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Synthesis, characterization and pronounced epoxidation activity of *cis*-dioxo-molybdenum(VI) tridentate Schiff base complexes using *tert*-butyl hydroperoxide

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ABSTRACT

The synthesis and catalytic performance of novel *cis*-dioxo-Mo(VI) complexes containing simple ONO tridentate Schiff base ligands in the epoxidation of various olefins using *tert*-butyl hydroperoxide in desired times with excellent chemo- and stereoselectivity have been described. The study of turnover numbers and the UV–Vis spectra of the Mo complexes in the present epoxidation system indicate well the high efficiency and stability of the catalysts during the reaction. The electron-deficient and bulky groups on the salicylidene ring of the ligand promote the effectiveness of the catalyst.

1. Introduction

High-valent molybdenum complexes have attracted continuing attention due to their important practical applications as catalysts in several industrial processes such as ammoxidation of propene, epoxidation of olefins, etc. [1–7] and as optoelectronic materials [8–10]. In this context, molybdenum(VI) dioxo-complexes have been extremely well investigated [11–18], particularly with respect to the catalytic role of transferase enzymes like nitrate reductase in which their active sites consist of a *cis* molybdenum dioxo moiety [19–21]. The ability of molybdenum to form stable complexes with oxygen-, nitrogen- and sulfur-containing ligands led to the development of molybdenum Schiff base complexes which are efficient catalysts both in homogeneous and heterogeneous reactions [22–28]. The activity of these complexes varies markedly with the type of ligands and coordination sites [29,30]. In continuation of our ongoing research on the development of biomimetic oxidation reactions [31–36], very recently we have introduced a dioxo-Mo(VI) Schiff base complex $[MoO_2(L^1)(CH_3OH)]$ (Scheme 1) containing a ONO tridentate Schiff base ligand, (L^1 = 2-[(2-hydroxypropylimino)methyl]phenol) as an efficient and selective catalyst for oxidation of sulfides to sulfoxides and sulfones [37]. In this report, the catalytic performance of this simple Mo catalyst in the highly selective epoxidation of olefins, which is a particular challenging problem in organic chemistry, has been described (Scheme 1). The influence of the electronic and structural requirements of the ligand on the catalytic activity of the catalyst has also been investigated (Scheme 1).

2. Experimental

2.1. General remarks

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

2.2. Instrumentation

Purity determinations of the products were accomplished by GC on a Shimadzu GC-16A instrument using a 25m CBP1-S25 (0.32 mm ID, 0.5 μm coating) capillary column. IR spectra were recorded on a Perkin–Elmer 780 instrument. UV–Vis spectra were recorded on a 160 Shimadzu spectrophotometer. NMR spectra were recorded on a Brucker Avance DPX 500 MHz instrument. Mass spectra were recorded on a Shimadzu GC–MS-QP5050A.

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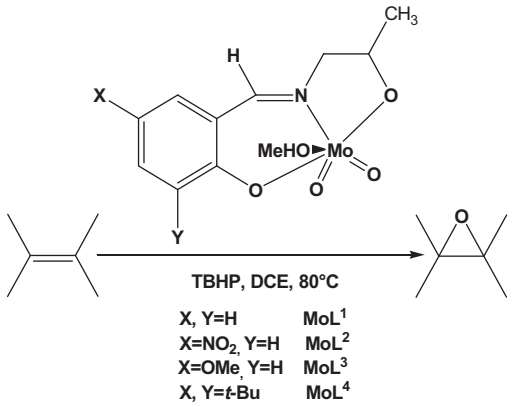


Scheme 1. Epoxidation of olefins catalyzed by the Mo^{VI} Schiff base complexes employed in this study.

2.3. Syntheses

2.3.1. H_2L^1 and MoL^1

The synthesis, characterization and crystal structure have previously been reported [37].

