Polyhedron 72 (2014) 19-26

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

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



POLYHEDRON

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ARTICLE INFO

Article history: Received 16 November 2013 Accepted 4 January 2014 Available online 11 January 2014

Keywords: Bis(oxazoline) Molybdenum(VI) complex Epoxidation Sulfoxidation

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, ¹H 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 MoO₂(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.

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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]. [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].

Since the first report on the synthesis of sulfoxides by Marcker

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 [Mo₂(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. ¹H 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 $5 \,^{\circ}\text{Cmin}^{-1}$ in the range 25–800 °C. FT-IR spectra were obtained as potassium bromide pellets in the range of $400-4000 \text{ cm}^{-1}$ 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



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

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%).

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



Fig. 1. (a) The crystal structure and (b) crystal packing for *bis*(oxazoline) ligand.

Table 1		
Epoxidation of alkenes with TBHP	catalyzed by [Mo ₂ (O) ₄ BOX(acac) ₂] in	refluxing 1,2-dichloroethane.

Row	Substrate	Product	Conversion (%) ^b	Epoxide yield (%)	Time (h)	TON	TOF (h^{-1})
1		ο	100	100	3	50	16.7
2		O OH	87	50	8	43.5	5.4
3			100	(1,2-epoxide) 83 (8,9-epoxide) 17	6	50	8.3
4	$\frown \frown \frown \frown$		53	53	10	26.5	2.7
5	$\checkmark \checkmark \checkmark \land \land \land$		44	44	10	22	2.2
6			30	30	10	15	1.5
7			18	18	10	9	0.9

^a Reaction conditions: Alkene (1 mmol), TBHP (2 mmol), catalyst (0.01 mmol, 0.02 mmol Mo), 1,2-dichloroethane (4 mL).

^b GC yield based on the starting alkene.

stirred under reflux conditions. The reaction progress was monitored by GC. After completion of the reaction, the mixture was directly passed through a short column of silica-gel (1:1, *n*-hexane–ethyl acetate) to remove the catalyst. The elute was evaporated under reduced pressure and the remaining residue was purified by silica-gel plate chromatography (eluted with $CCl_4:Et_2O = 9:1$) to afford the corresponding epoxide.

2.4. General procedure for oxidation of sulfides with TBHP catalyzed by Mo BOX complex

In a 25 mL round-bottom flask equipped with a magnetic stirring bar, a solution of sulfide (1 mmol), catalyst (6 mg, 0.008 mmol, 0.016 mmol Mo) in 1,2-dichloroethane (4 mL) was prepared. TBHP (2 mmol) was added to this solution and the reaction mixture was



Fig. 2. Optimization of the catalyst amount in the oxidation of cyclooctene with TBHP catalyzed by $[Mo_2(O)_4BOX(acac)_2]$.



Fig. 3. The effect of various oxidants in the oxidation of cyclooctene with TBHP catalyzed by $[Mo_2(O)_4BOX(acac)_2]$.

stirred under reflux conditions. The reaction progress was monitored by TLC. After the reaction was completed, the isolation and purification of the products were done as described above.

3. Results and discussion

3.1. Preparation and characterization of the BOX ligand

The synthetic route for ligand, [2,2'-(1,3-phenylene)*bis*(4,5-dihydrooxazole-4,2-diyl)]dimethanol, is shown in Scheme 3.

This ligand was characterized by elemental analysis, FT-IR, ¹H NMR and UV-Vis spectroscopic methods. All data was in agreement with the structure of the synthesized ligand. Initial evidence of the ligand is shown in the FT-IR spectra (Fig. S1). The very sharp band at 2234 cm⁻¹, relating to $v(C \equiv N)$ disappears upon ligand synthesis. ¹H NMR (Fig. S2) also confirmed the identity of the desired ligand. ¹H NMR (400 MHz, DMSO- d_6) δ = 8.34 (t, ⁴ J_{H-H} = 1.6 Hz, 1H), 7.94 (dd, ${}^{4}J_{H-H} = 1.6$ Hz, ${}^{3}J_{H-H} = 7.6$ Hz, 2H), 7.55 (t, ${}^{3}J_{\text{H-H}}$ = 7.6 Hz, 1H), 4.84–4.80 (m, 2H, 2 × CHN=C), 4.45–4.29 (m, 4H, $2 \times CH_2O$), 3.56–3.31 (m,4H, $2 \times CH_2OH$). TG and DTG data show that this ligand decomposes at about 400 °C (Fig. S3). This ligand shows two absorption peaks in ethanol at λ_{max} 224 and 250 nm (Fig. S4). The structure of this ligand was also confirmed by X-ray crystallography. The crystal structure of the ligand (CCDC 926630) along with its crystal packing is shown in Fig. 1 (Also see Tables S1, S2, and S3). The number of molecules in the unit cell is 2



