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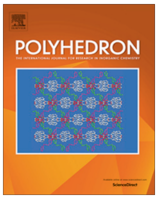

Oxidation of alkenes and sulfides catalyzed by a new binuclear molybdenum *bis*-oxazoline complex

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ABSTRACT

A novel *bis*(oxazoline) ligand derived from 1,3-dicyanobenzene was prepared and applied as a ligand for the preparation of a new binuclear molybdenyl complex. This ligand was characterized by UV–Vis, mass, ^{1}H NMR, and FT-IR spectroscopic methods, thermal and elemental analysis and X-ray diffraction. The molybdenum complex was prepared by the reaction of this ligand with $MoO_2(acac)_2$. The catalyst was also characterized by FT-IR, UV–Vis, and ICP spectroscopy, elemental and thermal analysis. This catalytic system was efficiently used for the oxidation of alkenes and sulfides in the presence of TBHP. The effect of different solvents and kind of oxygen donor was also studied in the oxidation reactions.

1. Introduction

The oxidation of organic substrates by transition metal complexes has become an important research area in both organic synthesis and bioinorganic modeling of oxygen transfer metalloenzymes. In the late 1960s, molybdenum complexes played a critical role in homogeneous industrial catalysis in the Arco and Halcon processes, involving the typical example of the industrial production of propylene oxide using alkyl hydroperoxides as oxidants, catalyzed by a homogeneous Mo(VI) (Scheme 1) [1].

Several oxomolybdenum(VI) complexes have recently been explored as catalysts for liquid-phase olefin epoxidation, usually employing *tert*-butyl hydroperoxide (TBHP) as the mono-oxygen source [2–4]. Partial oxidation of alkenes to epoxides and reaction products based on epoxides are both of academic and industrial interest. Different epoxides are among the most widely used intermediates in organic synthesis, pharmaceuticals together with polymer production, and act as precursors for complex molecules due to the strained oxirane ring [5]. They react to provide industrially essential products such as surfactants, detergents, antistatic agents and corrosion protection agents, lubricating oils, textiles and cosmetics [6].

Since the first report on the synthesis of sulfoxides by Marcker [7] in 1865, many processes for the conversion of sulfides to sulfoxides [8] using nitric acid [7], hydrogen peroxide [9], dinitrogen tetroxide [10], ozone [11], peracids [12], hydroperoxides [13] and many other reagentshave been developed. Sulfoxides and sulfones have found many applications in pharmacy [14,15] and other fields such as engineering plastics and polymers [16]. Oxidation of sulfides is the most direct approach for the synthesis of sulfoxides and sulfones [17]. Many different catalysts have been applied for oxidation of organic substrates but in order to make this process rapid, selective and consist of higher yields of products, the use of catalysts is mandatory. As a result of the apparent interest in the perfection of oxidation product synthesis, many explorations have been commenced to develop catalysts for oxidation, e.g. supported metal oxides [18,19] as well as homogeneous transition metal complexes [20,21]. Nevertheless, the reported methods rarely offer the ideal combination of simplicity of method and selectivity. Among all ligands used for example Schiff bases [22], porphyrins [23], and other ligands, metal complexes of the oxazoline ligand bearing a N–O coordination sphere have been reported [24,25] as one of the most efficient homogeneous catalysts. Their functions have grown quickly and a broad range of catalytic reactions has been described including oxidation, addition and reduction [26,27].

The aim of the present study is to find a highly active, selective, and stable catalyst, based on the oxazoline moiety that can be used under mild conditions.

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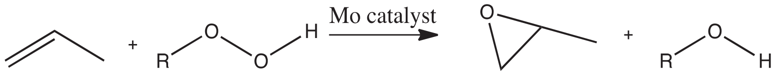
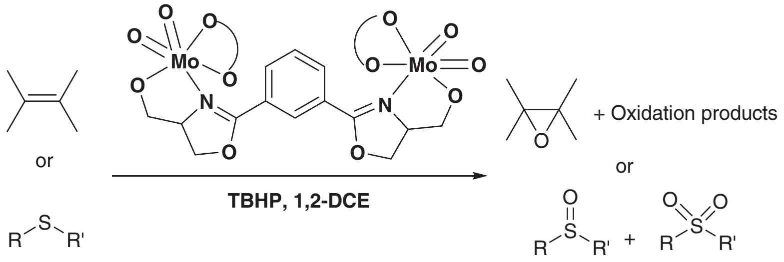


Scheme 1. Oxidation of propylene using alkyl hydroperoxides as oxidants, catalyzed by a homogeneous Mo(VI).



Scheme 2. Oxidation of alkenes and sulfides with TBHP catalyzed by $[Mo_2(O)_4BOX(acac)_2]$.

