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Synthesis, Crystal Structure, and Catalytic Properties of Novel Dioxidomolybdenum(VI) Complexes with Tridentate Schiff Base Ligands in the Biomimetic and Highly Selective Oxygenation of Alkenes and Sulfides

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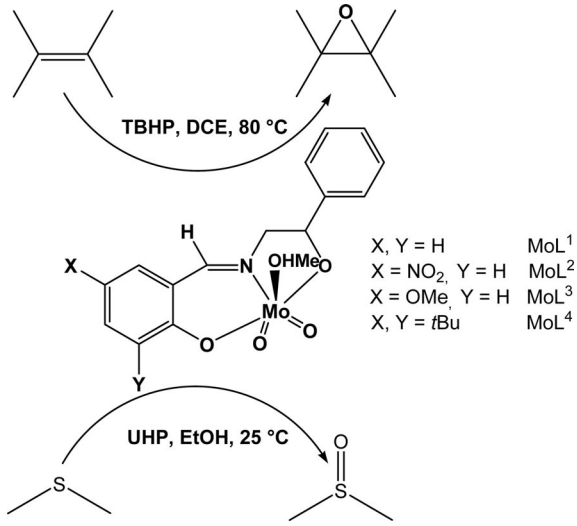
Keywords: Molybdenum / Oxido ligands / Peroxides / Oxygenation / Schiff bases / Epoxidation

Four novel dioxidomolybdenum(VI) complexes $[MoO_2(L^x)(CH_3OH)]$ have been synthesized, using 2[(*E*)-(2-hydroxy-2-phenylethylimino)methyl]phenol derivatives as tridentate ONO donor Schiff base ligands (H_2L^x) and $MoO_2(acac)_2$. A monoclinic space group was determined by X-ray crystallography from single-crystal data of a sample of these new complexes. The epoxidation of alkenes by using *tert*-butyl hydroperoxide and oxidation of sulfides to sulfoxides by urea hydrogen peroxide were efficiently enhanced with excellent selectivity under the catalytic influence these new Mo^{VI} complexes. The high efficiency and relative stability of the catalysts have been observed by turnover numbers and UV/Vis investigations. The electron-poor and bulky ligands promoted the effectiveness of the catalysts.

Introduction

The desire to construct biomimetic oxidation catalysts has prompted an extensive area of research into biologically important molybdenum complexes with various synthetic ligands.[1] In this context, dioxidomolybdenum(VI) complexes have been extremely investigated,[2] particularly with respect to the catalytic role of transferase enzymes like nitrate reductase, in which their active sites consist of a *cis* molybdenum dioxido moiety.[3] The ability of molybdenum to form stable complexes with oxygen-, nitrogen-, and sulfur-containing ligands led to the development of molybdenum Schiff base complexes that are efficient catalysts in both homogeneous and heterogeneous reactions.[4] The activity of these complexes varied markedly with the types of ligands and coordination sites.[4,5] In continuation of our ongoing research on the development of biomimetic oxidation reactions,[6] very recently we introduced a (dioxido)-Mo^{VI} Schiff base complex as an efficient and selective catalyst for the oxidation of sulfides to sulfoxides and sulfones.[7] Now, we wish to introduce four novel dioxidomolybdenum(VI) Schiff base complexes containing simple and easy-to-prepare asymmetric ONO tridentate ligands based on 2[(*E*)-(2-hydroxy-2-phenylethylimino)methyl]phenol and evaluate their catalytic activity in the oxygenation of alkenes to epoxides and sulfides to sulfoxides (Scheme 1) by using *tert*-butyl hydroperoxide (TBHP) and urea hydrogen peroxide (UHP) both of which are industrially and environmentally important oxidants.[8] The selective epoxidation of olefins and sulfoxidation of thioethers are particular challenging problems in organic synthesis, leading to a great interest in new and more efficient catalytic versions for these reactions.[9] We also report the crystal structure of a sample of these molybdenum complexes (MoL^3, Scheme 1) determined by single-crystal X-ray diffraction.



Scheme 1. Oxygenation of alkenes and sulfides catalyzed by different Mo^{VI}–Schiff base complexes utilized in this study.

