for 24 h using complex 1 (1.43 mmol) as catalyst precursor, cis-cyclooctene (143 mmol) as substrate, and TBHP (220 mmol, 5-6 M in decane) as oxidant (please see Section 2.5 for more details), the reaction mixture was cooled to ambient temperature, filtered, and kept under nitrogen in a fridge during one week, whereupon a small crop of yellow crystals of **2** was obtained. Yield: 0.08 g (17%). Anal. Calcd for C₇H₈MoN₄O₅: C, 25.94; H, 2.49; N, 17.29. Found: C, 25.82; H, 2.37; N, 17.37%. FT-IR (KBr, cm^{-1}): $\nu = 3147$ (w), 3138 (w), 3118 (m), 3100 (m), 3030 (w), 2987 (w), 1516 (m), 1457 (m), 1430 (m), 1403 (s), 1335 (w), 1295 (m), 1277 (s), 1225 (m), 1153 (w), 1110 (w), 1097 (w), 1082 (m), 1065 (m), 1000 (m), 949 (vs, v(Mo=0)), 925 (w), 914 (w), 866 (s, v(0-0)), 790 (m), 776 (m), 730 (m), 655 (m), 634 (w), 603 (m), 582 (m), 535 (m), 400 (m), 366 (w). FT-Raman (cm⁻¹): $\nu = 3146$ (m), 3119 (w), 3100 (w), 3030 (w), 2986 (w), 1517 (w), 1465 (w), 1431 (w), 1405 (w), 1335 (w), 1275 (w), 1247 (w), 1224 (w), 1152 (w), 1110 (w), 1099 (w), 982 (w), 950 (vs), 920 (m), 875 (s), 777 (w), 735 (w), 656 (w), 610 (w), 578 (m), 529 (m), 400 (w), 362 (w), 341 (w). ¹H NMR (300 MHz, 25 °C, DMSO- d_6): δ = 7.95 (d, 2H, 3-H pz), 7.49 (d, 2H, 5-H pz), 6.40 (s, 2H, CH₂), 6.29 (t, 2H, 4-H pz). ¹³C NMR (75 MHz, 25 °C, DMSO- d_6): δ = 140.1 (3-C pz), 130.6 (5-C pz), 106.3 (4-C pz), 64.2 (CH₂).

2.4. X-ray crystallography

Single crystals of $[MoO(O_2)_2(BPM)]$ (**2**) were manually harvested from the crystallization vial, immersed in silicone grease (Dow Corning) and mounted on a glass fibre with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data were collected on a Bruker X8 Kappa APEX II CCD areadetector diffractometer (Mo K α graphite-monochromated radiation, $\lambda = 0.71073$ Å) controlled by the APEX2 software package [8] and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad [9]. Images were processed using SAINT+ [10], and data were corrected for absorption by the multiscan semi-empirical method implemented in SADABS [11].

The structure was solved using the Patterson synthesis algorithm implemented in SHELXS-97 [12], which allowed the immediate location of the crystallographically independent Mo⁶⁺ centre and most of the heaviest atoms. The remaining non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on F^2 using SHELXL-97 [12a,13]. All non-hydrogen atoms were successfully refined using anisotropic displacement parameters. Hydrogen atoms bound to carbon were placed at their idealized positions using appropriate *HFIX* instructions in SHELXL: 23 for the $-CH_2-$ methylene group and 43 for the aromatic CH groups of the pyrazolyl rings. All these atoms were included in subsequent refinement cycles in riding motion approximation with isotropic thermal displacements parameters (U_{iso}) fixed at 1.2 × U_{eq} of the parent carbon atoms.

The last difference Fourier map synthesis showed the highest peak (0.285 e Å⁻³) located at 0.67 Å from Mo1, and the deepest hole ($-0.448 \text{ e } \text{Å}^{-3}$) at 0.70 Å from C5 close to the medium point of the bond with C6. Information concerning crystallographic data collection and structure refinement details is summarized in Table 1.