Fig. 4. The effect of various solvents in the oxidation of cyclooctene with TBHP catalyzed by $[Mo_2(O)_4BOX(acac)_2]$.



Fig. 5. The effect of temperature on the oxidation of cyclooctene with TBHP catalyzed by $[Mo_2(O)_4BOX(acac)_2]$.

and the space group of the ligand is C_2 . In the absence of sufficient anomalous dispersion (the absence of element heavier than Si in case of normal sealed tube Mo X-ray radiation) the absolute structure of the compound could not be determined by Mo X-ray radiation so the total 580 Friedel pairs were merged.

3.2. Preparation and characterization of the molybdenum oxazoline complex

The prepared catalyst was characterized by elemental analysis, FT-IR and UV–Vis spectroscopic methods. The FT-IR spectrum of homogeneous [Mo₂(O)₄BOX(acac)₂] (Fig. S5 shows a band at 1642 cm⁻¹ for *v*(C=N), and two bands at 945 and 906 cm⁻¹ attributed to the *v*(Mo=O) bonds. ¹H NMR (400 MHz, DMSO-*d*₆) δ = 8.31–7.52 (m, 6H, 4CH_{arom}, 2 × CH₃COCHCOCH₃), 4.68 (m, 4H, 2 × CH₂O), 4.00–3.98 (m, 4H, 2 × CH₂O), 3.35 (br, m,12H, 2 × CH₃COCHCOCH₃), 2.08–1.91 (m, 2H, 2 × CH–N).

As seen in Fig. S7, the $[Mo_2(O)_4BOX(acac)_2]$ shows a peak at $\lambda_{max} = 310$ nm which is attributed to the $O(p_\pi) \rightarrow Mo(d_\pi)$ charge-transfer transition [30].

TG and DTG data show that this complex decomposes at about 220 $^{\circ}$ C (Fig. S8). This is in accordance with the data obtained from melting point studies.

According to the ICP and CHN analyses, the ratio between Mo and the ligand was 2.07 that confirm that the catalyst consists of two molybdenum metals and is therefore binuclear.

Table 2

Comparison of the results obtained for epoxidation of cyclooctene catalyzed by [Mo₂(O)₄BOX(acac)₂] with some previously reported molybdenum systems.

Entry	Catalyst	Support	Oxidant	Conditions (°C)/Solvent	TOF (h^{-1})	Refs.
1	Mo ₂ O ₄ (acac) ₂ BOX	None	TBHP	Reflux/DCE	16.7	This work
2	$[MoI_2(CO)_3(trpH)]$	None	TBHP	55/DCE	9	[31]
3	[MoI ₂ (CO) ₃ (pheH)]	None	TBHP	55/DCE	2	[31]
4	HT-trp-Mo	Amino acid intercalated clay materials HT–trp)	ТВНР	55/DCE	10	[31]
5	HT-phe-Mo	Amino acid intercalated clay materials HT-phe)	ТВНР	55/DCE	17	[31]
6	$MoO_2(acac)_2$	Silica	TBHP	Reflux/DCE	16.0	[32]
7	$MoO_2(acac)_2$	MCM-41	TBHP	Reflux/DCE	15.5	[33]
8	$MoO_2(acac)_2$	MCM-41	TBHP	Reflux/DCE	14.7	[34]
9	MoO ₂ [1,2-diphenylethylene <i>bis</i> (3-oxyethylpyrrole)salicylideneiminate]	None	TBHP	Reflux/DCE	5	[35]



Fig. 6. Optimization of the catalyst amount in the oxidation of diphenyl sulfide with TBHP catalyzed by [Mo₂(O)₄BOX(acac)₂], along with the ratios of products formed.



