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Chiral molybdenum(VI) complexes with tridentate Schiff bases derived from *S*(+)-1-amino-2-propanol: Synthesis, characterization and catalytic activity in the oxidation of prochiral sulfides and olefins

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ABSTRACT

Seven chiral dioxidomolybdenum(VI) complexes with tridentate Schiff bases were synthesized by mono-condensation of *S*(+)-1-amino-2-propanol with salicylaldehyde and its derivatives. One- (^{1}H, ^{13}C) and two-dimensional (COSY, gHSQC and NOESY) NMR, IR, CD and UV–Vis spectroscopy were used for detailed characterization of the new molybdenum(VI) compounds. After optimization of the reaction conditions, the catalytic activities of these complexes were tested for the oxidation of olefins, *i.e.* styrene and cyclohexene, with aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as an oxidant. Moreover, the molybdenum(VI) Schiff base complexes were also able to catalyze the oxidation of prochiral sulfides [PhSR (R = Me, Bz)] to optically active sulfoxides in the presence of aqueous 30% H_2O_2.

1. Introduction

Molybdenum is essential transition metal for life, occurring as an important constituent of certain enzymes in plants and animals. In plants, nitrate reductase catalyzes nitrogen assimilation. In animals, xanthine dehydrogenase plays an important role in xanthine oxidation to uric acid, in purine catabolism and aldehyde oxidase in the final oxidation step of abscisic acid biosynthesis [1]. Moreover, as a trace element it is most abundant in seawater, with a concentration of *ca.* 100 nM, including marine sediments. All molybdenum enzymes found in living organisms are formed by different variants of the pterin-based cofactor (Moco) [2]. Such enzymes can be modelled by molybdenum complexes with an appropriate ligand. In this context, Schiff-base ligands have been particularly addressed due to their common availability via the condensation of amino compounds with aldehyde moieties [3]. The application of molybdenum(VI) complexes is mainly focused on the epoxidation of olefins and sulfoxidation reactions, but in the case of enantioselective sulfoxidation, molybdenum complexes are much less successful and explored [4,5].

N-salicyl-β-amino alcohol Schiff base ligands, especially chiral ones, are a member of the well-known "privileged ligands" group [6,7]. These "tridentate salen ligands" are very attractive due to their structural and electronic fine-tunability and extremely simple synthesis from naturally available chiral amino acids [8,9]. Moreover, their transition metal complexes, including dioxidomolybdenum(VI) compounds, have been successfully employed as catalysts for the very efficient epoxidation of olefins [10] and oxidation of sulfides to sulfoxides [11–13], the asymmetric alkynylation of aldehydes [13], the stereoselective synthesis of cyclic ethers [14,15] and trimethylsilylcyanations [16,17].

Transition metal complexes incorporating chiral Schiff base ligands have kept our continuing interest [18–20]. In this paper we describe new seven dioxidomolybdenum(VI) complexes with ONO donor Schiff bases, products of a single condensation of *S*(+)-1-amino-2-propanol with aromatic salicylaldehyde derivatives, presented in Fig. 1. Examination of the spectroscopic properties, *i.e.* UV–Vis, IR, circular dichroism, one- and two-dimensional NMR have been also performed. Moreover, the catalytic ability for the enantioselective sulfoxidation of methyl phenyl sulfide (PhSMe) and benzyl phenyl sulfide (PhSBz), utilizing aqueous 30% H_2O_2 as an oxidant, has been studied. Finally, the dioxidomolybdenum (VI) complexes have also shown their catalytic potential for the oxidation of styrene and cyclohexene in the presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as an oxidant.

2. Experimental

2.1. Measurements

All chemicals and reagents were obtained from commercial sources and used without further purification unless stated otherwise. Carbon, hydrogen and nitrogen contents were determined on

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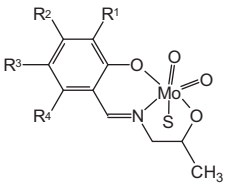

	R1	R2	R3	R4
1	H	H	H	H
2	OCH_3	H	H	H
3	H	H	OCH_3	H
4	$C(CH_3)_3$	H	H	H
5	$C(CH_3)_3$	H	$C(CH_3)_3$	H
6	Br	H	Br	H
7	H	H	$-(CH)_4-$	

Fig. 1. Structural formulae of the molybdenum(VI) complexes.