2.5. Catalytic olefin epoxidation

The liquid-phase catalytic epoxidation of *cis*-cyclooctene (Cy, 95%, Sigma–Aldrich) was carried out with magnetic stirring (800 rpm), under air, in closed borosilicate micro reactors (5 mL) equipped with a valve to allow sampling. Typically, the reaction mixtures consisted of an amount of catalyst equivalent to 43×10^{-3} mmol of molybdenum, 4.3 mmol of Cy and 6.6 mmol of oxidant. The olefin + oxidant mixture was pre-heated in a thermostated oil bath (55 °C) for 10 min, after which time the catalyst was added. This point was considered as time zero.

tert-Butylhydroperoxide (TBHP, 5–6 M in decane, Sigma–Aldrich) and aqueous H_2O_2 (30% w/w in water, Sigma–Aldrich) were used as oxidants. The reactions were performed without adding a co-solvent or by using 2 mL of 1,2-dichloroethane (DCE), nitromethane (MeNO₂), acetonitrile (ACN), *n*-hexane (hex) or ethanol (EtOH). The other substrates studied (without using co-solvents) were 1-octene, *trans*-2-octene, (*R*)-(+)-limonene and α -pinene. The influence of the temperature on the catalytic activity was evaluated using Cy without co-solvents.

The oxidation processes were monitored by gas chromatography (GC) using a GC Chrompack CP 9001 with a 25 m OPTIMA FFAP Macherey–Nagel capillary column and a flame ionization detector (FID), at regular intervals of 15 min during the first hour,

Table 1

Crystal data collection and structure refinement details for $[MoO(O_2)_2(BPM)]$ (2).

Formula	C ₇ H ₈ MoN ₄ O ₅
Formula weight	324.11
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	P21/c
a (Å)	11.0202(5)
b (Å)	7.7592(3)
<i>c</i> (Å)	12.7699(5)
β(°)	109.726(2)
Volume (Å ³)	1027.85(7)
Ζ	4
$D_{\rm c} ({\rm g} {\rm cm}^{-3})$	2.094
μ (Mo-K α) (mm ⁻¹)	1.295
Crystal size (mm)	$0.13 \times 0.08 \times 0.06$
Crystal type	Yellow block
θ range (°)	3.93 to 29.13
Index ranges	$-15 \le h \le 13, -10 \le k \le 10, -17 \le l \le 17$
Reflections collected	15 485
Independent reflections	2766 $[R_{int} = 0.0307]$
Completeness to $\theta = 29.13^{\circ}$	99.8%
Final <i>R</i> indices $[I > 2\sigma(I)]^{a,b}$	R1 = 0.0236, $wR2 = 0.0502$
Final R indices (all data) ^{a,b}	R1 = 0.0302, $wR2 = 0.0527$
Weighting scheme ^c	m = 0.0174, n = 0.6862
Largest diff. peak and hole	0.285 and -0.448 e Å ⁻³

^a $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$

^b wR2 = $\sqrt{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]}$

^c $w = 1/[\sigma^2(F_0^2) + (mP)^2 + nP]$ where $P = (F_0^2 + 2F_c^2)/3$.

then after each hour until a total of 6 h, and finally the last analysis was performed at 24 h of reaction. The results were determined directly from the chromatographic areas, using *n*-octane as internal standard. When necessary, the reaction products were identified by GC–MS (Agilent Technologies 5973 *invert* Series Mass Selective Detector) using He as the carrier gas and a 30 m AT-WAX MS Grace capillary column.

3. Results and discussion

3.1. Catalyst precursor preparation

The molybdenum tetracarbonyl complex *cis*-[Mo(CO)₄(BPM)] (1) was obtained directly from Mo(CO)₆ in excellent yield by heating a mixture of the molybdenum hexacarbonyl and the organic ligand in toluene at 110 °C for 4 h (Scheme 1). The solid-state FT-IR spectrum (KBr pellet) of 1 shows four active ν (C=O) normal modes in the 1800–2020 cm⁻¹ range, in agreement with the Nujol spectrum reported previously for the same complex [14]. When the ¹H NMR spectra (recorded in DMSO-*d*₆) of the coordinated and free ligand are compared, the signals for the pyrazolyl protons are shifted downfield upon coordination, while the CH₂ signal is unaffected.

3.2. Catalytic epoxidation of olefins

The tetracarbonyl complex **1** was explored as a catalyst precursor for the liquid-phase epoxidation of olefins by using *cis*-cyclooctene (Cy) as a model substrate, *tert*-butylhydroperoxide

(TBHP) as oxygen donor, and no co-solvent (other than the decane present in the oxidant solution and n-octane used as an internal standard for the GC measurements), at 55 °C (Table 2, Fig. 1). 1,2-Epoxy-cyclooctane (CyO) was always the only reaction product. In the absence of catalyst, the reaction rate was negligible. As shown in Table 3, the catalytic performance of **1**, measured in terms of turnover frequency calculated at 5 min reaction and epoxide yield at 24 h, compares quite favourably with that reported for other molybdenum carbonyl complexes used as catalyst precursors in the same reaction under similar conditions.