2.3.2. H_2l^2

The asymmetric tridentate Schiff base H_2L^2 was obtained by addition of a solution of 0.01 mol 1-amino-2-propanol (0.75 g) in methanol (10 ml) to a solution of 0.01 mol 5-nitro salicylaldehyde (1.67 g) in 10 mL methanol and the reaction mixture heated for 1 h, giving a yellow precipitate. The crude product was recrystallized from $CHCl_3$–hexane (1/4 v/v). Yield: 75% (1.68 g). M.p.: 162 °C. IR (KBr disc, cm^{-1}): 3346[1](ν_{OH}), 1667($\nu_{C=N}$), 1531($\nu_{C=C}$), 1265($\nu_{COphenolic}$); ^1H NMR (500 MHz, DMSO) δ_{ppm}: 1.19 (d, J = 6.2, 3H), 3.47 (dd, J_1 = 12.7 J_2 = 7.2, 1H), 3.70 (dd, J_1 = 12.7, J_2 = 3.0, 1H), 3.90 (m, 1H), 6.58 (d, J = 9.7, 1H), 8.02 (dd, J_1 = 9.6, J_2 = 3, 1H), 8.43 (d, J = 2.9, 1H), 8.69 (s, 1H), 14.21 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ_{ppm}: 21.60, 59.66, 65.46, 114.21, 123.83, 130.16, 133.64, 134.36, 168.69, 179.17; *Anal.* Calc. for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.49. Found: C, 53.52; H, 5.36; N, 12.52%. MS: m/z 224(M^+).

2.3.3. MoL^2

To 0.01 mol $\mathbf{H_2L^2}$ ligand (2.24 g) was added 0.01 mol dioxomolybdenum(VI) acetylacetonate (3.28 g) in 10 ml methanol. The reaction mixture was stirred under reflux condition for 2 h. After one day, a yellow precipitate was removed by filtration. By washing with cooled methanol, recrystallization from methanol and drying in vacuum, yellow crystals were secured in 62% yield (2.18 g). M.p.: >250 °C. IR (KBr disc, cm^{-1}): 1653($\nu_{C=N}$), 1605($\nu_{C=C}$), 899 and 930(ν_{Mo-O}); ^1H NMR (500 MHz, DMSO) δ_{ppm}: 1.26 (d, J = 6, 3H), 3.67–3.58 (dd, 1H), 4.22–4.11 (dd, 1H), 4.58–4.54 (m, 1H), 6.99 (d, J = 9.2, 1H), 8.23 (dd, J_1 = 9.2, J_2 = 3, 1H), 8.56 (d, J = 3, 1H), 8.84 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ_{ppm}: 20.15, 67.38, 79.08, 120.76, 121.41, 129.70, 130.98, 139.22, 163.53, 167.25; *Anal.* Calc. for $C_{10}H_{10}MoN_2O_6$: C, 34.30; H, 2.88; N, 8. Found: C, 34.28; H, 2.85; N, 8%. UV–Vis: λ_{max} = 328 nm.

2.3.4. H_2l^3

The asymmetric tridentate Schiff base $\mathbf{H_2L^3}$ was obtained by addition of a solution of 0.01 mol 1-amino-2-propanol (0.75 g) in methanol (10 ml) to a solution of 0.01 mol 5-methoxy salicylaldehyde (1.52 g) in 10 mL methanol. The reaction mixture was heated for 1 h, giving a yellow precipitate. The crude product was recrystallized from $CHCl_3$–hexane (1/4 v/v). Yield: 81% (1.69 g). M.p.: 58 °C. IR (KBr disc, cm^{-1}): 3193(ν_{OH}), 1645($\nu_{C=N}$), 1521($\nu_{C=C}$), 1153($\nu_{COphenolic}$); ^1H NMR (500 MHz, DMSO) δ_{ppm}: 1.12 (d, J = 6.3, 3H), 3.47 (dd, J_1 = 11.8, J_2 = 6.3, 1H), 3.57 (dd, J_1 = 11.85, J_2 = 4.8, 1H), 3.41 (s, 3H), 3.87–3.83 (m, 1H), 6.8 (d, J = 8.9, 1H), 6.94 (dd, J_1 = 8.9, J_2 = 3.1, 1H), 7.04 (d, J = 3.0, 1H), 8.45 (s, 1H), 13.00 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ_{ppm}: 22.22, 56.42, 66.56, 67.26, 115.75, 118.02, 119.34, 120.01, 152.31, 155.59, 167.06; *Anal.* Calc. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.16; H, 7.18; N, 6.70%. MS: m/z 209 (M^+).