a Carlo Erba MOD 1106 elemental analyzer. Electronic spectra were recorded on a Perkin-Elmer LAMBDA 18 spectrophotometer. Circular dichroism spectra were measured with a Jasco J-815 spectropolarimeter. IR spectra of solid samples (KBr pellets) were run on a Bruker IFS 66. NMR spectra were obtained in DMSO-d_6 solutions with a Bruker AVANCE III 700 MHz spectrometer using TMS as a reference. A Shimadzu GC-2025 gas chromatograph with a Zebron ZB-5 capillary column (30 m × 0.25 mm × 0.25 mm) and FID detector were used to analyze the reaction products from the oxidation of olefins. Confirmation of the identity of the reaction products has been made with a GC–MS model Shimadzu GCMS-QP2010 SE.

2.2. Catalytic activity

2.2.1. Sulfoxidation

To a solution of catalyst (0.010 mmol) in 3 ml of CH_2Cl_2/MeOH mixture (7:3), thioanisole or benzyl phenyl sulfide (1.00 mmol) was added at −20 °C or room temperature, with 1,3,5-trimethoxybenzene as an internal standard. Aqueous 30% H_2O_2 was added (1.10 mmol) in small portions and the resulting mixture was stirred. After the appropriate reaction time, the solution was quenched with 3 ml of sodium sulfite solution (0.1 M) and extracted with ethyl acetate (3 × 3 ml). The combined organic layers were evaporated to dryness. The solid product, dissolved in $CDCl_3$, was analyzed (yield and *ee* value) by ^{1}H NMR spectra in the presence of the chiral shift reagent Eu(hfc)$_3$ [21].

2.2.2. Oxidation of olefins

In typical procedure, styrene or cyclohexene (1.00 mmol), an oxidant (2.00 mmol), *i.e.* aqueous 30% H_2O_2 or 5.5 M *tert*-butyl hydroperoxide (TBHP) in decane, and the catalyst (0.010 mmol) were heated at 80 °C for 1 h in 10 ml of 1,2-dichloroethane (DCE) or for 5 h in 10 ml of acetonitrile (MeCN). The reactions were monitored by GC and the yields were recorded as the GC yield based on the starting styrene or cyclohexene. The identities of the oxidation products were confirmed by GC–MS. Different amounts of catalysts and oxidants were also added to study their effect on the conversion and selectivity of the reaction products.

2.3. Synthesis of the dioxidomolybdenum(VI) complexes

The complexes were obtained in the following example procedure. A solution of 1 mmol of *S*(+)-1-amino-2-propanol in methanol (10 ml) was added to 1 mmol of an aromatic *o*–hydroxyaldehyde (salicylaldehyde, 3-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 3-*tert*-butylsalicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde, 3,5-dibromosalicylaldehyde or 2-hydroxy-1-naphthaldehyde) in MeOH (10 ml) and heated with stirring under reflux for 1 h. Bis(acetylacetonato)dioxidomolybdenum(VI) (1 mmol) in MeOH (10 ml) was then added and stirred at room temperature for 2 h. After cooling, a precipitate separated and was filtered off, washed and recrystallized from MeOH.

2.3.1. {S(+)-2-[(2-oxidopropyl)iminomethyl]phenolato-κ^3N,O,O′}dioxidomolybdenum(VI) (**1**)

Yield 87%. *Anal.* Calc. for $C_{10}H_{11}NO_4Mo{\cdot}CH_3OH$: C, 39.2; H, 4.5; N, 4.2. Found: C, 39.0; H, 4.5; N, 4.2%. IR (KBr, cm^{-1}): 1640 ($\nu_{C=N}$); 931, 901 ($\nu_{Mo=O}$). UV–Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 271 (8300), 347 (2360). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 278 (13.07), 349 (5.52). ^{1}H NMR (DMSO-d_6, ppm) δ: 8.70 (1H, s) (azomethine); 7.55 (1H, d, ^3J = 7.7 Hz), 7.47 (1H, t, ^3J = 7.7 Hz), 6.95 (1H, t, ^3J = 7.7 Hz), 6.87 (1H, d, ^3J = 8.3 Hz) (aromatic); 4.46–4.48 (1H, m) (methine); 4.17 (1H, dd, ^3J = 13.3 Hz, ^4J = 4.1 Hz), 3.57 (1H, dd, ^3J = 13.3 Hz, ^4J = 9.6 Hz) (methylene); 1.28 (1H, d, ^3J = 6.1 Hz) (methyl); 4.11 (1H, br s), 3.18 (3H, s) (MeOH). ^{13}C NMR (DMSO-d_6, ppm) δ: 164.1 (azomethine); 162.2, 135.2, 134.4, 121.4, 119.8, 119.7 (aromatic); 77.9 (methine); 67.1 (methylene); 49.1 (MeOH); 20.3 (methyl).

