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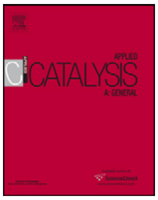

Heterogeneous oxidation catalysts formed in situ from molybdenum tetracarbonyl complexes and *tert*-butyl hydroperoxide

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ABSTRACT

The tetracarbonyl complexes *cis*-[Mo(CO)$_4${2-[3(5)-pyrazolyl]pyridine}] (**1**) and *cis*-[Mo(CO)$_4${ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate}] (**2**) were obtained in excellent yields by microwave-assisted heating of a mixture of Mo(CO)$_6$ and the organic ligand in toluene at 110 °C for 30 min. Complexes **1** and **2** are air stable, storable catalyst precursors for the epoxidation of olefins by *tert*-butyl hydroperoxide (TBHP). In situ oxidative decarbonylation of **1** gives the tetranuclear compound [Mo$_4$O$_{12}${2-[3(5)-pyrazolyl]pyridine}$_4$] (**3**). Elemental analysis and infrared data indicate that the oxidation of **2** gives an octameric species with the molecular formula [Mo$_8$O$_{24}${ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate}$_4$] (**4**). The molybdenum oxide/pyrazolylpyridine compounds **3** and **4**, which can be readily prepared in very good yields from the parent carbonyls upon reaction with TBHP in *n*-decane/CH$_2$Cl$_2$ at room temperature, are active and stable heterogeneous catalysts for the epoxidation of *cis*-cyclooctene (Cy) by TBHP, giving 1,2-epoxycyclooctane as the only product. The highest activity is found for **4**: ca. 90% epoxide yield after 6 h reaction at 55 °C. Further experiments confirmed that **2** is an effective catalyst precursor for (i) the epoxidation of Cy by aqueous TBHP, giving the corresponding epoxide as the only product, (ii) the selective epoxidation of *R*-(+)-limonene by TBHP (in *n*-decane), and (iii) the selective oxidation of methyl phenyl sulfide to the corresponding sulfoxide by aqueous TBHP or H$_2$O$_2$ at 35 °C.

1. Introduction

Transition metal carbonyl complexes have been widely exploited in different areas such as luminescence [1], nonlinear optics [2], medicine (e.g., as carbon monoxide-releasing molecules [3]) and catalysis [4–9]. A wide range of molybdenum carbonyl complexes have recently been applied as precursors to molybdenum(VI) catalysts for the epoxidation of olefins [4a,4b,5], the *cis*-dehydroxylation of olefins [6], and the oxidation of amines [7], alcohols [8] and sulfides [9]. In addition to the extensively studied tricarbonyl complexes of the type Cp′Mo(CO)$_3$X (Cp′ = η^5-C$_5$R$_5$; X = halide, alkyl, acetylide) [4a,4b,5a], the complexes Cp′Mo(CO)$_2$(η^3-allyl) [5b], (Cp^x-NHC)Mo(CO)$_2$X (with an *ansa* bridge between Cp^x and an N-heterocyclic carbene) [5c], CpMo(CO)$_2$(NHC)X [5d], [Mo(η^3-allyl)X(CO)$_2$(bis-NHC)] [5e], [Mo(η^3-allyl)X(CO)$_2$(N–N)] [5f] and *cis*-[Mo(CO)$_4$(N–N)] [5g] (X = halide, N–N = bidentate diimine ligand) have been studied. Most of these complexes are available effortlessly from Mo(CO)$_6$. For example, the tetracarbonyl complexes can be obtained quickly and in high yields by a microwave-assisted synthesis employing Mo(CO)$_6$ and the organic ligand as starting materials. When used directly as catalyst precursors, the molybdenum carbonyl complexes undergo oxidative decarbonylation by reaction with the oxidant, which is usually *tert*-butyl hydroperoxide (TBHP) or H$_2$O$_2$. The Mo^{VI} species formed include Cp′MoO$_2$X, Cp′MoO(O$_2$)X, [Cp′MoO$_2$]$_2$(μ-O) and [Cp′MoO(O$_2$)]$_2$(μ-O) from Cp′Mo(CO)$_3$X, [CpMoO$_2$(NHC)]BF$_4$ from CpMo(CO)$_2$(NHC)X, [MoO$_2$(N–N)]$_2$(μ-O)$_2$ from [Mo(η^3-allyl)X(CO)$_2$(N–N)], polymeric [MoO$_3$(bipy)] from *cis*-[Mo(CO)$_4$(bipy)] (bipy = 2,2′-bipyridine), and octameric [Mo$_8$O$_{24}$(di-*t*-Bu-bipy)$_4$] from *cis*-[Mo(CO)$_4$(di-*t*-Bu-bipy)] (di-*t*-Bu-bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine).