2.3.5. MoL^3

To 0.01 mol $\mathbf{H_2L^3}$ ligand (2.09 g), was added 0.01 mol dioxomolybdenum(VI) acetylacetonate (3.28 g) in 10 mL methanol. The reaction mixture was stirred under reflux condition for 1 h. After one day, a yellow precipitate was removed by filtration. By washing with cooled methanol, recrystallization from methanol and drying in vacuum, yellow crystals were secured in 80% yield (2.68 g), M.p.: >250 °C. IR (KBr disc, cm^{-1}): 1644($\nu_{C=N}$), 1478($\nu_{C=C}$), 881 and 916(ν_{Mo-O}); ^1H NMR (500 MHz, DMSO) δ_{ppm}: 1.26 (d, J = 6.0, 3H), 3.59–3.52 (dd, 1H), 4.15 (dd, J_1 = 13.4, J_2 = 3.7, 1H), 3.74 (s, 3H), 4.45–4.41 (m, 1H), 6.82 (d, J = 8.9, 1H), 7.08–7.13 (m, 2H), 8.66 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ_{ppm}: 20.73, 56.50, 67.51, 77.96, 116.91, 120.93, 121.45, 122.89, 152.72, 156.92, 164.23; *Anal.* Calc. for $C_{11}H_{13}MoNO_5$: C, 39.42; H, 3.91; N, 4.18. Found: C, 39.38; H, 3.88; N, 4.2%. UV–Vis: λ_{max} = 346 nm.

2.3.6. H_2l^4

The asymmetric tridentate Schiff base $\mathbf{H_2L^4}$ was obtained by addition of a solution of 0.01 mol 1-amino-2-propanol (0.75 g) in methanol (10 ml) to a solution of 0.01 mol 3,5-di-*tert*-butyl salicylaldehyde (2.34 g) in 10 ml methanol. The reaction mixture was heated at reflux for 1 h, giving a yellow oil. IR (KBr, cm^{-1}): 3347(ν_{OH}), 1628($\nu_{C=N}$), 1477($\nu_{C=C}$), 1271($\nu_{COphenolic}$); ^1H NMR (500 MHz, $CDCl_3$) δ_{ppm}: 1.75 (d, J = 6.2, 3H), 1.29 (s, 9H), 1.40 (s, 9H), 3.58 (dd, J_1 = 12.2, J_2 = 7.2, 1H), 3.75 (dd, J_1 = 12.04, J_2 = 2.9, 1H), 4.27–4.13 (m, 1H), 7.15 (s, 1H), 7.43 (s, 1H), 8.43 (s, 1H), 13.65 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_{ppm}: 21.28, 29.85, 31.92, 67.67, 67.74, 118.22, 126.50, 127.58, 137.19, 140.64, 158.49, 168.36; *Anal.* Calc. for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.21; H, 9.96; N, 4.80%. MS: m/z 291 (M^+).

2.3.7. MoL^4

To 0.01 mol $\mathbf{H_2L^3}$ (2.91 g), was added 0.01 mol dioxo-molybdenum(VI) acetylacetonate (3.28 g) in 10 ml methanol. The reaction mixture was stirred under reflux conditions, the solution color changed to deep yellow and yellow crystals started to precipitate after 5 min. The reflux was continued for 1 h. The product was filtered and washed with cooled methanol (78% yield, 3.5 g). M.p.: >250 °C. IR (KBr disc, cm^{-1}): 1634($\nu_{C=N}$), 1477($\nu_{C=C}$), 910 and 925(ν_{Mo-O}); ^1H NMR (500 MHz, DMSO) δ_{ppm}: 1.26 (s, 9H), 1.36 (s, 9H), 3.17 (d, J = 4.9, 3H), 4.13–4.07 (m, 2H), 4.44 (m, 1H), 7.39 (s, 1H), 7.46 (s, 1H), 8.69 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ_{ppm}: 20.75, 30.42, 32.08, 34.78, 35.78, 49.47, 67.42, 77.75, 121.43, 129.01, 129.48, 138.89, 141.33, 159.54, 165.23; *Anal.* Calc. for $C_{19}H_{31}MoNO_5$: C, 50.78; H, 6.95; N, 3.12. Found: C, 50.80; H, 6.92; N, 3.10%. UV–Vis: λ_{max} = 344 nm.