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Results and Discussion

Structural Discussion of (Dioxido)Mo^{VI} Complexes

Dioxidomolybdenum complexes (MoL^1–MoL^4) were prepared by the reaction of 2[(*E*)-(2-hydroxy-2-phenylethylimino)methyl]phenol derivatives (Scheme 1) and dioxidomolybdenum(VI) acetylacetonate,[10] and these complexes were characterized by elemental analysis, IR, NMR, and UV/Vis spectroscopy, and mass spectrometry (Supporting Information, Scheme S1). The Schiff base ligand is bonded to the MoO_2^{+2} ion through two phenolic oxygen atoms and an imine nitrogen atom *trans* to an oxido group in a meridional arrangement. For example, the IR spectra of MoL^3 in KBr matrix confirm the presence of an imine bond (C=N) at 1638 cm^{-1}, the C=C vibration band of the aromatic ring at 1476 cm^{-1}, and Mo–O vibration bands at 909 and 920 cm^{-1}. The ORTEP plot of MoL^3 with relevant bond lengths and angles is given in Figure 1. The O=Mo=O angle is 106.36° and the Mo=O distances are 1.707 and 1.699 Å. According to the spectroscopic data and also the molecular structure, which was determined for MoL^3 by crystal data, a methanol molecule is coordinated to the Mo^{VI} central metal. The Mo–O–C angle and Mo–O distance for Mo–$OHCH_3$ in MoL^3 are 125.94° and 2.3877 Å, respectively. The crystal packing diagram (Figure 2) shows the formation of the O–H···O hydrogen bonded centrosymmetric dimer. The electronic spectra of the H_2L^3 ligand (λ_{max} = 345 nm) and the MoL^3 complex (λ_{max} = 285 nm) are shown in Figure 3.

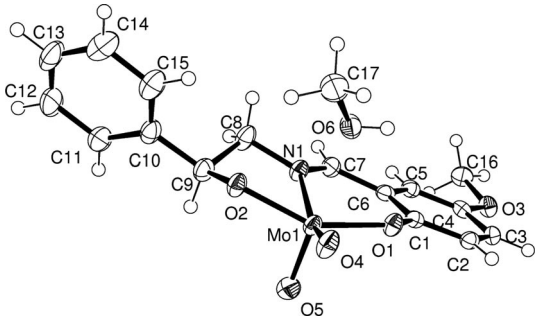


Figure 1. A view of the molecular structure of MoL^3, showing the numbering scheme and displacement ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Mo1–O1 1.9520(16), Mo1–O2 1.9213(16), Mo1–O4 1.707(2), Mo1–O5 1.6992(16), Mo1–O6 2.3877(17), Mo1–N1 2.268(2), N1–C7 1.282(3), N1–C8 1.457(3), O1–C1 1.342(3), O2–C9 1.425(3), O3–C4 1.383(3), O3–C16 1.432(3); O4–Mo1–O5 106.36(9), O4–Mo1–O6 85.66(8), O1–Mo1–O2 150.19(6), O1–Mo1–O4 99.79(7), O1–Mo1–O5 98.18(8), O2–Mo1–O4 97.47(7), O2–Mo1–O5 100.04(8), O1–Mo1–N1 80.30(7), O2–Mo1–N1 75.21(7), Mo1–O6–C17 125.94(16), O2–Mo1–O1–C1 –61.9(2), O4–Mo1–O1–C1 173.6(2), O5–Mo1–O1–C1 65.3(2), N1–Mo1–O2–C9 28.58(15), C16–O3–C4–C5 6.5(3), C8–C9–C10–C15 –77.9(3).

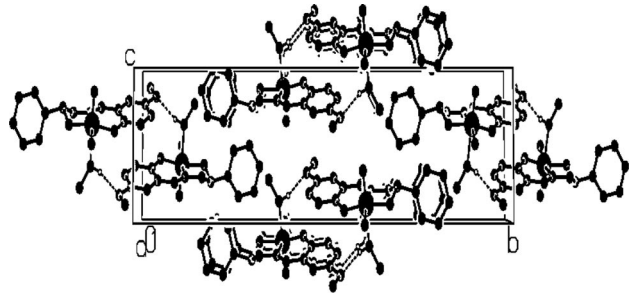


Figure 2. Crystal packing of MoL^3 viewed down the *b* axis, showing the formation of the O–H···O hydrogen bonded centrosymmetric dimer (hydrogen bonds are shown as dashed lines).

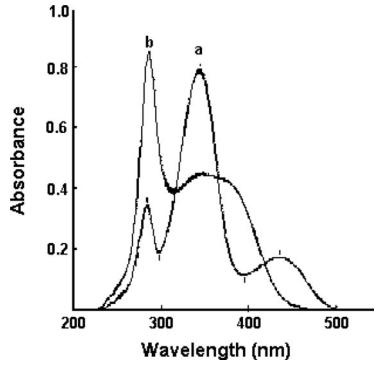


Figure 3. Electronic spectra of H_2L^3 (a) and MoL^3 (b) in methanol.

Catalytic Epoxidation of Alkenes

The oxidation of cyclooctene by using TBHP, which did not proceed in the absence of catalyst under mild and reflux conditions, was used as a model reaction. To find optimum reaction conditions, the influence of different factors that may affect the conversion and selectivity of the reaction was investigated. A systematic examination of cyclohexene oxidation in various solvents was performed in the presence of 1 mol-% of the simple MoL^1 (Scheme 1) catalyst at different temperatures. Considering the yield and reaction time, dichloroethane (DCE) was found to be the best reaction solvent; however, completion of the reaction required a temperature of 80 °C (Table 1). The poorer yields obtained with CH_2Cl_2 and $CHCl_3$ is probably caused by the lower reaction temperature at their reflux conditions.