The compounds [MoO$_3$(bipy)] and [Mo$_8$O$_{24}$(di-*t*-Bu-bipy)$_4$] exhibit high selectivity and moderate activity for the epoxidation of *cis*-cyclooctene (used as a model substrate) [5g]. Changing the nature of the bidentate ligand in the tetracarbonyl precursors may influence not only the species formed by oxidative decarbonylation but also their catalytic performance. One family of ligands that have led to highly active catalysts of the type [MoO$_2$Cl$_2$(L)] and [MoO(O$_2$)$_2$(L)] are pyrazolylpyridines [10,11]. In a continuation of our previous study [5g] we now describe the synthesis of the tetracarbonyl complexes [Mo(CO)$_4$L] (L = 2-[3(5)-pyrazolyl]pyridine (**1**), ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate (**2**))

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and their application as precatalysts for the epoxidation of *cis*-cyclooctene and *R*-(+)-limonene, and the oxidation of methyl phenyl sulfide. The oxidation of the complexes gives tetrameric $[Mo_4O_{12}L_4]$ from **1** and a cubane-based complex from **2**, and both compounds can be used as recyclable heterogeneous catalysts.

2. Experimental

2.1. Preparation of the catalyst precursors

Anhydrous toluene (Scharlau), dichloromethane, *n*-hexane and pentane (Aldrich), $Mo(CO)_6$ and 5–6 M TBHP in *n*-decane (Aldrich) were obtained from commercial sources and used as received. Literature procedures were used to prepare 2-[3(5)-pyrazolyl]pyridine [12] and ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate [11b,13].

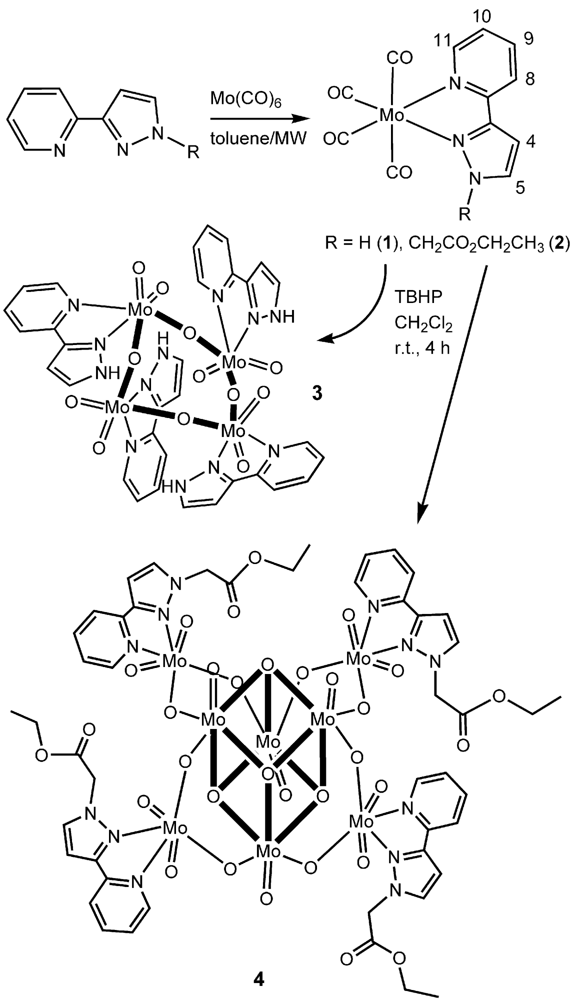
To prepare *cis*-$[Mo(CO)_4\{$2-[3(5)-pyrazolyl]pyridine$\}]$ (**1**), a glass vessel with a capacity of 35 mL was loaded with toluene (20 mL), $Mo(CO)_6$ (0.50 g, 1.90 mmol) and 2-[3(5)-pyrazolyl]pyridine (0.28 g, 1.90 mmol), and the mixture was heated at 110 °C for 30 min using a Discover S-Class (CEM 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 IR sensor was used for temperature measurement, and the reaction temperature was reached and maintained using a dynamic control mode in which the power (max. 150 W) was automatically adjusted based on the temperature feedback. After cooling to room temperature, the mixture was transferred to a Schlenk tube, and the resultant solid was washed with *n*-hexane (30 mL) and pentane (10 mL), and vacuum-dried. Yield: 0.64 g (95%). Anal. calcd for $C_{12}H_7N_3MoO_4$ (353.14): C, 40.81; H, 2.00; N, 11.90. Found: C, 40.87; H, 2.30; N, 11.98. Selected IR (KBr, cm^{-1}): ν = 3360 (s) (ν_{NH}), 2009 (s), 1873 (vs), 1831 (m), 1798 (vs) (ν_{CO}), 1608 (m), 1513 (m), 759 (s), 364 (m). ^1H NMR (300 MHz, 25 °C, $CDCl_3$): δ = 11.06 (br, 1H, NH), 8.96 (d, 1H, H^{11}), 7.80 (dt, 1H, H^9), 7.71 (d, 1H, H^8), 7.69 (d, 1H, H^5), 7.23 (ddd, 1H, H^{10}), 6.83 (d, 1H, H^4) (see Scheme 1 for atom numbering) ppm.