2.4. General oxidation procedure

To a solution of olefin (0.5 mmol) and $\mathbf{MoL^x}$ (Scheme 1) (0.005 mmol) in 5 ml DCE was added TBHP (1 mmol) and the reaction mixture was stirred under 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 analysis. Further purification was achieved by silica chromatography eluting with *n*-hexane/ethyl acetate (10/2).

Table 1
Analytical and selected spectral data of the Mo(VI) complexes.

Complex	Selected spectral data					
	Elem. *Anal.* (Calc.)	$\nu_{C=N}$ (cm^{-1})	$\nu_{Mo=O}$ (cm^{-1})	$\delta_{-CH=N-}$(ppm)	$\delta_{(methanol)}$(ppm)	λ_{max} (nm)
$[MoO_2L^1(CH_3OH)]$	C, 39.2(39.18), H, 4.45(4.48), N, 4.17(4.15)	1638	900, 924	8.70	3.18 (J = 5,3H)	341 (LMCT)
$[MoO_2L^2]$	C, 34.31(34.30), H, 2.85(2.88), N, 7.92(8)	1653	899, 930	8.84	–	328 (LMCT)
$[MoO_2L^3]$	C, 39.39(39.42), H, 3.93(3.91), N, 4.2(4.18)	1644	881, 916	8.66	–	346 (LMCT)
$[MoO_2L^4(CH_3OH)]$	C, 50.75(50.78), H, 6.92(6.95), N, 3.2(3.12)	1632	910, 925	8.69	3.17 (J = 4.9,3H)	344 (LMCT)

3. Results and discussion

3.1. Structural discussion of the cis-dioxo-Mo(VI) complexes

The Schiff base ligands $\mathbf{H_2L^1}$–$\mathbf{H_2L^4}$ (Scheme 1) were prepared by the condensation of 1-amino-2-propanol with a number of salicylaldehydes substituted by different electronic and steric groups (5-NO_2-, 5-OCH_3- and 3,5-di-*tert*-butyl salicylaldehyde) in methanol and could be isolated by precipitation on the addition of $CHCl_3$–*n*-hexane (1/4 v/v). The corresponding Mo complexes (Scheme 1, MoO_2L^1–MoO_2L^4) of these ligands were synthesized by the reaction of $MoO_2(acac)_2$ and the related Schiff base ligands in methanol. All the new complexes were recrystallized from methanol and are quite air stable as solids and also in solution. Analytical and selected spectral data of the Mo complexes are given in Table 1.

In addition to crystal data for $\mathbf{MoL^1}$ [37], spectroscopic and elemental analyses are consistent with a monomeric complex with a ligand:Mo ratio of 1:1. When the synthesis reactions were performed using two equivalents of the ligands, the same products were formed as observed with one equivalent of the ligand. The infrared spectra of the Mo complexes exhibit two strong $\nu_{Mo=O}$ bands in the regions 880–910 and 916–930 cm^{-1}, characteristic of the symmetric and asymmetric stretching vibrations of *cis*-$[MoO_2]^{2+}$ fragments [11–18]. The absence of a broad band around 3354–3193 cm^{-1} in the spectra of the molybdenum complexes compared to the Schiff base ligands indicates the coordination of the phenolic oxygen after deprotonation. The characteristic imine bands in the ligands (1635–1667 cm^{-1}) are shifted to lower wavenumbers after coordination of the azomethine nitrogen to the Mo center, and appeared at 1632–1653 cm^{-1}. A sharp singlet at 8.36–8.69 ppm, which be rationalized as the azomethine proton of the ligands, shifted downfield and appeared at 8.66–8.84 ppm, resulting from the coordination of the azomethine nitrogen [38,39]. The appearance of a signal at 3.17–3.18 ppm in the ^1H NMR spectra of $[MoO_2(L^1)(CH_3OH)]$ and $[MoO_2(L^4)(CH_3OH)]$ confirms the coordination of a methanol molecule to the Mo(VI) center of these complexes [35,37].

The electronic spectra of the Mo(VI) complexes revealed a high intensity charge transfer band (LMCT) in the region 300–350 nm and a regular trend between λ_{max} and the electronic requirements of the complexes was observed. As expected the complex containing an electron-deficient Schiff base ligand ($\mathbf{H_2L^2}$) requires higher energy for the LMCT [38–41]. The electronic spectra of the $\mathbf{H_2L^2}$ ligand (λ_{max} = 346, 360 nm) and the $\mathbf{MoL^2}$ complex (λ_{max} = 328 nm) are shown in Fig. 1.