Different catalyst/alkene molar ratios have been used in the oxidation of cyclooctene for different reaction times (Figure 4). It was observed that oxidation of cyclooctene required 45 min for completion with the use of 1 mol-% of the catalyst and an increase in this ratio up to 5 mol-% did not affect noticeably the reaction rate (Figure 4).

The examination of various molar ratios of TBHP/alkene in the catalytic oxidation of cyclooctene in DCE showed that full oxidation of the starting material was obtained by two equivalents of TBHP (Figure 5).

The influence of axial nitrogenous bases having dramatic effects on the rate and selectivity in the oxidation reaction catalyzed by various transition-metal complexes such as

Table 1. The influence of the nature of the solvent on the epoxidation of cyclooctene by using TBHP catalyzed by MoL[1].[a]

Solvent	% yield of epoxide[b] (T, °C)[c]
CH_3CN	0
$(CH_3)_2CO$	0
C_2H_5OH	0
CH_2Cl_2	35
$CHCl_3$	76
DCE	5 (30), 60 (60), 100 (80)

[a] The molar ratio of cyclooctene/TBHP/catalyst was 100:200:1. [b] GC yield based on the starting alkene after 45 min. [c] The reactions were run in air under reflux except for DCE, which was performed at different temperatures.

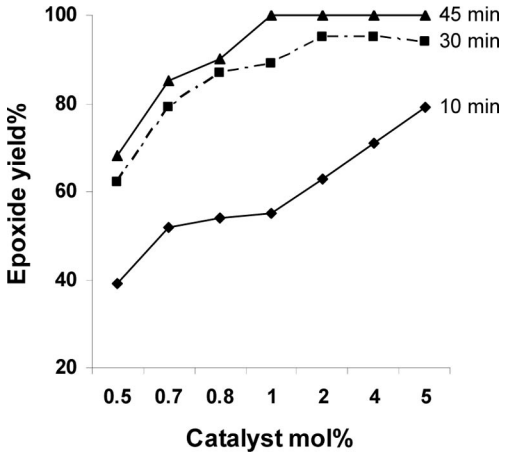


Figure 4. The influence of catalyst concentration on the reaction rate and yield of cyclooctene epoxide.

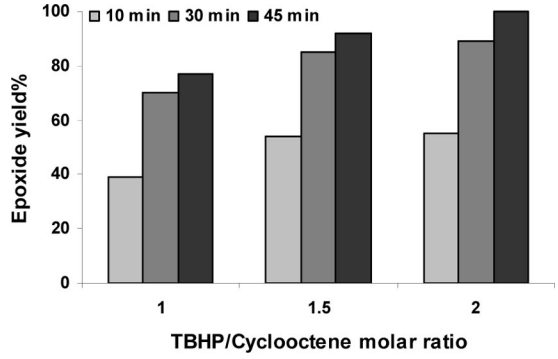
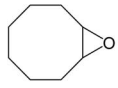
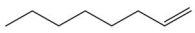
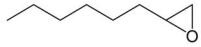
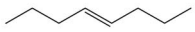
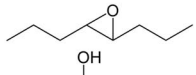
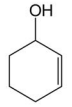
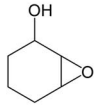
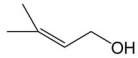
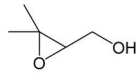
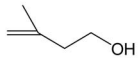
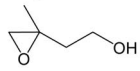
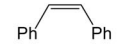
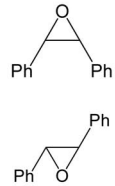
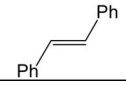
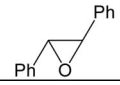


Figure 5. The influence of TBHP/alkene molar ratio on the reaction rate and yield of cyclooctene epoxide.

porphyrin[11] and salen catalysts[12] has also been studied. However, the addition of imidazole to this catalytic system retarded significantly the oxidation of cyclooctene (12% yield after 45 min).[13] Under the optimized conditions (100:200:1 molar ratio for alkene/TBHP/catalyst in DCE at 80 °C), cyclooctene converted completely within 45 min and 95% of epoxide product was secured as the sole product.

In order to establish the general applicability of the method, various alkenes were subjected to the oxidation protocol under the influence of the MoL[1] catalyst (Table 2). As summarized in Table 3, different alkenes are generally excellent substrates for this catalyst (Table 2, entries 1–11). It led to complete conversion of cyclohexenes, cyclooctene, and norbornene with the formation of the corresponding epoxides as the sole products. Inspection of the results in Table 2 indicates several useful features of this catalytic method. The least reactive aliphatic terminal and nonterminal alkenes were oxidized in desired times in high/excellent yields and excellent selectivities (Table 2, Entries 5 and 6). The chemoselectivity of the procedure was notable. The oxidative hydroxy group was tolerated under the influence of this catalytic system and the corresponding epoxide was obtained in 100% selectivity (Table 2, Entries 7–9). A novel feature of this simple catalytic method is its excellent stereoselectivity. Complete retention of configuration in the epox-