2.3.2. {S(+)-2-[(2-oxidopropyl)iminomethyl]-6-methoxyphenolato-κ^3N,O,O′}dioxidomolybdenum(VI) (**2**)

Yield 91%. *Anal.* Calc. for $C_{11}H_{13}NO_5Mo{\cdot}CH_3OH$: C, 39.3; H, 4.7; N, 3.8. Found: C, 39.1; H, 4.6; N, 3.9%. IR (KBr, cm^{-1}): 1642 ($\nu_{C=N}$); 1256 ($\nu_{asym(C-O)}$); 1040 ($\nu_{sym(C-O)}$); 924, 901 ($\nu_{Mo=O}$). UV–Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 273 (8480), 377 (2510). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 284 (9.46), 374 (3.39). ^{1}H NMR (DMSO-d_6, ppm) δ: 8.68 (1H, s) (azomethine); 7.14 (2H, t, ^3J = 7.9 Hz), 6.89 (1H, t, ^3J = 7.9 Hz) (aromatic); 4.43–4.45 (1H, m) (methine); 4.16 (1H, dd, ^3J = 13.3 Hz, ^4J = 4.1 Hz), 3.56 (1H, dd, ^3J = 13.3 Hz, ^4J = 9.6 Hz) (methylene); 3.78 (3H, s) (methoxy); 1.27 (1H, d, ^3J = 6.1 Hz) (methyl); 4.12 (1H, q), 3.18 (3H, d) (MeOH). ^{13}C NMR (DMSO-d_6, ppm) δ: 164.1 (azomethine); 152.3, 149.7, 125.6, 121.5, 119.5, 116.7 (aromatic); 77.9 (methine); 66.9 (methylene); 56.1 (methoxy); 49.2 (MeOH); 20.2 (methyl).

2.3.3. {S(+)-2-[(2-Oxidopropyl)iminomethyl]-4-methoxyphenolato-κ^3N,O,O′}dioxidomolybdenum(VI) (**3**)

Yield 94%. *Anal.* Calc. for $C_{11}H_{13}NO_5Mo{\cdot}CH_3OH$: C, 39.3; H, 4.7; N, 3.8. Found: C, 39.1; H, 4.7; N, 3.8%. IR (KBr, cm^{-1}): 1643 ($\nu_{C=N}$); 1259 ($\nu_{asym(C-O)}$); 1032 ($\nu_{sym(C-O)}$); 926, 898 ($\nu_{Mo=O}$). UV–Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 276 (7780), 375 (3120). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 279 (14.31), 385 (4.76). ^{1}H NMR (DMSO-d_6, ppm) δ: 8.67 (1H, s) (azomethine); 7.13 (1H, d, ^3J = 3.2 Hz), 7.10 (1H, dd, ^3J = 8.9 Hz, ^4J = 3.2 Hz), 6.82 (1H, d, ^3J = 8.9 Hz) (aromatic); 4.42–4.44 (1H, m) (methine); 4.14 (1H, dd, ^3J = 13.3 Hz, ^4J = 4.1 Hz), 3.55 (1H, dd, ^3J = 13.3 Hz, ^4J = 9.6 Hz) (methylene); 3.75 (3H, s) (methoxy); 1.27 (1H, d, ^3J = 6.1 Hz) (methyl); 4.11 (1H, q), 3.18 (3H, d) (MeOH). ^{13}C NMR (DMSO-d_6, ppm) δ: 163.8 (azomethine); 156.5, 152.3, 122.5, 121.0, 120.5, 116.5 (aromatic); 77.6 (methine); 67.1 (methylene); 56.0 (methoxy); 49.0 (MeOH); 20.3 (methyl).