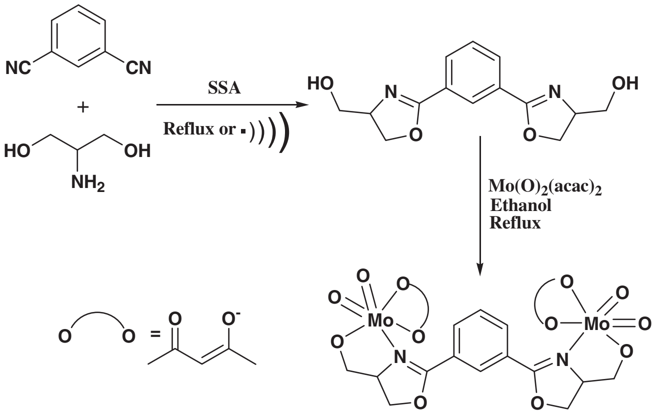
In this article, a novel binuclear molybdenum oxazoline compound was synthesized and used as a homogeneous and efficient catalyst for the epoxidation of olefins and oxidation of sulfides with *tert*-BuOOH (Scheme 2). The effect of different solvents, oxidants, and temperatures on the activity and selectivity of the catalyst was also studied.

2. Experimental

All materials and chemicals were of commercial reagent grade and prepared from Merck, Aldrich or Fluka chemical companies. Alkenes were obtained from Merck or Fluka and were passed through a column containing active alumina and/or silica to remove peroxide impurities. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using DMSO-d_6 as solvent. Elemental analysis was performed on a LECO, CHNS-932 analyzer. Thermogravimetric analysis (TGA) were carried out on a Mettler TG50 instrument under air flow at a uniform heating rate of 5 °Cmin^{-1} in the range 25–800 °C. FT-IR spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} by a JASCO 6300 spectrophotometer. Gas chromatography experiments (GC) were performed on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. UV–Vis spectra were obtained on a Shimadzu UV 265 spectrometer. The Mo content of the catalyst was determined by a Jarrell-Ash 1100 ICP analysis. Mass spectra were recorded by a Platform II spectrometer from Micromass, EI mode at 70 eV.

2.1. General procedure for ligand (BOX) synthesis

The novel *bis*-oxazoline ligand, BOX, was synthesized using our previously reported methods with slight modifications [28,29]. A mixture of 1,3-dicyanobenzene (4 mmol), 2-amino-1,3-propanediol (16 mmol) and silica sulphoric acid, SSA, (200 mg) was stirred at 100 °C for 3 days. The progress of the reaction was monitored by TLC (eluent:*n*-hexane/EtOAc, 2:1). After completion of the reaction, the mixture was cooled to room temperature and dissolved in methanol to remove the unreacted aminoalcohol. The mixture was filtered and the solid material was dissolved in hot methanol, and the *bis*-oxazoline light pink needle-like crystals were obtained by the slow evaporation of methanol. The same reaction was also carried out under ultrasonic irradiation as following: a mixture of 1,3-dicyanobenzene (4 mmol), 2-amino-1,3-propanediol (16 mmol) and SSA (200 mg) was exposed to ultrasonic irradiation for 3 h (6 discontinuous 30 min. exposures). The reaction progress was monitored by TLC (eluent:*n*-hexane/EtOAc, 2:1). The *bis*-oxazoline crystals were obtained as described above. Yield 91%; Mp 198 °C; Elemental *Anal.* Calc. for $C_{14}H_{16}N_2O_4$ (M_W = 276.29) C, 60.86; H, 5.84; N, 10.14. Found: C, 58.69; H, 6.23; N, 10.16%. Exact Mass: 276.11; *m*/*z*: 276.11 (100.0%), 277.11 (15.9%), 278.12 (1.9%).



Scheme 3. The synthesis route for BOX ligand and its Mo complex.

2.2. General procedure for synthesis of Mo complex

The *bis*-oxazoline was metallated as follows: a degassed ethanol solution (40 ml) of the corresponding *bis*-oxazoline (0.276 g, 1 mmol) was added to a solution of $Mo(O)_2(acac)_2$ (1 mmol, 0.326 g) in absolute ethanol (20 ml) under argon atmosphere. The reaction was stirred under reflux conditions for 24 h. The solution was then cooled, filtered and evaporated under reduced pressure. Dissolving this crude product in methanol and evaporation under reduced pressure for a second time, gave the pure product. Yield: (0.257 g, 35%, light green powder). Elemental analysis: *Anal.* Calc. for $C_{24}H_{28}Mo_2N_2O_{12}$ (M_W = 728.41): C, 39.57; H, 3.87; N, 3.85. Found: C, 39.45; H, 3.76; N, 4.15%.

2.3. General procedure for oxidation of alkenes with TBHP catalyzed by Mo BOX complex

In a round-bottom flask (25 mL) equipped with a reflux condenser, a gas inlet and a magnetic stirrer, a solution of alkene (1 mmol) in 1,2-dichloroethane (4 mL) was prepared. The molybdenum BOX complex (8 mg, 0.01 mmol, 0.02 mmol Mo) and TBHP (2 mmol) was added to this solution and the reaction mixture was