The kinetic profile with complex **1** as catalyst precursor is typical of many complexes of the type $[MoO_2X_2L_n]$ used as catalysts in the same reaction under similar conditions in a batch reactor (Fig. 1) [16–18]. Initially the reaction rate is high, with 50% conversion being reached after 5 min, and then the reaction rate drops as the substrate is consumed, with full conversion being reached at 3 h.

When 30% aqueous H₂O₂ was used as the oxidant instead of TBHP, with **1** as catalyst precursor, no epoxidation of Cy took place. This behaviour brings us to the studies of Mimoun and co-workers [19], who found that the monoperoxo and diperoxo complexes of the type $[MoO(O_2)Cl_2L_2]$ and $[MoO(O_2)_2L_2]$ showed only weak activity as catalysts for olefin epoxidation with H₂O₂ or Ph₃COOH. Better results have been reported in a few selected cases [20], in particular oxodiperoxomolybdenum/ionic liquid/H2O2 olefin epoxidation systems [20a-d]. Generally, the epoxidation activity of oxoperoxomolybdenum complexes is much greater when using TBHP as oxidant, which led Mimoun and co-workers to conclude that alkyl-peroxidic rather than peroxo species are active intermediates in the reaction [19]. Accordingly, experimental and theoretical studies carried out by Kühn et al. showed that the complexes $[MoO_2X_2L_n]$ (X = Cl, Br, CH₃) carrying Lewis-bases ligands undergo an equilibrium reaction with excess TBHP to give seven-coordinate molybdenum η^1 -alkylperoxo complexes that selectively catalyze the epoxidation of olefins [16].

The influence of solvent on the epoxidation of *cis*-cyclooctene in the presence of **1** was investigated at 55 °C (Table 2, Fig. 1). Depending on the type of the solvent, 1,2-dichloroethane (DCE), ethanol (EtOH), nitromethane (MeNO₂), acetonitrile (ACN) or *n*hexane (hex), the catalytic activity changes considerably without affecting the selectivity to the epoxide, which was always 100%. A decrease in the initial rate was observed for all solvents, which could be partially related with dilution effects and, eventually, with changes in the reaction system that did not favour the formation of actives species. Nevertheless, apart from hex, a full conversion of Cy (with 100% selectivity) was obtained after 24 h for all the other solvents, in spite of the different reaction rates observed in the first hours.

The lack of a clear relationship between the dielectric properties (Table 2) of the solvents and the catalytic activity may be partly related to differences in solubility. Thus, the higher reaction rate observed for DCE may be largely explained by the fact that complex 1 is evidently more soluble in the system containing this polar, non-coordinating solvent. The low solubility of the catalyst in hexane, due to the non-polar and aprotic nature of this solvent, is probably the reason for the low epoxidation rate since it causes a decrease in



Scheme 1. Preparation of the catalyst precursor 1.

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Table 2
Olefin epoxidation with TBHP using complex 1 as catalyst precursor

Olefin	<i>T</i> (°C)	Co-solvent ^a	TON (mol mol_{Mo}^{-1})	TOF (mol $mol_{Mo}^{-1} h^{-1})^b$	Olefin conversion (%) ^c	Epoxide selectivity (%) ^c
cis-Cyclooctene	20	None	5	63	26/38	100/100
	55	None	48	579	100/100	100/100
	(2nd batch at 55 °C)	None	38	379	100/100	100/100
	75	None	100	1175	100/100	100/100
	(2nd batch at 75 °C)	None	40	480	100/100	100/100
	55	MeNO ₂ (38)	-	340	98/100	100/100
	55	ACN (35)	-	174	90/100	100/100
	55	EtOH (24)	-	270	98/100	100/100
	55	DCE (10.4)	-	391	100/100	100/100
	55	Hex (1.9)	_	202	89/94	100/100
1-Octene	55	None	4	21	27/46	100/100
trans-2-Octene	55	None	3	36	67/96	100/100
Limonene	55	None	44	527	93/99	3/4 ^d
α-Pinene	55	None	28	331	53/68	4/2 ^e

^a Dielectric constants are given in parentheses.

^b Calculated from the conversion at 5 min of reaction.