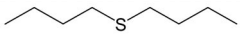
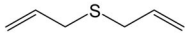
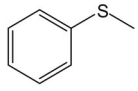
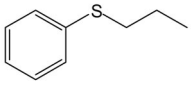
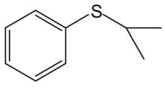
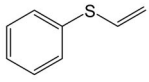
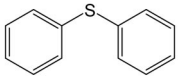
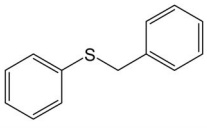
Table 2. Epoxidation of alkenes by using TBHP catalyzed by MoL[1] in DCE.[a]

Entry	Alkene	Conversion (%)[b]	Product[c]	Selectivity (%)[b]
1		100		100
2		100		100
3		68 (5 min) 85 (20 min) 94 (30 min) 100 (45 min)		100
4		100		100
5		91		100
6		100		100
7		100		100
8		64		100
9		100		100
10		100[d]		>98[d] <2[d]
11		83[d]		100[d]

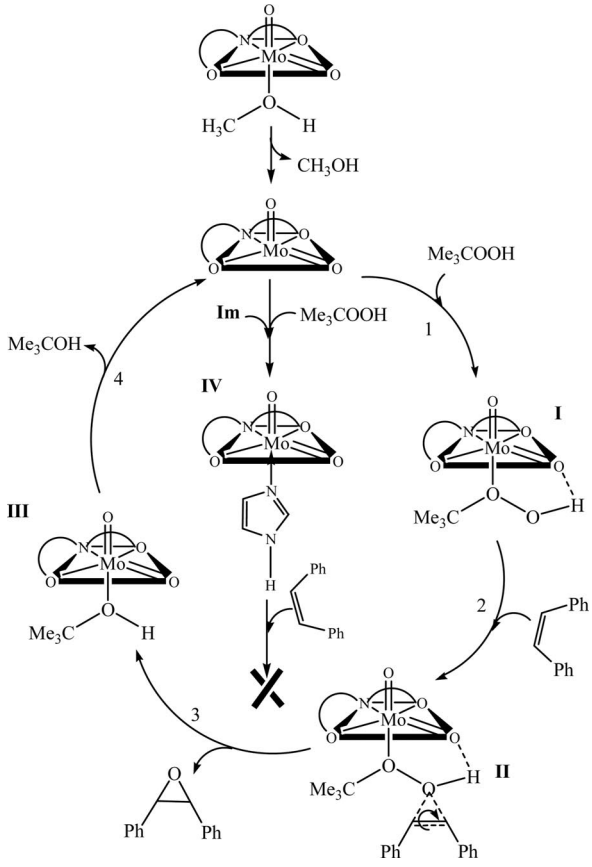
[a] The reactions were run for 45 min in air in DCE at 80 °C with a molar ratio of alkene/TBHP/catalyst, 100:200:1. [b] Conversions and selectivities were determined by GC based on the starting alkenes. [c] All products were identified by their IR, ^{1}H NMR, and GC–MS spectroscopic data in comparison with authentic samples. [d] Determined by ^{1}H NMR spectroscopy.

idation of *trans*-stilbene and excellent stereoselectivity in the oxidation of *cis*-stilbene (>98%) were obtained (Table 2, Entries 10 and 11). Although the mechanism of epoxidation of alkenes is still controversially discussed, the ideas of Sobczak[14] may be accepted on the basis of structural analogy of the catalyst (Scheme 2). According to this suggested mechanism the second stage of process is the interaction between the alkene and the TBHP molecule, activated in the coordination sphere of the molybdenum complex (Scheme 2, **I**). The Lewis acidity of the Mo center increases the oxidizing power of the peroxido group and the alkene is subsequently oxygenated by nucleophilic attack on an electrophilic oxygen atom of the coordinated peroxide.[15] Spectroscopic and computational methods applied to molybdenum dioxido and oxidodiperoxido complexes support a reaction mechanism involving an activation state formed between the complex, oxidant, and alkene (Scheme 2, **II**).[16,17] In this process, in higher conversions, *tert*-butyl alcohol can compete with TBHP for coordination to the molybdenum center, forming a less reactive species (Scheme 2, **III**) that leads to the decreasing reaction rate.[16] Similarly, for complex MoL^1, the initial reaction rates were much higher than those observed later in the reactions (Table 2, Entry 3). This suggestion may be supported by addition of a strong π-donor imidazole ligand to the reaction containing the MoL^1 complex, making it a sluggish catalyst for epoxidation of cyclooctene (12% conversion after 45 min at 80 °C). Presumably, imidazole forms an inactive species (Scheme 2, **IV**) by coordinating to the molybdenum ion,[13] and/or interference with the catalytic cycle by forming a hydrogen bond with TBHP and stabilizing the wrong species.[18]

Table 3. Oxidation of various sulfides by UHP catalyzed by MoL^1 in ethanol.[a]

Entry	Sulfide	Conversion (%)[b]	Selectivity (%)[b,c]	
			Sulfoxide	Sulfone
1		>98	100	0
2		100	100	0
3		96	100	0
4		95	97	3
5		90	100	0
6		94	98	2
7		78	94	6
8		88	98	2

[a] The reactions were run in air at room temperature with a molar ratio of sulfide/UHP/catalyst, 100:100:1. [b] Conversions and yields were measured by GC based on the starting sulfides after 10 min for Entries 1 and 2 and 35 min for all others. [c] All products were identified by their IR, ^{1}H NMR, and GC–MS spectroscopic data in comparison with authentic samples.