2.3.4. {S(+)-2-[(2-Oxidopropyl)iminomethyl]-6-tert-butylphenolato-κ^3N,O,O′}dioxidomolybdenum(VI) (**4**)

Yield 89%. *Anal.* Calc. for $C_{14}H_{19}NO_4Mo{\cdot}CH_3OH$: C, 45.8; H, 5.9; N, 3.6. Found: C, 46.0; H, 5.7; N, 3.7%. IR (KBr, cm^{-1}): 1646 ($\nu_{C=N}$); 925, 889 ($\nu_{Mo=O}$). UV–Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 288 (6280), 366 (1560). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 282 (11.57), 358 (4.79). ^{1}H NMR (DMSO-d_6, ppm) δ: 8.68 (1H, s) (azomethine); 7.44 (1H, d, ^3J = 7.6 Hz), 7.41 (1H, d, ^3J = 7.6 Hz), 6.89 (1H, t, ^3J = 7.6 Hz) (aromatic); 4.46–4.48 (1H, m) (methine); 4.15 (1H, dd, ^3J = 13.3 Hz, ^4J = 4.1 Hz), 3.57 (1H, dd, ^3J = 13.3 Hz, ^4J = 9.6 Hz) (methylene); 1.36 (9H, s) (*tert*-butyl); 1.27 (1H, d, ^3J = 6.1 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d) (MeOH). ^{13}C NMR (DMSO-d_6, ppm) δ: 165.7 (azomethine); 159.6, 142.3, 139.7, 132.6, 132.0, 119.3 (aromatic); 77.6 (methine); 67.0 (methylene); 49.0 (MeOH); 34.2, 30.1 (*tert*-butyl); 20.6 (methyl).

*2.3.5. {S(+)-2-[(2-Oxidopropyl)iminomethyl]-4,6-di-tert-butylphenolato-κ³N,O,O'}dioxidomolybdenum(VI) (**5**)*

Yield 85%. *Anal.* Calc. for $C_{18}H_{27}NO_4Mo{\cdot}CH_3OH$: C, 50.8; H, 7.0; N, 3.1. Found: C, 50.5; H, 6.9; N, 3.2%. IR (KBr, cm^{-1}): 1637 ($\nu_{C=N}$); 929, 897 ($\nu_{Mo=O}$). UV–Vis spectrum in DMSO [λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)]: 284 (6880), 362 (1980). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ ($M^{-1}\,cm^{-1}$)]: 283 (11.67), 368 (4.24). ^{1}H NMR (DMSO-d_6, ppm) δ: 8.70 (1H, s) (azomethine); 7.47 (1H, d, ^3J = 2.5 Hz), 7.40 (1H, d, ^3J = 2.5 Hz) (aromatic); 4.44–4.46 (1H, m) (methine); 4.13 (1H, dd, ^3J = 13.3 Hz, ^4J = 4.1 Hz), 3.55 (1H, dd, ^3J = 13.3 Hz, ^4J = 9.6 Hz) (methylene); 1.37 (9H, s), 1.29 (9H, s) (*tert*-butyl); 1.26 (1H, d, ^3J = 6.1 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d) (MeOH). ^{13}C NMR (DMSO-d_6, ppm) δ: 165.1 (azomethine); 158.8, 140.6, 138.0, 129.1, 128.7, 120.5 (aromatic); 77.4 (methine); 67.0 (methylene); 49.0 (MeOH); 35.2, 34.3, 31.6, 30.1 (*tert*-butyl); 20.4 (methyl).

*2.3.6. {S(+)-2-[(2-Oxidopropyl)iminomethyl]-4,6-dibromophenolato-κ³N,O,O'}dioxidomolybdenum(VI) (**6**)*

Yield 87%. *Anal.* Calc. for $Br_2C_{10}H_9NO_4Mo{\cdot}CH_3OH$: C, 26.7; H, 2.7; N, 2.8. Found: C, 26.6; H, 2.7; N, 2.9%. IR (KBr, cm^{-1}): 1644 ($\nu_{C=N}$); 927, 900 ($\nu_{Mo=O}$). UV–Vis spectrum in DMSO [λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)]: 272 (12950), 361 (4940). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ ($M^{-1}\,cm^{-1}$)]: 281 (10.86), 361 (2.86). ^{1}H NMR (DMSO-d_6, ppm) δ: 8.69 (1H, s) (azomethine); 7.99 (1H, d, ^3J = 2.5 Hz), 7.82 (1H, d, ^3J = 2.5 Hz) (aromatic); 4.52–4.54 (1H, m) (methine); 4.19 (1H, dd, ^3J = 13.3 Hz, ^4J = 4.1 Hz), 3.63 (1H, dd, ^3J = 13.3 Hz, ^4J = 9.6 Hz) (methylene); 1.28 (1H, d, ^3J = 6.1 Hz) (methyl); 4.10 (1H, br s), 3.17 (3H, s) (MeOH). ^{13}C NMR (DMSO-d_6, ppm) δ: 163.0 (azomethine); 157.7, 139.1, 135.9, 123.6, 115.6, 109.7 (aromatic); 78.6 (methine); 67.2 (methylene); 49.0 (MeOH); 20.3 (methyl).