The complex *cis*-$[Mo(CO)_4\{$ethyl[3-(2-pyridyl)-1-pyrazolyl] acetate$\}]$ (**2**) was prepared in 95% yield by using the procedure described above for **1**. Satisfactory elemental analyses were obtained, and the spectroscopic data (^1H NMR and FT-IR) were in agreement with those published in Ref. [14].

2.2. Preparation of the molybdenum oxide/pyrazolylpyridine catalysts

To prepare $[Mo_4O_{12}\{$2-[3(5)-pyrazolyl]pyridine$\}_4]$ (**3**), a solution of 5–6 M TBHP in *n*-decane (1.5 mL, 8.5 mmol) was added dropwise to a magnetically stirred suspension of **1** (0.30 g, 0.85 mmol) in dichloromethane (20 mL), and the mixture was stirred at room temperature for 4 h. The initially dark brown suspension turned violet during the first 15 min of reaction. After 4 h, a pale violet solid was isolated by filtration, washed several times with diethyl ether, and vacuum-dried. Yield: 0.20 g, 81%. Anal. calcd for $C_{32}H_{28}Mo_4N_{12}O_{12}$ (1156.40): C, 33.24; H, 2.44; N, 14.53; Mo, 33.18. Found: C, 33.42; H, 2.66; N, 14.10; Mo, 33.40. Selected IR (KBr, cm^{-1}): ν = 3420 (br), 3136 (w), 3112 (w), 1609 (s), 1568 (m), 1538 (w), 1521 (m), 1472 (m), 1448 (s), 1435 (s), 1371 (s), 935 (w), 921 (w), 849 (vs), 817 (vs), 778 (vs), 710 (w), 694 (w), 644 (w), 401 (s), 377 (m). ^1H NMR (300 MHz, 25 °C, DMSO-d_6): δ = 13.06 (br, 1H, NH), 8.58 (d, 1H, H^{11}), 8.0–7.7 (series of overlapping broad peaks and multiplets, 3H, $H^{5,8,9}$), 7.31 (t, 1H, H^{10}), 6.84 (d, 1H, H^4) ppm.

To prepare $[Mo_8O_{24}\{$ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate$\}_4]$ (**4**), a solution of 5–6 M TBHP in *n*-decane (1.2 mL, 6.8 mmol) was added dropwise to a magnetically stirred suspension of **2** (0.30 g, 0.68 mmol) in dichloromethane (20 mL), and the mixture was stirred at room temperature for 4 h. The initially dark brown suspension turned olive during the first 15 min of reaction. After 4 h, a pale brown solid was isolated by filtration, washed several times with diethyl ether, and vacuum-dried. Yield: 0.15 g, 85%. Anal. calcd for $C_{48}H_{52}Mo_8N_{12}O_{32}$ (2076.51): C, 27.76; H, 2.52; N, 8.09; Mo, 36.96. Found: C, 27.70; H, 2.96; N, 8.52; Mo, 36.20. Selected IR (KBr, cm^{-1}): ν = 3480 (br), 3122 (m), 1744 (s), 1612 (s), 1440 (s), 1374 (s), 1249 (m), 1221 (s), 943 (m), 908 (s), 844 (m), 776 (vs), 701 (m), 671 (vs). ^1H NMR (300 MHz, 25 °C, DMSO-d_6): δ = 8.58 (m, 1H, H^{11}), 7.91–7.79 (series of overlapping multiplets, 3H, $H^{5,8,9}$), 7.31 (ddd, 1H, H^{10}), 6.86 (d, 1H, H^4), 5.16 (s, 2H, NCH_2), 4.17 (q, 2H, CH_2CH_3), 1.22 (t, 3H, CH_2CH_3) ppm.



Scheme 1. Schematic representations of the tetranuclear compound **3** and the proposed structure of compound **4**.

2.3. Characterisation methods

Microanalyses for CHN and ICP-OES analysis for Mo were performed at the University of Aveiro. Powder X-ray diffraction (XRD) data were collected on a Philips X'pert MPD diffractometer equipped with an X'Celerator detector, a graphite monochromator (Cu-K_α X-radiation filtered by Ni (λ = 1.5418 Å)) and a flat-plate sample holder, in a Bragg-Brentano para-focusing optics configuration (40 kV, 50 mA). Samples were step-scanned in 0.04° 2θ steps with a counting time of 50 s per step. Transmission IR spectra 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