Scheme 2. Suggested mechanism of *cis*-stilbene epoxidation with TBHP catalyzed by MoL^x complexes.

The excellent stereoselectivity obtained in the oxidation of *cis*-stilbene indicates that the closure of the epoxide ring occurs faster than the rotation around the C–C bond during the oxygen transfer step from the active oxidizing species to the alkene (Scheme 2, **II**).

Catalytic Oxidation of Sulfides to Sulfoxides

On the basis of the promising results obtained in the previous report on green oxidation of sulfides catalyzed by $[MoO_2(L)(CH_3OH)]$ using UHP in ethanol,[7] we evaluated the sulfoxidation activity of these new Mo^{VI} catalysts in the oxidation of thioanisole, which did not proceed in the absence of a catalyst. Performing the reaction in the presence of 1 mol-% of MoL^1 by using an equimolar ratio of UHP and sulfide in ethanol under mild conditions afforded the related sulfoxide as the sole product in excellent yield (>96%) within 35 min. It should be mentioned that the use

of dried ethanol as the reaction media decreases the selectivity of sulfoxide (86%) and the conversion rate was not affected. Encouraged by the excellent catalytic performance for the thioanisole oxidation to sulfoxide, different sulfides were subjected to the reaction system in the presence of MoL^1 and the results are listed in Table 3. All substrates could be smoothly converted into sulfoxides with high to excellent conversion rates, and excellent selectivities were obtained under mild conditions. The highest yields were obtained for dialkyl and diallyl sulfide (98–100%) after 10 min. Replacement of one or both alkyl or aryl groups with a phenyl or benzyl group enhanced the reaction times (35 vs. 10 min); however, no regular trends in electronic and steric requirements have been observed. A salient feature of the present sulfoxidation system is its excellent selectivity. Sulfoxides could be nearly stoichiometrically produced and the generation of the corresponding sulfones was well controlled, which makes this process a good alternative for sulfoxide production. Also, a sulfide having a carbon–carbon double bond (Table 3, Entries 2 and 6) was cleanly transformed into the corresponding sulfoxide in excellent yield. In addition, benzyl phenyl sulfide (Table 3, Entry 8) was selectively oxidized to its corresponding sulfoxide without formation of any benzylic oxidation byproducts.

It is noteworthy that the easy preparation method of the catalyst offered ready scalability. Performing the oxidation reaction with the use of 100 mmol of thioanisole as substrate gave 89% of the related sulfoxide after purification over silica chromatography, eluting with *n*-hexane/ethyl acetate (10:3).

Activity and Stability of (Dioxido)Mo^{VI} Complexes

The high/excellent yields of epoxides (64–100%) and sulfoxides (78–100%) obtained by using these new catalytic methods in relatively short times (10–45 min) display the superior catalytic activity of the present (dioxido)Mo^{VI} complexes.[4] More evidence in this matter have been obtained by determining the turnover numbers (TON) of the MoL^1 catalyst in the oxidation of sulfides by UHP and alkenes by TBHP by using a 5000:10000:1 molar ratio for substrate/oxidant/catalyst. The impressive turnover frequency (TOF = 1640/h) and turnover number (TON ≈ 5000/24 h) obtained in the oxidation of thioanisole by using UHP indicate the high efficiency and relative stability of the catalyst, respectively. This was further supported by the study of the electronic spectra of the complex in the oxidation of thioanisole (Figure 6). The intensity of the characteristic absorption band at 287 nm remains approximately unchanged during a 1-h reaction time, indicating the high stability of the Mo catalyst under the oxidation reaction conditions. The initial decrease in the intensity upon addition of the oxidant may be attributed to the formation of active species in the oxidation reaction (Supporting Information, Figure S1).[19] However, the lower TOF (1250/h) and TON (4700/24 h) observed in the oxidation of less reactive norbornene by using TBHP can be related to some competing destruction of the catalyst, as confirmed by UV/Vis spectral changes in the complex during the oxidation reaction (Figure 6; Supporting Information, Figure S2). By comparing the absorbance (λ_{max} = 287 nm) at the end of the reaction (A = 0.46 after 45 min) with that observed before the addition of oxidants (A = 0.86) we found that 53% of the catalyst remained intact.