*2.3.7. {S(+)-2-[(2-Oxidopropyl)iminomethyl]naphtholato-κ³N,O,O'}dioxidomolybdenum(VI) (**7**)*

Yield 87%. *Anal.* Calc. for $C_{14}H_{13}NO_4Mo{\cdot}CH_3OH$: C, 46.5; H, 4.4; N, 3.6. Found: C, 46.5; H, 4.4; N, 3.6%. IR (KBr, cm^{-1}): 1625 ($\nu_{C=N}$); 931, 897 ($\nu_{Mo=O}$). UV–Vis spectrum in DMSO [λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)]: 273 (8810), 310 (10710), 378 (3980). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ ($M^{-1}\,cm^{-1}$)]: 283 (7.11), 298 (7.11), 379 (5.60). ^{1}H NMR (DMSO-d_6, ppm) δ: 9.61 (1H, s) (azomethine); 8.40 (1H, d, ^3J = 8.6 Hz), 8.03 (1H, d, ^3J = 9.0 Hz), 7.90 (1H, d, ^3J = 8.0 Hz), 7.62 (1H, t, ^3J = 7.5 Hz), 7.42 (1H, t, ^3J = 7.5 Hz), 7.13 (1H, d, ^3J = 9.0 Hz) (aromatic); 4.54–4.56 (1H, m) (methine); 4.38 (1H, dd, ^3J = 13.3 Hz, ^4J = 4.1 Hz), 3.70 (1H, dd, ^3J = 13.3 Hz, ^4J = 9.6 Hz) (methylene); 1.31 (1H, d, ^3J = 6.1 Hz) (methyl); 4.11 (1H, q), 3.18 (3H, d) (MeOH). ^{13}C NMR (DMSO-d_6, ppm) δ: 159.7 (azomethine); 163.0, 136.1, 133.5, 129.4, 128.6, 128.2, 124.4, 122.3, 121.4, 112.4 (aromatic); 77.5 (methine); 67.6 (methylene); 49.1 (MeOH); 20.3 (methyl).

3. Results and discussion

3.1. Spectroscopic properties

The spectroscopic properties of the complexes, i.e. infrared, UV–Vis, circular dichroism, ^{1}H and ^{13}C NMR data, are listed in Section 2.

Strong C=N vibrations (at 1625–1646 cm^{-1}) are displayed in the IR spectra of the complexes, which may be assigned the azomethine group of the Schiff base ligands coordinated to the dioxidomolybdenum(VI) moiety [22]. In the case of compounds **2** and **3**, with methoxy substituents attached to the aromatic ring of the salicyl moiety, asymmetric and symmetric C—O stretches have been found at *ca.* 1260 and 1040 cm^{-1}, respectively. In addition, complexes **1–7** display two sharp bands at 924–931 and 889–901 cm^{-1} due to the ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O) modes, respectively, which indicate the presence of a *cis*-[$Mo^{VI}O_2$] structure [23].

Circular dichroism and UV–Visible absorption spectra of the molybdenum(VI) complexes were recorded in DMSO. The intraligand π–π^* transitions are strong and appear as very intense bands in the 270–310 nm region with ε_{max} = 6280–12950 $dm^3\,mol^{-1}\,cm^{-1}$. On the other hand, the low-energy absorptions recorded for all compounds between 347 and 385 nm (ε_{max} = 1560–4940 $dm^3\,mol^{-1}\,cm^{-1}$) are assigned to a ligand-to-metal charge transfer (LMCT) transition arising from the phenolate oxygen p_π orbital to an empty d orbital of the molybdenum atom [24]. The circular dichroism spectra revealed the same bands in the 278–284 and 349–385 nm ranges, having the same origin as the electronic spectra with a very strong positive sign of the Cotton effects, *i.e.* with $\Delta\varepsilon$ values in the 7.11–14.31 and 2.86–5.60 $M^{-1}\,cm^{-1}$ ranges, respectively.