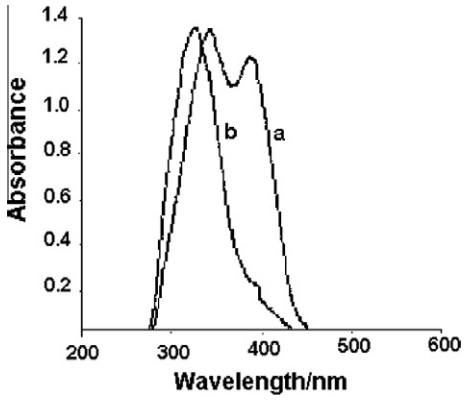


Fig. 1. Electronic spectra of $\mathbf{H_2L^2}$ (a) and $\mathbf{MoL^2}$ (b) in methanol.

3.2. Catalytic activity

The oxidation of cyclohexene using *tert*-butyl hydroperoxide (TBHP), which did not proceed in the absence of catalyst under mild and reflux conditions, was used as a model reaction. To find the 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 such as EtOH, MeOH, MeCN, $(Me)_2CO$, CH_2Cl_2, $CHCl_3$ and 1,2-$C_2H_4Cl_2$ (DCE) was carried out in the presence of 1 mol% of the simple $\mathbf{MoL^1}$ catalyst. While coordinative solvents inhibited the reaction completely under mild and reflux conditions, cyclohexene oxidation proceeded in CH_2Cl_2, $CHCl_3$ and DCE at various temperatures. Considering the yield and reaction rate, DCE was found to be the best solvent; however the reaction required a temperature of 80 °C for completion in the desired time (Fig. 2). The poorer yields obtained with CH_2Cl_2 (34%) and $CHCl_3$ (66%) is probably caused by the lower reaction temperature for their reflux conditions.

Different catalyst/alkene molar ratios have been used in the oxidation of cyclohexene with different reaction times (Fig. 3). It was observed that oxidation of cyclohexene required 40 min for completion using 1 mol% of the catalyst and an increase in this ratio up to 5 mol% did not noticeably affect the reaction rate (Fig. 3).

The examination of various molar ratios of TBHP/alkene in the catalytic oxidation of cyclohexene in DCE showed that the full oxidation of the starting material was obtained by two equivalents of

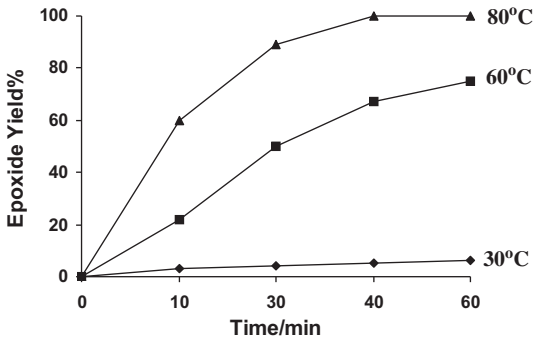


Fig. 2. The influence of temperature on the oxidation of cyclohexene using TBHP catalyzed by $\mathbf{MoL^1}$. The reactions were run under air in DCE and the molar ratio of cyclohexene:TBHP:catalyst was 100:200:1.

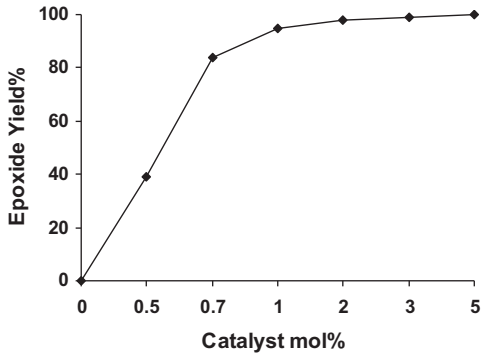


Fig. 3. The influence of catalyst concentration on the oxidation of cyclohexene using TBHP catalyzed by **MoL^1**. The reactions were run under air in DCE and the molar ratio of cyclohexene:TBHP:catalyst was 100:200:*X*.