Fig. 7. The effect of various solvents in the oxidation of diphenyl sulfide with TBHP catalyzed by [Mo₂(O)₄BOX(acac)₂].



Fig. 8. Time interval for the oxidation of diphenylsulfide with various TBHP amounts in 20 min.

3.3. Catalytic alkene epoxidation with TBHP catalyzed by [Mo₂(O)₄BOX(acac)₂]

In order to find the optimized conditions, cyclooctene was used as a model substrate using *tert*-BuOOH as an oxidant and in the presence of catalytic amounts of $[Mo_2(O)_4BOX(acac)_2]$. The optimum conditions used for the oxidation of cyclooctene by this catalytic system was catalyst, substrate, and oxidant in a molar ratio of 1:100:200, respectively (Table 1). In this reaction cyclooctene oxide was produced with 100% selectivity.

First, we optimized the catalyst amount in the oxidation of cyclooctene. The results showed that when 0.01 mmol (8 mg) of catalyst was used in the oxidation of cyclooctene with 2 mmol of TBHP, the highest yield was obtained. Whereas trace amounts of products (10%) was detected when the same reaction was carried out in the absence of catalyst (Fig. 2).

The effect of different oxidants such as H_2O_2 , $NaIO_4$, *tert*-BuOOH and H_2O_2 /urea (UHP) was also investigated in the oxidation of cyclooctene. The results showed that *tert*-BuOOH is the best oxygen source (Fig. 3).

Different solvents were also used in the oxidation of cyclooctene with *tert*-BuOOH and amongst them, 1,2-dichloroethane gave the most conversion (Fig. 4).

The reaction temperature was also optimized by repeating the reaction in various temperatures. At room temperature ($25 \,^{\circ}$ C), the product yields were low and with increasing the reaction temperature better results and higher yields were obtained (Fig. 5).

Under the optimized reaction conditions, different alkenes including cyclic and linear ones were oxidized by this catalytic

Table 3

Sulfide oxidation with TBHP catalyzed by [Mo₂(O)₄BOX(acac)₂] in refluxing 1,2-dichloroethane.^a

Row	Sulfide	Time (min)	Conversion (%) ^b	Product ^a		TOF (h^{-1})
				Sulfoxide (%)	Sulfone (%)	
1	NO ₂	5 60	55 95	5 0	50 95	412.5 59.4
2	CH ₃	5 30	100 100	95 70	5 30	750.0 125.0
3	SCH3	10 15	95 100	95 95	0 5	356.3 250.0
4	но С S ОН	5 20	90 100	90 0	0 100	675.0 187.5
5	s s	30 60	95 100	75 0	20 100	118.8 62.5
6	S S	45 90	100 100	75 20	25 80	83.3 41.7
7	S√S√S	5	100	90	10	750.0
8	CH ₃	5 30	100 100 100	100 10	0 90	750.0 125.0
9	s s	10	100	100	0	375.0
10	∕S	35 5 30	100 100 100	0 100 0	0 100	107.1 750.0 125.0
11	S S	20 45	65 100	60 30	5 70	121.9 83.3

^a Reaction conditions: sulfide (1 mmol), TBHP (2 mmol), catalyst (0.008 mmol, 0.016 mmol Mo), 1,2-dichloroethane (4 mL).

^b GC yield based on the starting sulfide.

system. As can be seen in Table 1, both cyclic and linear alkenes were converted to their corresponding epoxides with TBHP in the presence of $[Mo_2(O)_4BOX(acac)_2]$ catalyst. In this catalytic system, cyclooctene was completely converted to its corresponding epoxide with 100% selectivity. In the epoxidation of styrene, the major product was styrene oxide (50%) and about 37% benzaldehyde was also produced. This catalytic system exhibits a promising regioselectivity in the epoxidation of (R)-(+)-limonene. The ratio among 1,2- and 8,9-epoxides was found to be 4.88. In the case of linear alkenes such as 1-heptene, 1-octene, 1-decene and 1-dodecene, the corresponding epoxides were obtained in good to high yields with 100% selectivity.