The NMR spectra of all the molybdenum(VI) complexes were recorded in DMSO-d_6. The assignment of all the proton and carbon signals were made on the basis of their intensity, coupling patterns and chemical shifts using one- (^{1}H and ^{13}C) and two-dimensional (COSY, gHSQC and NOESY) techniques. The ^{1}H spectra of all the complexes **1–7** show the presence of azomethine proton signals, proving the monocondensation of all the salicylaldehyde derivatives with *S*(+)-1-amino-2-propanol, as reported earlier for the vanadium(V) complexes derived from the same Schiff base ligand [25]. Two-dimensional NMR experiments were used for the complete assignment and identification of all the ^{1}H and ^{13}C signals and for establishing connections and proximity between all protons and carbon atoms. Taking compound **3** as an example, we found the appearance of cross peaks in its COSY spectrum between two methylene protons doublet of doublets (at δ 4.14 and 3.55 ppm) and the methine proton signal at δ 4.43 ppm. Furthermore, a cross-peak between the methyl proton doublet at δ 1.27 and 4.43 ppm signal has been also observed. On the basis of structural information from through space dipole–dipole couplings in the NOESY spectra, cross-peaks between the signals of two of the methylene protons (δ 4.14 and 3.55 ppm) and the azomethine proton at δ 8.67 ppm have been found. Finally, just as expected, no corresponding cross-peaks between the signals of the azomethine proton and the methyl proton (δ 1.27 ppm) or the methine proton (δ 4.43 ppm) could be observed. Moreover, the coordination of one methanol molecule to the molybdenum atom in the case of all complexes was confirmed by the appearance of signals at δ 3.17–3.18 and 4.10–4.12 ppm.

3.2. Catalytic activity studies

3.2.1. Sulfoxidation

The catalytic activity of the dioxidomolybdenum(VI) complexes **1–7** under optimized reaction conditions for the enantioselective oxidation of model prochiral sulfides, *i.e.* methyl phenyl sulfide (thioanisole) and benzyl phenyl sulfide into their corresponding sulfoxides (Fig. 2) have been tested. A slight excess of 1.10 equivalents of aqueous 30% H_2O_2 was used as an oxidant basing on the sulfide substrate. Furthermore, optimized amounts of 1 mol% of catalyst were used in the sulfoxidation reactions, based on a substrate in a mixture of CH_2Cl_2 and CH_3OH (7:3). The best enantioselectivities were achieved with dichloromethane, but methanol was necessary for a better mixing of the aqueous oxidant with the halogenated solvent [26]. Moreover, protic solvents can significantly enhance yield and selectivity of sulfoxide [27]. The catalytic studies results are listed in Table 1.

Complexes **1**, **2**, **3** and **7** showed the best results as catalysts in the oxidation of thioanisole (Table 1, entries 1, 2, 3 and 7). All the molybdenum(VI) catalysts yielded 79–93% overall conversion

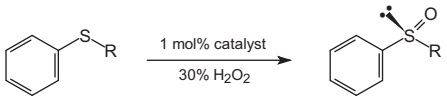

Fig. 2. Sulfoxidation of thioethers catalyzed by the molybdenum(VI) complexes.

Table 1
Catalytic oxidation of PhSMe and PhSBz by aqueous 30% H_2O_2 in the presence of 1 mol % of the molybdenum(VI) Schiff base complexes as catalysts.

Entry	Catalyst	Substrate	Yield (%)	*T* (°C)	*t* (min)	TON	*ee*[a] (%)
1	**1**	PhSMe	88	Rt	45	88	6
2	**2**	PhSMe	93	Rt	45	93	11
3	**3**	PhSMe	90	Rt	45	90	9
4	**4**	PhSMe	79	Rt	45	79	3
5	**5**	PhSMe	78	Rt	45	78	rac
6	**6**	PhSMe	74	Rt	45	74	rac
7	**7**	PhSMe	82	Rt	45	82	7
8	**1**	PhSBz	73	Rt	45	73	3
9	**2**	PhSBz	84	Rt	45	84	6
10	**3**	PhSBz	79	Rt	45	79	5
11	**7**	PhSBz	74	Rt	45	74	3
12	**1**	PhSMe	93	−20	210	93	11
13	**2**	PhSMe	97	−20	210	97	17
14	**3**	PhSMe	95	−20	210	95	15
15	**7**	PhSMe	91	−20	210	91	12