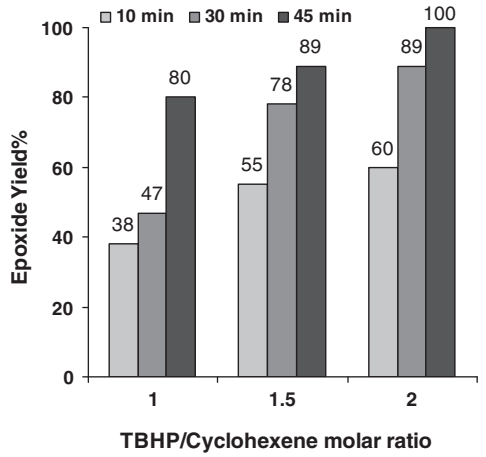


Fig. 4. The influence of TBHP/alkene molar ratios on the oxidation of cyclohexene catalyzed by **MoL^1** in DCE.

TBHP (Fig. 4). Under the optimized conditions (100:200:1 M ratio for alkene:TBHP:catalyst in DCE at 80 °C), cyclohexene converted completely within 40 min and 95% of the epoxide product was secured as the sole product.

In order to establish the general applicability of the method, various olefins were subjected to the oxidation protocol under the influence of the **MoL^1** catalyst (Table 2). As summarized in Table 2, 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. Inspections of the results in Table 2 indicate several useful features of this catalytic method. The least reactive aliphatic terminal and non-terminal alkenes were oxidized in desired times in good/excellent yields and excellent selectivities (Table 2, entries 5, 6). The chemoselectivity of the procedure was notable. The oxidative hydroxyl 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. The complete retention of configuration in the epoxidation of *trans*-stilbene and excellent stereoselectivity in the oxidation of *cis*-stilbene (>94%) were obtained (Table 2, entries 10, 11).

According to the suggested mechanism (Scheme 2) [42,43], the second stage of the process is the interaction between the olefin and the TBHP molecule, activated in the coordination sphere of the molybdenum complex (Scheme 2). The Lewis acidity of the Mo center increases the oxidizing power of the peroxo group and the alkene is subsequently oxygenated by nucleophilic attack on an electrophilic oxygen atom of the coordinated TBHP peroxide [44]. Spectroscopic and computational methods applied to molybdenum dioxo and oxodiperoxo complexes support a reaction mechanism involving an activation state formed between the complex, oxidant and olefin (Scheme 2, **IV**) [45,46]. 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 this active oxidizing species to the olefin (Scheme 2, **IV**). In this process, in higher conversions, *tert*-butanol can compete with TBHP for coordination to the molybdenum center, forming a less reactive species (Scheme 2, **V**) that leads to the decreasing reaction rate [45]. Similarly, for complex **MoL^1**, the initial reaction rates were much higher than those observed later in the reactions (Fig. 5, none). The inhibiting effect of coordinative solvents used in the preliminary experiments may be more evidence for this suggestion. This was further supported by the retarding effect of nitrogenous bases on the catalytic activity of **MoL^1**. The addition of pyridine and imidazole to the reaction mixture containing the **MoL^1** complex in DCE under the same conditions retarded remarkably the epoxidation of cyclohexene (Fig. 5). Presumably, pyridine and in particular strong π-donor imidazole form an inactive species (Scheme 2, **VI**) by coordinating to the molybdenum ion [47–49], making it a sluggish catalyst for activation of TBHP.

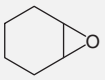
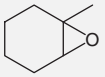
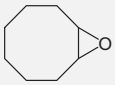
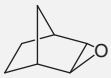
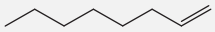
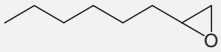
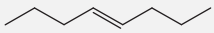
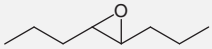
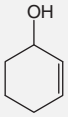
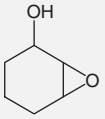
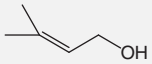
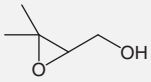
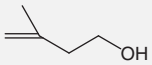
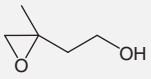
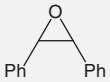
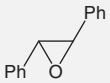
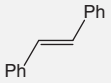
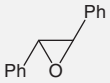
It is noteworthy that the easy preparation method of the Mo-Schiff base catalyst and advantages of TBHP as an oxidant for industrial synthesis offer ready scalability. The performance of the oxidation reaction using 100 mmol norbornene as a substrate gave 92% of the related epoxide after purification over silica chromatography eluting with *n*-hexane/ethyl acetate (10/2).