^c Olefin conversion and epoxide selectivity at 6/24 h.

^d Selectivities to other products were 6/6% for carvone and 48/41% for limonene-1,2-diol.

^e Selectivities to other products were 13/11% for campholenic aldehyde and 9/11% for campholenic aldehyde oxide.

the number of available active species in the reaction mixture. The much slower reactions observed in the presence of the coordinating solvents ACN and ethanol (as opposed to the non-coordinating solvents DCE and MeNO₂) may be due to the participation of solvent molecules in the reaction, probably by coordination to the metal site, thereby influencing the overall kinetics (e.g., the formation of the active oxidizing species may become rate-limiting) [17]. As a result, interactions between the olefin/oxidant and the solvated and/or coordinated molybdenum species may become unfavourable. Nitromethane, whose polarity is very similar to that of ACN, is a non-coordinating solvent and, therefore, the results were slightly better (98% at 6 h) than those of ACN (90% at 6 h). DCE showed a kinetic profile very similar to MeNO₂.

It is known that the catalytic activity of Mo^{VI} complexes for olefin epoxidation is highly dependent on the reaction temperature. Raising the temperature may have two different effects: (a)



Fig. 1. Kinetic profiles for *cis*-cyclooctene epoxidation with TBHP, at 55 °C, using *cis*- $[Mo(CO)_4(BPM)]$ (1) as catalyst precursor and either no co-solvent (\Box) or in the presence of DCE (\bigcirc), MeNO₂ (\times), EtOH (\triangle), hex (+) or ACN (\diamond).

the reaction rate increases, as observed in most cases; (b) the stability of the catalyst decreases, resulting in deactivation. Usually, a moderate increase in the temperature gives rise to an increase in the reaction rate; however, high temperatures may be detrimental due to the possibility of complex decomposition. In the present study, when the reaction was run at room temperature (20 °C, Cy as substrate and TBHP as oxidant), the initial TOF decreased to 63 mol mol_{Mo}^{-1} h⁻¹, keeping the selectivity to epoxide at 100% (Table 2). After 6 h, a yield of about 26% was obtained, in contrast to 100% obtained at 3 h for the reaction run at 55 °C, and 98% obtained at 5 min for the reaction run at 75 °C (Fig. 2). Increasing the reaction temperature from 55 to 75 °C resulted in an increase in the TOF from 597 to 1175 mol mol_{Mo}^{-1} h⁻¹ (Table 2).

These data show that a higher reaction temperature is beneficial in terms of initial reaction rate, which could be related with the accelerated formation of the active species via decarbonylation of the precursor. On the other hand, a low temperature (20 °C) gives rise to a significant decrease in the reaction rate probably due to an ineffective formation of the active species. Despite the better results obtained at 75 °C, carrying out the reaction at 55 °C may be advantageous since a high yield of epoxide can be obtained in a relatively short reaction time (practically 100% after 2 h), which is very attractive regarding the reduction in energy costs of the process.

In order to evaluate the performance of the catalytic system with **1** for the epoxidation of other olefins, a thorough study was carried out using the structurally different substrates 1-octene, *trans*-2-octene, (*R*)-(+)-limonene (present in citrus peel) and α -pinene (component of turpentine that can be extracted from pine resin) (Scheme 2). Data in Table 2 summarize the results of the catalytic activity for the different olefins tested, and Fig. 3 shows the kinetic profiles. Both TON and TOF values follow the sequence 1-octene < *trans*-2-octene < α -pinene < (*R*)-(+)-limonene < *cis*-cyclooctene. This order is in accordance with the increasing presence of alkyl substituents that cause an increase in electron density on the double bond, thus increasing its nucleophilicity.

A comparison of the catalytic activities for the linear octenes indicates that the catalytic system is more active in the epoxidation of internal double bonds than of terminal ones, as would be expected based on mechanistic findings [16–18]. The respective epoxides were the only reaction products in both reactions. *trans*-2-Octene was more reactive than 1-octene, which suggests that the catalyst promotes epoxidation of more nucleophilic olefins. This is consistent with the fact that for (*R*)-(+)-limonene the epoxidation

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Epoxidation of cis-cyclooctene at 55	C with IBHP (in decane)) and different molybdenum	carbonyl complexes as catalyst precursors.