[a] All sulfoxides are in the *S* configuration.

within 45 min reaction time and enantiomeric excesses of up to 11% for the *S*-configured sulfoxide were obtained. We also employed a substrate with a more bulky substituent, *i.e.* benzyl phenyl sulfide. In this case (Table 1, entries 8–11) the overall yield of benzyl phenyl sulfoxide was slightly lower (73–84%) and a considerable decrease in the enantioselectivities (⩽6%) was noticed. When the sulfoxidation was carried out at −20 °C with **1**, **2**, **3** and **7** as catalysts, the enantioselectivities significantly increased to value of 11–17% for methyl phenyl sulfide and also the conversions improved up to 97% after 210 min reaction time (Table 1, entries 12–15). It was reported earlier by Mimoun et al. that a sufficient nucleophilic center is very important for the catalytic oxidation processes of a number of types of organic substrates [28]. Compounds **2** and **3** have achieved the best enantioselectivity in comparison to the remaining catalysts. In our opinion, the reason for such behavior is the highest electron-donating resonance effect of the ortho- and para-substituted methoxy groups, where a higher electron density on the phenolate oxygen atom is observed, helping to improve attainment of sufficient nucleophilicity of the metal centre.

In general, when a smaller steric demand of the substrate was involved, *i.e.* using thioanisole as compared to benzyl phenyl sulfide, much better results in both yield and enantioselectivity of the corresponding sulfoxide were obtained in the sulfoxidation reactions. In addition it is noteworthy that under the given conditions no over oxidation to the sulfone could be observed.

3.2.2. Oxidation of styrene

The oxidation of styrene with complexes **1**–**7** as catalysts in 1,2-dichloroethane was performed in the presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as an oxidant. Under these reaction conditions styrene oxide, 1-phenylethane-1,2-diol, phenylacetaldehyde, benzaldehyde and benzoic acid were obtained as the oxidation products (Fig. 3). To achieve optimized reaction conditions for the maximum conversion of styrene oxidation, different parameters were taken under consideration, *i.e.* amount of catalyst (0.5, 1 and 2 mol%) and oxidant (1:1, 2:1 and 3:1 M ratios to substrate), different solvents and temperature of

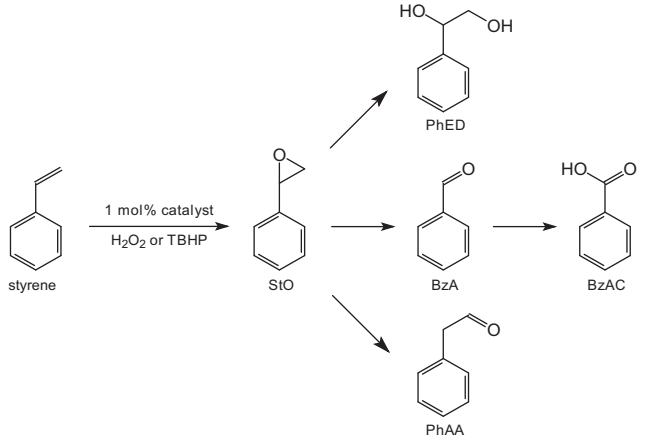

Fig. 3. Various oxidation products of styrene catalyzed by the molybdenum(VI) complexes.

the reaction mixture with the representative catalyst, **2**, were tested.

Considering the highest conversion and reaction rate, we found 1,2-dichloroethane (DCE) to be the best solvent during our examination of olefin oxidation in different solvents, such as methanol, ethanol, acetonitrile, chloroform, methylene chloride and 1,2-dichloroethane [24,29]. Moreover, as reported earlier [30], it was concluded that a higher reactions temperature can also be responsible for obtaining better yields and reaction rates.