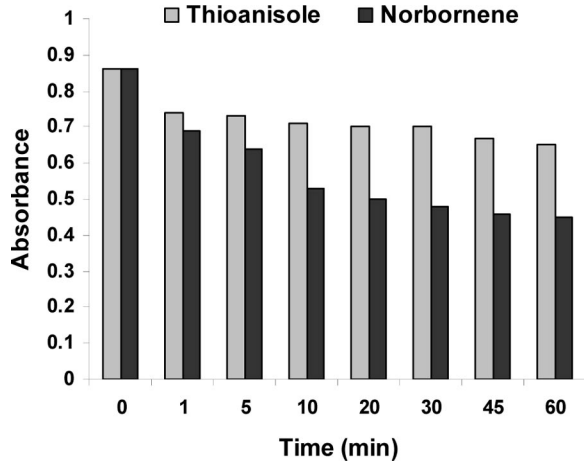


Figure 6. Plot of absorbance at 286 nm of MoL^1 vs. time in the oxidation of thioanisole by using UHP in ethanol at 25 °C and epoxidation of cyclooctene by using TBHP in DCE at 80 °C.

These results encouraged us to investigate the influence of electronic and structural requirements in the Schiff base ligand on the catalytic activity and stability of Mo complexes in the epoxidation reaction.[6c–6e] As outlined in Figure 7, the order of catalytic activities of different electronically and structurally Mo complexes was found to be $MoL^4 > MoL^2 > MoL^1 > MoL^3$. As expected, an electron-withdrawing group in the salicylidene ring (MoL^2) increases the effectiveness of the catalyst, resulting from elevating the Lewis acidity of the molybdenum center and therefore activation of TBHP (Scheme 2, **I**), promoting the catalytic activity of epoxidation.[4g,17] However, the introduction of the bulky and electron-rich *tert*-butyl substituents on the salicylidene ring near the coordination site (MoL^4) enhanced remarkably the catalytic performance of the catalyst. Presumably, the partial ligand dissociation would open a coordination site at the molybdenum center of hindered MoL^4 for coordination/activation of the TBHP and additionally its Lewis acidity.[19a,19b,20] Also, the absence of a methanol molecule as a ligand in the coordination site of the MoL^4 complex, facilitating the coordination of TBHP to the five-coordinate molybdenum center, should be taken into account. Moreover, the higher catalytic activity of the electron-deficient MoL^2 complex, as well as the hindered MoL^4 complex, is probably caused by their resistance to formation of catalytically inactive species[21] during the oxidation process, enhancing the stability of the catalysts towards oxidative degradation (Supporting Information, Figures S3 and S4) as is well established for porphyrin- and salen-complex-catalyzed oxidation reactions.[6c–6e,11,12,22,23] This suggestion was further supported by high TONs of the MoL^2 and

MoL^4 catalysts in the epoxidation of norbornene (TON ≈ 5000/24 h). However, general statements such as this have to be regarded with caution, as the catalytic mechanisms may be different for oxidation reactions using different catalytic systems.

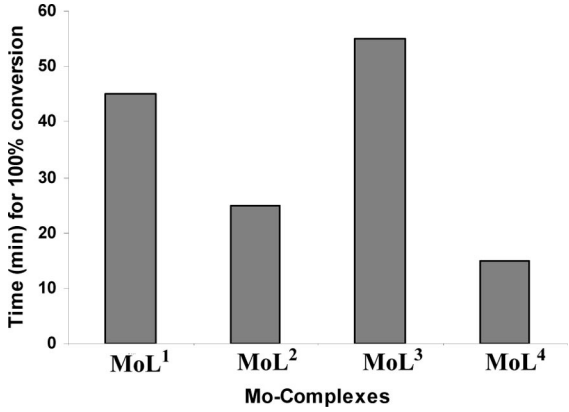


Figure 7. The influence of electronic and structural requirements on the catalytic activity of the Mo catalysts in the epoxidation of cyclooctene by using TBHP in DCE at 80 °C.

The promising results for activity and stability of these easily prepared molybdenum Schiff base complexes during the oxidation reactions leading to high/excellent yields of products at reasonably low reaction times, in particularly for full epoxidation of aliphatic alkenes, along with excellent chemoselectivity in both epoxidation and sulfoxidation reactions and absolute stereoselectivity in the epoxidation of stilbenes, are strong points of the present *cis*-(dioxido)-Mo^{VI} Schiff base complexes as oxidation catalysts.[4c–4e,4g,4h,5,12] It is noteworthy that, as the ligand backbone is chiral, a complex bearing enantiomerically pure ligand may offer enantioselective reactions.