Complex ^a	Mo:Cv:TBHP	Co-solvent	TOF (mol mol \overline{M}_{2}^{1} h ⁻¹) ^b	Epoxide vield at 24 h (%)	Ref.
				_p	
$cis-[Mo(CO)_4(BPM)](1)$	1:100:150°	None	579 (5)	100	This work
<i>cis</i> -[Mo(CO) ₄ (di- ^t Bu-bipy)]	1:100:150 ^d	DCE	9 (10)	82	[1t]
cis-[Mo(CO) ₄ (pzpy)]	1:100:150 ^d	None	67 (10)	92	[1u]
<i>cis</i> -[Mo(CO) ₄ (pyim)]	1:100:150 ^c	None	372 (5)	100	[1v]
[Mo(η ³ -allyl)Cl(CO) ₂ (DAB)]	1:100:150 ^d	None	297 (10)	95	[1m]
CpMo(CO) ₃ Cl	1:100:200 ^d	CHCl ₃	900 (5)	100	[15]
CpMo(CO) ₃ Cl	1:100:150 ^d	None	500 (10)	100	[10]
CpMo(CO) ₃ Me	1:100:200 ^d	None	820 (5)	100	[1d]
CpMo(CO) ₃ Me	1:100:150 ^d	None	313 (5)	100	[1j]
$CpMo(CO)_2(\eta^3-allyl)$	1:100:150 ^d	None	310 (10)	100	[10]
CpMo(CO) ₂ (NHC)Cl	1:100:200 ^d	None	40 (15)	27	[1p]
[Cp ^{ox} Mo(CO) ₂ (MeCN)]BF ₄	1:100:200 ^d	CHCl ₃	960 (5)	100	[1r]
Cp ^{PPh2} Mo(CO) ₂ Cl	1:100:200 ^d	None	1400 (2)	100	[1s]

^a Di-^fBu-bipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine; pzpy = ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate; pyim = N-(n-propyl)-2-pyridylmethanimine; DAB = 1,4-(2,6-dimethyl) phenyl-2,3-dimethyldiazabutadiene; NHC = 1,3-dibenzylimidazol-2-ylidene; (Cp^{Ox} and Cp^{PPh2}) pendant oxazoline or diphenylphosphine groups are coordinated through the N or P-atoms to the molybdenum centre.

^b The reaction time used to calculate the TOF is given in parentheses.

^c Order of addition of reagents = [(Cy + TBHP) + Mo complex].

^d Order of addition of reagents = [(Mo complex + Cy) + TBHP].

is mainly promoted at the double bond of the ring (C_1-C_2) instead of the terminal double bond (C_8-C_9) . However, α -pinene, a substituted and cyclo-olefin, has a significantly lower reactivity because it is a bicyclic molecule with a proximal dimethyl bridge that may cause steric hindrance when it approaches the active species.

No correlation could be established between the polarity of the substrate molecules and the catalytic activity (this could be important since in the absence of solvent the volume of substrate in the reaction medium is considerable): for example, the dielectric constants of (*R*)-(+)-limonene and α -pinene are similar (2–3, at 20 °C), but the respective conversions were not. The reactions of *cis*-cyclooctene, 1-octene and *trans*-2-octene gave the corresponding epoxide as the only product throughout 24 h reaction. In contrast, the reactions of (*R*)-(+)-limonene and α -pinene were not



Fig. 2. Kinetic profiles for *cis*-cyclooctene epoxidation with TBHP using *cis*- $[Mo(CO)_4(BPM)]$ (1) as catalyst precursor and no co-solvent, at 20 °C (\bullet run 1), 55 °C (\Box run 1, × run 2), and 75 °C (+ run 1, \bigcirc run 2).

selective to the corresponding epoxide, under the applied reaction conditions, originating a wide spectrum of products, which included carvone and limonene-1,2-diol from (*R*)-(+)-limonene, and campholenic aldehyde and campholenic aldehyde oxide from α -pinene (Scheme 2). After 24 h, 99% conversion of (*R*)-(+)-limonene was achieved, while the epoxide and diol yields were only 4 and 41%, respectively. For both the (*R*)-(+)-limonene and α -pinene reactions, small amounts of other unidentified products were detected. The multiplicity of reaction products obtained from these monoterpenes results in low concentrations of the final products, thereby increasing the cost of recovery of these compounds.