The results obtained with this catalytic system were compared with some of those reported in the literature (Table 2). As can be seen, this catalytic system is an efficient system in the epoxidation of alkenes.

3.4. Oxidation of sulfides with tert-BuOOH catalyzed by [Mo₂(O)₄BOX(acac)₂]

The reaction conditions were also optimized in the oxidation of sulfides with TBHP in which diphenyl sulfide was used as a model substrate. In the optimization of catalyst amount, the best results were obtained when 0.008 mmol (6 mg, 0.016 mmol Mo) of catalyst was applied with 2 mmol of TBHP after 20 min. Under these conditions, the conversion was 81% and the sulfoxide to sulfone ratio was 4.4. No better results were obtained when higher amounts of catalyst were used. When the reaction was continued for 45 min, the amount of sulfoxide decreased to 30% and the amount of sulfone reached to 70%. Trace amounts of the products were detected when the same reaction was carried out in the absence of catalyst (Fig. 6).

In order to choose the reaction media, different solvents were also tested and 1,2-dichloroethane was chosen as solvent because of the higher amount of sulfoxide was produced (Fig. 7).

Various TBHP molar amounts were also tested. The results showed that when 2 mmole of the oxidant were used, the highest yields of sulfoxide were obtained (Fig. 8).

This catalytic system is extremely efficient and catalyzes the oxidation of a wide range of sulfides and the sulfoxide and sulfone are produced using catalyst, substrate, and oxidant in a molar ratio of 1:125:250, respectively. The results are summarized in Table 3. Most sulfides were completely converted to their products. In all cases, two different reaction times are reported. In the cases of benzyl-4-methylbenzyl sulfide and 4-phenylthiobenzyl alcohol, the reaction favors sulfoxide formation over the sulfone, even after long reaction times. Among the sulfides used, 2-hydroxylethylphenyl sulfide, benzothiophen, dibenzothiophen, diallyl sulfide, methylphenyl sulfide, dibutyl sulfide, dipropyl sulfide, and diphenyl sulfide are selective towards the corresponding sulfoxide in short reaction times. However, when the reaction times are increased, the selectivity changes and more sulfone is observed. This is very interesting concerning the fact that the selectivity can be changed by altering the reaction time. For example, in the case of dipropyl sulfide, stopping the reaction at 5 min gives 100% conversion to the corresponding sulfoxide. Conversely, continuing the reaction up to 30 min gives 100% transformation to the equivalent sulfone. In the case of 4-nitrobenzyl-4-methylphenyl sulfide, the progress of the reaction favors sulfone production over sulfoxide production. On the basis of the previously reported mechanisms, it seems that the oxidation of sulfides and sulfoxides with peroxides proceeds by a one-step oxygen-transfer mechanism with the simultaneous electrophilic attack of the sulfur on the peroxide and the breaking of the O-O bond and formation of the S=O bond [36]. Electronwithdrawing groups such as NO₂ increase the electrophilicity of the corresponding sulfoxide and consequently the tranquil attack of the peroxide to the sulfoxide sulfur ultimately facilitates the formation of the sulfone. However electron-donating groups, e.g. CH₃ tend to favor the first step and form the consistent sulfoxide.

4. Conclusion

In summary, we synthesized a new binuclear molybdenum complex and demonstrated its high catalytic activity in the selective oxidation of various alkenes and sulfides under homogeneous conditions using TBHP as the terminal oxidant. The excellent chemoselectivity of this complex towards alkenes and the sulfur group, as well as the high yields makes it a good choice for oxidation.

Acknowledgments

We gratefully acknowledge The University of Isfahan Council of Research for the support of this work. The authors also thank Dr. Reza Kia for his valuable helps.

Appendix A. Supplementary data

The data corresponding to the FT-IR, ¹H NMR, TG-DTG, and electronic absorption data of the BOX ligand are provided (Figs. S1, S2, S3, and S4). The data corresponding to the FT-IR, TG-DTG, and electronic absorption data of the molybdenum complex are provided (Figs. S5, S6, S7, and S8). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2014.01.004.

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