Conclusions

In summary, the synthesis of four novel Mo^{VI} complexes $[MoO_2(L^x)(CH_3OH)]$ based on 2[(*E*)-(2-hydroxy-2-phenylethylimino)methyl]phenol as a ONO tridentate Schiff base ligand was described. The crystal structure of a sample of these complexes showed a monoclinic space group $P2_1/n$. A highly efficient epoxidation method with the use of TBHP activated by these simple Mo^{VI} complexes in desired times with excellent chemo- and stereoselectivity has been developed. Also, green oxidation of sulfides by using UHP was efficiently enhanced with excellent selectivity in ethanol under the influence of these Mo catalysts. Electron-poor and bulky groups on the salicylidene ring of the ligand promoted the effectiveness of the catalyst. The relatively high TOFs and TONs obtained in the oxidation of sulfides and alkenes, along with good/high percentages of the remaining catalysts at the end of the reactions, confirmed clearly the high activity and also relative stability of the Mo catalysts towards oxidative degradation. The applicability of these easily prepared Mo–Schiff base complexes in both epoxidation and sulfoxidation reactions with high efficiency and stability in combination with TBHP and UHP as desired oxygen sources highlight the novelty of these new Mo^{VI} catalysts and make the present catalytic methods more attractive for applied goals.

Experimental Section

General: All reagents were used as received. Solvents were purified by standard methods and dried if necessary. Methanol was distilled from magnesium methoxide. Acetyl acetate and ammonium heptamolybdate was purchased from Fluka Company and these reagents were used as received. All reactions and workups were carried out in air.

Instrumentation: X-ray data collections were recorded with a Stoe Image Plate Diffraction System. Purity determinations of the products were accomplished by GC with a Shimadzu GC-16A instrument by using a 25-m CBP1–S25 (0.32 mm ID, 0.5 μm coating) capillary column. IR spectra were recorded with a Perkin–Elmer 780 instrument. UV/Vis spectra were recorded with a 160 Shimadzu spectrophotometer. NMR spectra were recorded with a Bruker Avance DPX 500 MHz instrument. Mass spectra were recorded with a Shimadzu GC–MS-QP5050A.

Synthesis of H_2L^3 Ligand: The asymmetric tridentate Schiff base (H_2L^3) was obtained by addition of a solution of 1-amino-2-phenylethanol (1.37 g, 0.01 mol) in methanol (10 mL) to a solution of 5-methoxysalicylaldehyde (1.52 g, 0.01 mol) in methanol (10 mL), and the reaction mixture was stirred in air at reflux for 2 h, giving an orange precipitate. The crude product was recrystallized from $CHCl_3$/hexane (1:4). Yield: 75% (2.03 g). M.p. 166–168 °C. IR (KBr): $\tilde{\nu}$ = 3159 (υ_{OH}), 1640 ($\upsilon_{C=N}$), 1488 ($\upsilon_{C=C}$), 1263 ($\upsilon_{COphenolic}$) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.8 (dd, J = 6.9, 7.8 Hz, 1 H, CH_2), 3.8 (S, 3 H, OMe), 4.0 (dd, J = 14.8, 2.8 Hz, 1 H, CH_2) 5.1 (dd, J = 8.9, 6.0 Hz, 1 H, CH), 6.8 (d, J = 2.8 Hz, 1 H, aromatic proton), 6.9 (d, J = 8.9 Hz, 1 H, aromatic proton), 6.9 (dd, J = 7.5, 2.8 Hz, 1 H, aromatic proton), 7.3 (t, J = 7.2 Hz, 1 H, aromatic proton), 7.42 (t, J = 7.2 Hz, 2 H, aromatic proton), 7.5 (d, J = 7.09 Hz, 2 H, aromatic proton), 8.4 (s, 1 H,C=N),12.6 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 56.37, 67.72, 74.0, 115.44, 118.22, 118.72, 120.08, 126.41, 128.44, 142.11, 152.48, 155.63, 167.32 ppm. $C_{16}H_{17}NO_3$ (271.13): calcd. C 70.85, H 6.28, N 5.17; found C 70.80, H 6.35, N 5.20. MS: m/z = 271 [M^+]. UV/Vis: λ_{max} = 345 nm.

Synthesis of MoL^3 Complex: To the H_2L^3 ligand (2.71 g) was added dioxidomolybdenum(VI) acetylacetonate[10] (3.28 g, 0.01 mol) in methanol (10 mL). The reaction mixture was stirred under reflux for 1 h. The yellow precipitate was removed by filtration after 1 d. By washing with cold methanol, recrystallizing from methanol, and drying in vacuo, yellow rod crystals were secured in 70% (3.01 g) yield. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 1638 ($\upsilon_{C=N}$), 1476 ($\upsilon_{C=C}$), 909 and 920 (υ_{Mo-O}) cm^{-1}. ^1H NMR (500 MHz, DMSO, 25 °C): δ = 3.17 (d, J = 5.2 Hz, 3 H, methanol), 3.75 (s, 3 H, OMe), 4.08 (dd, J = 10.5, 5.2 Hz, 1 H, CH_2), 4.39 (dd, J = 13.5, 7.1 Hz, 1 H, CH_2), 5.28 (dd, J = 10.7, 4.0 Hz, 1 H, CH), 6.87 (d, J = 8.9 Hz, 1 H, aromatic proton), 7.13 (dd, J = 8.9, 3.2 Hz, 1 H, aromatic), 7.17 (d, J = 3.2 Hz, 1 H, aromatic proton), 7.32 (t, J = 7.2 Hz, 1 H, aromatic proton), 7.39 (t, J = 7.7 Hz, 2 H, aromatic proton), 7.46 (d, J = 7.4 Hz, 2 H, aromatic proton) 8.74 (s, 1 H,C=N) ppm. ^{13}C NMR (125 MHz, DMSO, 25 °C): δ = 48.55, 55.62, 66.91, 82.36, 116.14, 120.04, 120.56, 122.11, 126.06, 127.58, 128.25, 141.45, 151.98, 156.00, 163.49 ppm. $C_{17}H_{19}MoNO_6$ (429.50): calcd. C 47.54, H 4.42, N 3.26; found C 47.61, H 4.39, N 3.31. UV/Vis: λ_{max} = 285 nm.