The catalytic stability of the active species formed from 1 was investigated by carrying out two 24 h runs at 55 °C, using a substrate:oxidant molar ratio of 1:1.6. After the first run, the reaction vessel was recharged with substrate and oxidant in identical amounts to those used in the first run. Initially, the reaction was somewhat slower in the second run (Table 2), but after 3 h the kinetic curves converged to give the same conversion of 100% at 6 h (Fig. 2). As mentioned above, for a reaction temperature of 75 °C, complete conversion of Cy was achieved in the first run after 5 min. To assess the stability of the catalyst at this higher temperature, a second run was carried out as described above. The same effect was observed, i.e., the reaction was somewhat slower in the second run (Table 2), but after 3 h the kinetic curves converged to give similar conversion in the range of 95-100% up to 6 h (Fig. 2). For both reaction temperatures, since the catalyst was not separated from the reaction products of the first run, the accumulation of tert-BuOH, a possible coordinating solvent, could cause a lower initial reaction rate [16,17]. Additionally, a more dilute reaction mixture and a decrease in the reaction temperature that occurred when the new amounts of substrate and oxidant were added may also contribute to the lower initial rate. Nevertheless, the same level of conversion is achieved at longer times, which attests to the high stability of the catalyst.

With the aim of obtaining a better understanding of the molybdenum species formed upon use of complex **1** as a catalyst precursor for the epoxidation of olefins, a separate reaction was performed with the same precursor:Cy:TBHP ratios (1:100:152) but involving larger quantities (please see Section 2.3 for details). After 24 h of reaction at 55 °C, the reaction mixture was cooled to ambient temperature, filtered, and kept in a fridge during one week, whereupon a small crop of yellow crystals suitable for X-ray diffraction was obtained. As will be described below, the XRD



Scheme 2. Substrates and their respective epoxidation products using 1 as catalyst precursor and TBHP as oxidant, at 55 °C, without co-solvent.

analyses identified the structure as the oxodiperoxo complex $[MoO(O_2)_2(BPM)]$ (2). Complex 2 could also be obtained in 47% yield by carrying out the reaction of **1** with TBHP in the absence of Cy. The complex was characterized by FT-IR, FT-Raman, ¹H and ¹³C NMR spectroscopy. In the solid-state, the FT-IR spectrum of 2 shows bands at 949 cm⁻¹ (ν (Mo=O)), 866 cm⁻¹ (ν (O-O)), 656, 582 and 535 cm⁻¹ (ν (Mo(O₂)₂)), which are all characteristic of [MoO(O₂)₂L_n] complexes bearing either two monodentate ligands or one bidentate ligand (L) [21]. The corresponding bands appear at 950, 875, 656, 578 and 529 cm⁻¹ in the Raman spectrum. No ν (C=O) bands were observed. The ¹H and ¹³C NMR spectra of **2** in DMSO- d_6 show pyrazole ($\delta_{\rm H}$ = 7.95, 7.49, 6.29 ppm; $\delta_{\rm C}$ = 140.1, 130.6, 106.3 ppm) and CH_2 ($\delta_H = 6.40$ ppm; $\delta_C = 64.2$ ppm) signals. When compared to the spectra of the free ligand in the same solvent [14], the signals for **2** are unshifted, which may mean that the ligand BPM is weakly coordinated to the metal centre and/or is displaced by the deuterated solvent molecules.

As mentioned above, seven-coordinate molybdenum peroxo complexes of the type $[MoO(O_2)_2L_n]$ are well known catalysts for the epoxidation of olefins with TBHP, especially when L is a neutral

bidentate N,N-ligand such as a substituted pyrazolylpyridine [21a,22]. A catalytic run for the epoxidation of *cis*-cyclooctene carried out with **2** under the same conditions used for the catalyst precursor **1** gave a kinetic profile similar to that obtained with **1** (Fig. 4). Hence, there is a high probability that the active catalyst formed *in situ* from **1** is the oxodiperoxo complex [MoO(O₂)₂(BPM)] (**2**). The initial catalytic activity for **2** (TOF \approx 550 mol mol_{M0}⁻¹ h⁻¹) is slightly higher than that reported for [MoO₂Cl₂(2,2-di(1-pyrazolyl) propane)] under similar conditions (TOF = 460 mol mol_{M0}⁻¹ h⁻¹) [6a]; after 4 h reaction the epoxide yield with **2** was 99.2% vs. 62% for the dichlorodioxomolybdenum(VI) complex.