3.3. Activity and stability of dioxo-Mo(VI) complexes

The high/excellent yields of the epoxides (66–100%) obtained using these new catalytic methods in relatively short times (45 min) display the superior catalytic activity of the present dioxo-Mo(VI) complexes [22–26]. This was further supported by the impressive turnover number of the **MoL^1** catalyst (4925/24 h) in the oxidation of cyclooctene by TBHP using a 5000:10000:1 M ratio for the substrate/oxidant/catalyst. More evidences in this matter have been obtained by monitoring the electronic spectra of the **MoL^1** complex in the epoxidation of the less reactive 1-octene (Fig. 6). The intensity of the characteristic absorption bands remains approximately unchanged during the hour reaction time, indicating the high stability of the Mo catalyst under the oxidation 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 [50–53].

The influence of the electronic and structural requirements of the Schiff base ligand on the catalytic activity and stability of the Mo catalyst was investigated. Different electronically and structurally Mo complexes (Scheme 1) were subjected to the epoxidation of cyclooctene by TBHP using a 10 000:20 000:1 M ratio for the substrate/oxidant/catalyst. The order of catalytic activity was found to be **MoL^4** > **MoL^2** > **MoL^1** > **MoL^3** according to turnover frequency of the catalysts per hour (Fig. 7). As expected, an electron-withdrawing group in the salicylidene ring (**MoL^2**) increases the effectiveness of the catalyst, resulting from the elevated Lewis acidity of the molybdenum centre and therefore the activation of TBHP (Scheme 2, **II**), promoting the catalytic activity of epoxidation [46,54]. However, the introduction of the bulky and electron-rich *tert*-Bu substituents on the salicylidene ring near the coordination

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

Entry	Alkene	Conversion %[b] (isolated yield%)	Product[c]	δ_{ppm} (C–H oxiran ring)	Selectivity %[b]
1		100 (94)		3.1	100
2		100 (91)		2.9	100
3		100 (95)		2.9	100
4		100 (96)		2.9	100
5		66 (58)		2.5–2.9	100
6		100 (90)		2.7	100
7		100 (92)		3.1–3.3	100
8		100 (94)		2.7	100
9		100 (90)		2.5	100
10		78[d] (75)		4.4	94[d]
				3.9	6[d]
11		68[d] (60)		3.9	100[d]

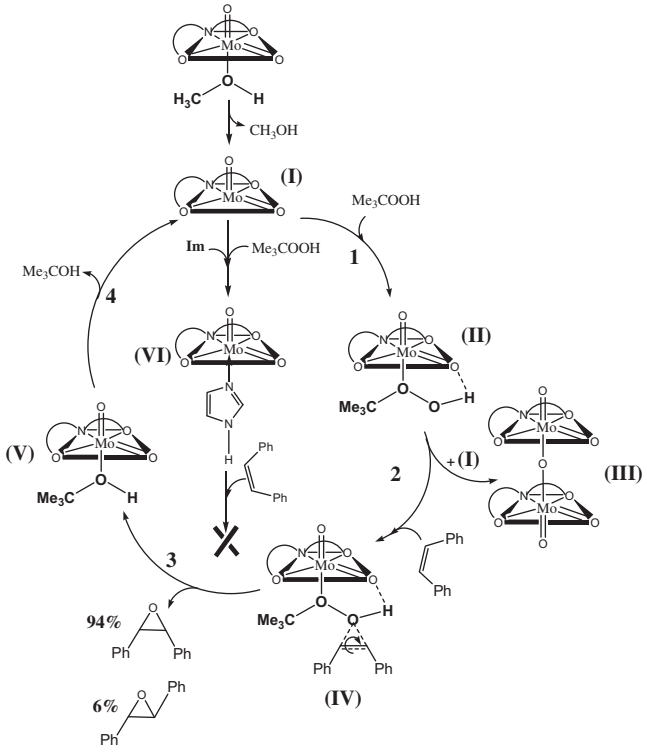
[a] The reactions were run for 45 min under air in DCE at 80 °C and the molar ratio of alkene:TBHP:catalyst was 100:200:1.
[b] Conversions and selectivities were determined by GC based on the starting alkene.
[c] All products were identified by their IR, ^{1}H NMR and GC–MS spectral data in comparison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