Epoxidation Procedure: To a solution of the alkene (0.5 mmol) and MoL^x (Scheme 1; 0.05 mmol) in DCE (5 mL) was added TBHP (1 mmol), and the reaction mixture was stirred in air at 80 °C for the required time. The reaction progress was monitored by GC, and the yields of the products were determined by GC and NMR spectroscopic analysis. Further purification was achieved by silica chromatography (*n*-hexane/ethyl acetate, 10:1). Assignments of products were made by comparison with authentic samples or were identified by their IR, ^{1}H NMR and MS spectroscopic data.

Sulfoxidation Procedure: To a solution of the sulfide (0.5 mmol) and MoL^x (Scheme 1) (0.05 mmol) in ethanol (5 mL) was added urea hydrogen peroxide (0.5 mmol), and the reaction mixture was stirred in air at room temperature for the required time. The reaction progress was monitored by TLC, and the yields of the products were determined by GC analysis. Higher purification of products was achieved by chromatography over silica gel (*n*-hexane/ethyl acetate, 10:3). Assignments of products were made by comparison with authentic samples or were identified by their IR, ^{1}H NMR, and MS spectroscopic data.

Crystallographic Data Collection and Structure Refinement: Suitable X-ray quality crystals of MoL^3 were obtained as yellow rods by slow evaporation of solvent from a methanol solution of the complex at room temperature. The intensity data were collected at 173°K with a Stoe Image Plate Diffraction System[24] using Mo-K_α graphite monochromated radiation. Image plate distance was 70 mm, ω oscillation scans 0–200°, step $\Delta\omega$ = 0.8°, exposures of 1 min, 2θ range 4.3–51.8°, d_{min}–d_{max} = 12.45–0.81 Å. The structure was solved by direct methods by using SHELXS-97.[25] The refinement and all further calculations were carried out by using SHELXL-97.[25] The OH H atom was located in a difference electron-density map and freely refined. The remainder of the H atoms could also be located from Fourier difference maps but were included in calculated positions and treated as riding atoms by using SHELXL default parameters. The non-H atoms were refined anisotropically by using weighted full-matrix least-squares on F^2. The ORTEP plot of the MoL^3 complex was drawn by using ORTEP3,[26] at 50% probability level with atomic numbering along with selected bond lengths and angles. The crystal packing diagram (Figure 2) was drawn by using PLATON.[27] Data collection and refinement processes are summarized in Table 4. CCDC-736287 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data and structure refinement for the MoL^3 complex.

	$[MoO_2(L^3)(CH_3OH)]$
Empirical formula	$C_{17}H_{19}MoNO_6$
Formula weight	429.27
Temperature (K)	173
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	7.1829(6)
b (Å)	31.2340(19)
c (Å)	7.7220(7)
α (°)	90
β (°)	96.918(10)
γ (°)	90
V (Å^3)	1719.8(2)
Z	4
$D_{calcd.}$ (g/cm^3)	1.658
Absorption coefficient (1/mm)	0.796
$F(000)$	872
Crystal size (mm)	$0.19 \times 0.23 \times 0.45$
θ range for data collection (°)	2.55 to 26.10
Index ranges	$-8 \le h \le 7$ $-35 \le k \le 38$ $-9 \le l \le 9$
Reflections collected	11617
Independent reflections	3320 (R_{int} = 0.053)
Completeness to θ = 26° (%)	98
Absorption correction	multiscan
Max. and min. transmission	0.8610 and 0.7108
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3320/1/232
Goodness-of-fit on F^2	1.04
Final R indices [$I > 2\sigma(I)$]	R_1[a] = 0.0299, wR_2[b] = 0.0757
R indices (all data)	R_1[a] = 0.0348, wR_2[b] = 0.0781
Largest diff. peak and hole	0.419, –0.413

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma w\{(F_o^2 - F_c^2)^2/\Sigma w[(F_o^2)^2]^{1/2}\}$.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of tridentate Schiff base ligands H_2L^1, H_2L^2, and H_2L^4 and their dioxidomolybdenum(VI) complexes MoL^1, MoL^2, and MoL^4; UV/Vis spectral changes of the MoL^1, MoL^2, and MoL^4 complexes during the oxidation reactions.

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