3.3. Crystal structure description of $[MoO(O_2)_2(BPM)]$ (2)

Compound **2** crystallized in the monoclinic space group $P2_1/c$, with the asymmetric unit being composed of a whole complex molecule ultimately formulated as [MoO(O₂)₂(BPM)]. The metal centre is heptacoordinated to a terminal oxido, two η^2 -O,O'-peroxido and one κ^2 -*N*,N'-bispyrazolylmethane ligands. If each of the peroxido ligands is considered as a single coordination site, the





Fig. 3. Oxidation of *cis*-cyclooctene (\Box) , (*R*)-(+)-limonene (×), α -pinene (+), *trans*-2-octene (\bullet) and 1-octene (\triangle) with TBHP using *cis*-[Mo(CO)₄(BPM)] (1) as catalyst precursor, at 55 °C, without co-solvent.

coordination environment around the metal centre can be envisaged as a highly distorted trigonal bipyramid (Fig. 5). The polyhedron distortion can be related with either the internal angles or the coordination distances. In this geometry the apical positions are occupied by the oxido ligand O1 and by one of the nitrogen atoms of the neutral ligand (N3 in this case). The Mo–O distances are 1.6854(15) Å for the Mo=O bond and in the 1.9160(15)– 1.9597(15) Å range for the single Mo–O bonds. The *trans* influence of the former double bond is remarkable in this molecule, with the two Mo–N bonds being statistically very distinct [2.1913(16)



Fig. 4. Epoxidation of *cis*-cyclooctene with TBHP in the presence of *cis*- $[Mo(CO)_4(BPM)]$ (1) (\Box) or $[MoO(O_2)_2(BPM)]$ (2) (+), at 55 °C, without co-solvent.

Fig. 5. Asymmetric unit of [MoO(O₂)₂(BPM)] (**2**) showing a whole molecular unit. Nonhydrogen atoms are represented as thermal ellipsoids drawn at the 50% probability level, while hydrogen atoms are represented as small spheres with arbitrary radii. The atomic labelling is provided for all non-hydrogen atoms. For selected bond lengths and angle ranges referring to the Mo^{6+} coordination sphere see Table 4.

and 2.3666(16) Å], with the longest being attributed to the apical nitrogen atom (see Table 4 for additional geometry details). This structural feature has been observed in a series of compounds having the general formula $[MoO(O_2)_2(L)_2]$ (where L represents a pyrazole or pyridine group) and similar coordination geometry, as revealed by a systematic search of the Cambridge Structural Database (CSD, version 5.33, November 2011 with three updates – May 2012) [23]. For this family of compounds, which comprises 11 members, the Mo–N distances range from *ca*. 2.16 to *ca*. 2.25 Å for the equatorial nitrogen atom and from *ca*. 2.28 to *ca*. 2.43 Å for the apical one [20b,c,22b,24], which agree well with the results for **2**. While the internal polyhedral angles in **2** involving the apical and the equatorial atoms range from 77.83(6) to 104.25(8)°, those subtended by the medium points of the peroxido ligands and the equatorial nitrogen atoms range from *ca*. 109 to *ca*. 111° (see Table 4

Table 4

Selected bond lengths (in Å) and angles (in degrees) for the Mo^{6+} coordination environment present in [MoO(O₂)₂(BPM)] (**2**).

· · · · · ·	1 1 2)2(11()	
Mo1-01	1.6854(15)		
Mo1-02	1.9597(15)		
Mo1-03	1.9219(16)		
Mo1-04	1.9468(16)		
Mo1-05	1.9160(15)		
Mo1-N1	2.1913(16)		
Mo1-N3	2.3666(16)		
02-03	1.466(2)		
04–05	1.472(2)		
01-Mo1-05	104.25(8)	O1-Mo1-N1	90.93(7)
01-Mo1-03	103.68(8)	O5-Mo1-N1	131.55(7)
O5-Mo1-O3	89.35(7)	O4-Mo1-N1	87.63(7)
01-Mo1-04	100.34(8)	O2-Mo1-N1	88.05(6)
05-Mo1-04	44.80(7)	O5-Mo1-N3	83.00(7)
03-Mo1-04	132.42(7)	O1-Mo1-N3	168.72(7)
01-Mo1-02	101.34(7)	O3-Mo1-N3	84.81(6)
05-Mo1-02	131.38(7)	O4-Mo1-N3	78.55(6)
03-Mo1-02	44.36(6)	O2-Mo1-N3	79.40(6)
04-Mo1-O2	157.95(7)	N1-Mo1-N3	77.83(6)

