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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_{Mo}^{-1} h^{-1} at 55 °C and 1175 mol mol_{Mo}^{-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 [$MoO(O_2)_2$(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**.

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, 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

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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. ^{1}H 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 (≥99%, Sigma–Aldrich), DMSO (≥99%, Lab-Scan), $MgSO_4$ (José M. Vaz Pereira), chloroform (≥99%, Sigma–Aldrich), CH_2Br_2 (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 (^{1}H 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-yellow precipitate was washed with diethyl ether (3 × 20 mL), and finally vacuum-dried. Yield: 2.45 g (90%). Anal. Calcd for $C_{11}H_8MoN_4O_4$: 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, ν(CO)), 1927 (vs, ν(CO)), 1871 (vs, ν(CO)), 1804 (vs, ν(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). ^{1}H 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, CH_2). ^{13}C NMR (75 MHz, 25 °C, DMSO-d_6): $\delta = 220.4$ (CO), 146.2 (3-C pz), 133.9 (5-C pz), 107.3 (4-C pz), 62.6 (CH_2).

2.3. *[MoO(O$_2$)$_2$(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 $C_7H_8MoN_4O_5$: 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, ν(Mo=O)), 925 (w), 914 (w), 866 (s, ν(O–O)), 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). ^{1}H NMR (300 MHz, 25 °C, DMSO-d_6): $\delta = 7.95$ (d, 2H, 3-H pz), 7.49 (d, 2H, 5-H pz), 6.40 (s, 2H, CH_2), 6.29 (t, 2H, 4-H pz). ^{13}C NMR (75 MHz, 25 °C, DMSO-d_6): $\delta = 140.1$ (3-C pz), 130.6 (5-C pz), 106.3 (4-C pz), 64.2 (CH_2).

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 area-detector diffractometer (Mo Kα 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 Mo^{6+} 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 e 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 ($MeNO_2$), 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,