site (**MoL^4**) enhanced remarkably the catalytic performance of the catalyst. Presumably, partial ligand dissociation would open a coordination site at the molybdenum centre of the hindered **MoL^4** for coordination/activation of the TBHP and additionally enhance its Lewis acidity [50,51,55]. Moreover, the higher catalytic activity of the electron-deficient **MoL^2** as well as the hindered **MoL^4** complex is probably caused by their resistance to formation of catalytically inactive species, such as a μ-oxo dimer (Scheme 2, **III**), during the oxidation process, thus enhancing the stability of the catalysts towards oxidative degradation [56–58]. This suggestion is further supported by high total TONs of the **MoL^2** and **MoL^4** catalysts in the epoxidation of cyclooctene after 24 h (TON = 9667 and 9732/24 h for **MoL^2** and **MoL^4,** respectively).

The promising results for the 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, along with excellent chemo- and stereoselectivity in the epoxidation reactions are strong points of the present *cis*-dioxo-Mo(VI) Schiff base complexes as oxidation catalysts [22–26].

4. Conclusion

In summary, a highly efficient epoxidation method using TBHP activated by simple Mo(VI)-Schiff base complexes in desired times with excellent chemo- and stereoselectivity has been developed. To investigate the influence of the electronic and steric demands of the ligands on the catalytic activity of Mo complexes, three novel Mo(VI) complexes, **MoL^x**, based on 2-[(2-hydroxypropylimino)methyl]phenol as ONO tridentate Schiff base ligands have been synthesized. It was observed that electron-poor and bulky groups on the salicylidene ring of ligand promote the effectiveness of the catalyst. The relative high TOF and TON obtained in the oxidation of olefins, along with the high percentage of catalyst remaining at the end of the reactions confirms 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 the epoxidation of diverse olefins with excellent chemo- and stereoselectivity, and ready scalability, highlights the novelty of this epoxidation method and makes it more attractive for applied goals.



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

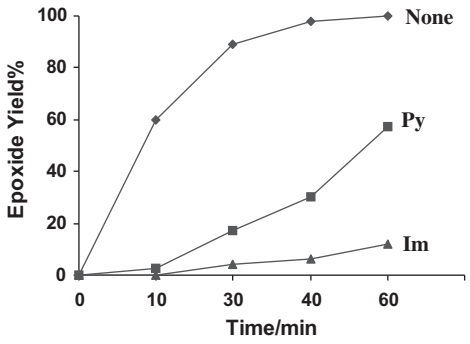


Fig. 5. The influence of nitrogenous donors on the oxidation of cyclohexene using TBHP catalyzed by **MoL**^{1} in DCE at 80 °C.

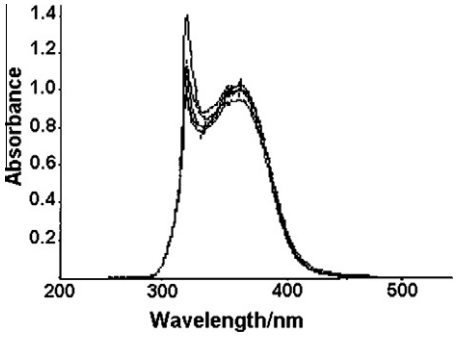


Fig. 6. UV–Vis spectral changes of the **MoL**^{1} complex during the oxidation of 1-octene using TBHP in DCE at 80 °C.

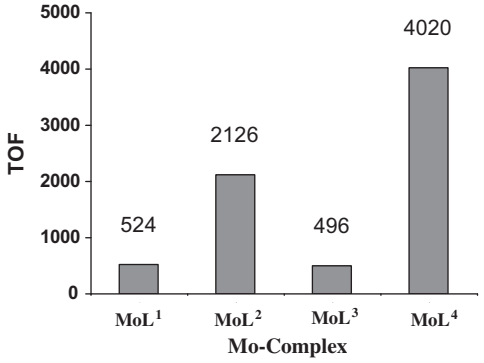


Fig. 7. The TOF of the **MoL**^{x} complexes in the epoxidation of cyclooctene by TBHP in DCE at 80 °C after 1 h using 10 000:20 000:1 M ratio for olefin:TBHP:catalyst.

Acknowledgements

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