Table 5

Weak interactions (distances in Å and angles in degrees) present in the crystal structure of $[MoO(O_2)_2(BPM)]~({\bf 2}).^a$

$\begin{array}{l} \pi \cdots \pi^b \\ C_g A \cdots C_g A^i \\ C_g B \cdots C_g B^{ii} \end{array}$	Intercentroid distance 3.7338(12) 3.3414(14)	
$D-H\cdots Cg$ $C2-H2\cdots C_gB^i$	d(D…Cg) 3.414(3)	<(DHCg) 144
$\begin{array}{l} D-H\cdots A \\ C1-H1\cdots O4^{iii} \\ C4-H4A\cdots O1^{iv} \\ C4-H4B\cdots O2^{c} \\ C5-H5\cdots O2^{v} \\ C7-H7\cdots O3^{iv} \end{array}$	d(D…A) 3.486(3) 3.359(3) 3.046(3) 3.212(3) 3.476(3)	<(DHA) 175 141 123 129 169

^a Symmetry operations used to generate equivalent atoms: (i) 2 - x, 1 - y, 2 - z; (ii) 1 - x, 1 - y, 2 - z; (iii) 2 - x, -y, 2 - z; (iv) x, $\frac{1}{2} - y$, $\frac{1}{2} + z$; (v) x, 1 + y, z.

^b $C_gA =$ centroid of the ring {N1, N2, C1–C3}, $C_gB =$ centroid of the ring {N3, N4,

C5-C7}.

^c Intramolecular interaction.

for detailed geometrical details). One remarkable aspect of the coordination geometry around the Mo^{6+} metal centre concerns the fact that the atoms of the coordination sphere are distributed in two almost perpendicular medium planes [angle between of 89.68(10)°]: one comprising the peroxido ligands [largest deviation of 0.014(2) Å for both O3 and O5] and the other comprising the atoms Mo1, N1, N3 and O1 [largest deviation of 0.007(2) Å for O1]. Atom Mo1, which is located in the second plane, is displaced only 0.371(1) Å from the first plane.

In the absence of strong supramolecular interactions, the crystal packing in **2** is mainly governed by the need to fill the available space and by a handful of weak interactions such as C–H···O, C–H··· π and π – π stacking interactions (see Table 5 for geometrical details and Fig. 6 for a schematic representation). Each of the aromatic rings interacts through π – π stacking with symmetry-related aromatic rings, with the distances between centroids being smaller than 3.7338(12) Å. This leads to the formation of a supramolecular chain parallel to the *a*-axis of the unit cell. A C–H··· π interaction [C···C_g distance of 3.414(3) Å] also participates in the constitution of this chain. Supramolecular chains close pack with the assistance of weak C–H···O interactions [C···O distance smaller than 3.486(3) Å].



Fig. 6. Crystal packing of $[MoO(O_2)_2(BPM)]$ (**2**) viewed in perspective along the [010] direction of the unit cell. Weak supramolecular interactions are represented as follows: C-H···O as dashed green lines, C-H··· π as dashed pink lines, and π - π stacking interactions as dashed orange lines. Table 5 summarizes the geometrical data for the represented supramolecular interactions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

The present work has shown that a molvbdenum tetracarbonyl complex bearing a bis(pyrazolyl)methane ligand is a precursor to a very active and stable catalyst for olefin epoxidation, with the catalytic activity comparing favourably with that previously found for analogous complexes bearing either bipyridine, pyrazolylpyridine or pyridylimine derivatives as ligands. Whereas the reactions of cis-cyclooctene, 1-octene and trans-2-octene gave the corresponding epoxide as the only product, the reactions of (R)-(+)-limonene and α -pinene were not selective to the corresponding epoxide, under the applied reaction conditions, originating a wide spectrum of products. Taking into account that the oxodiperoxo complex $[MoO(O_2)_2(BPM)]$ (2) was isolated in a small amount from the catalytic reaction mixture obtained after epoxidation of *cis*-cyclooctene, and that the catalytic performance of **2** for cis-cyclooctene epoxidation matches that observed for 1, it seems reasonable to conclude that fast oxidative decarbonylation of cis-[Mo(CO)₄(BPM)] (1) may occur in situ to give 2 as the active catalyst. In the future, spectroscopic investigations of the reaction of the precursor with the oxidant may help to confirm the nature of the molybdenum species formed.

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Appendix A. Supplementary material

CCDC-890671 contains the supplementary crystallographic data (including structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2012.09.019.

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