To study the effect of the amount of oxidant, *i.e. tert*-butyl hydroperoxide (TBHP) in decane or aqueous 30% H_2O_2, to styrene, different molar ratios (1:1, 2:1 and 3:1) styrene (1.00 mmol) and catalyst **2** (0.010 mmol) were employed in DCE (10 ml), and the oxidation was carried out with a contact time of 45 min at 80 °C. Taking the 1:1 M ratio of H_2O_2 to styrene, no more than 18% conversion was observed. The conversion improved to 30% with a 2:1 ratio, and finally with 3:1 M ratio a maximum of 32% conversion was achieved. Further addition of the oxidant did not improve the overall conversion yield, therefore a 2:1 M ratio has been shown to be adequate. When TBHP was taken into consideration, we tested the same molar ratios of TBHP:styrene (1:1 to 2:1 and 3:1) and the conversion changed from 32 to 53 and 55%, respectively. Addition of this oxidant in higher molar ratios improved the conversion only marginally, so again the 2:1 M ratio was chosen for further studies.

Continuing the optimization of the oxidation conditions, different amounts of catalyst **2** (0.5, 1 and 2 mol%) with the 2:1 M ratio of oxidant to styrene have been studied. Adding 0.5 mol% catalyst, only 12% (with 30% H_2O_2) and 27% (with TBHP) conversion was achieved. Furthermore, when 1 and 2 mol% of the catalyst were added to the reaction mixture, we found very similar results, with 30 and 53% conversion for 30% H_2O_2 and TBHP, respectively, for 45 min of contact time. With the above results we concluded to perform all oxidation reaction with 1 mol% of catalysts. Under the same conditions, reactions without the presence of any catalysts were tested, giving only *ca.* 3–5% conversion for both oxidants.

The selectivity for all the reaction products and the percentage conversion of styrene are summarized in Table 2. Using *tert*-butyl hydroperoxide (TBHP) in decane as an oxidant, under the optimized reaction conditions, all the complexes gave significantly higher conversions (68–76%) in comparison to the other earlier reported dioxidomolybdenum(VI) complex with a Schiff base derived from 2-[(1-hydroxy-2-methylpropane-2-ylimino)methyl]-naphthol, which gave 50% conversion, but with less excess of the oxidant and only 0.1 mol% of the catalyst [30]. The selectivities in

Table 2
Catalytic oxidation of styrene by aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) in the presence of 1 mol% molybdenum(VI) Schiff base complexes.

Entry	Catalyst	Oxidant	Conv. (%)	Solvent	TON	Product selectivity[a] (%)				
						StO	BzA	BzAC	PhAA	PhED
1	**1**	H_2O_2	17	DCE	17	68	28	–	–	4
2	**2**	H_2O_2	30	DCE	30	59	32	–	–	9
3	**3**	H_2O_2	24	DCE	24	56	33	–	–	11
4	**4**	H_2O_2	27	DCE	27	58	38	–	–	4
5	**5**	H_2O_2	26	DCE	26	55	39	–	–	6
6	**6**	H_2O_2	20	DCE	20	51	42	–	–	7
7	**7**	H_2O_2	23	DCE	23	55	40	–	–	5
8	**1**	TBHP	68	DCE	68	85	14	–	–	1
9	**2**	TBHP	73	DCE	73	77	19	–	–	4
10	**3**	TBHP	76	DCE	76	81	17	–	–	2
11	**4**	TBHP	70	DCE	70	84	14	–	–	2
12	**5**	TBHP	71	DCE	71	78	19	–	–	3
13	**6**	TBHP	70	DCE	70	85	13	–	–	2
14	**7**	TBHP	74	DCE	74	73	24	–	–	3
15	**1**	H_2O_2	26	MeCN	26	7	79	1	6	7
16	**2**	H_2O_2	29	MeCN	29	8	83	1	3	5
17	**3**	H_2O_2	28	MeCN	28	5	85	1	4	5
18	**4**	H_2O_2	21	MeCN	21	7	80	1	6	5
19	**5**	H_2O_2	30	MeCN	30	6	78	1	7	8
20	**6**	H_2O_2	27	MeCN	27	4	84	1	4	7
21	**7**	H_2O_2	18	MeCN	18	5	88	1	4	2
22	**1**	TBHP	88	MeCN	88	25	65	5	2	3
23	**2**	TBHP	91	MeCN	91	29	59	7	2	3
24	**3**	TBHP	93	MeCN	93	34	56	7	3	4
25	**4**	TBHP	79	MeCN	79	31	61	4	2	2
26	**5**	TBHP	81	MeCN	81	33	55	5	3	4
27	**6**	TBHP	85	MeCN	85	25	64	6	2	3
28	**7**	TBHP	82	MeCN	82	23	67	4	2	4

[a] StO – styrene oxide, BzA – benzaldehyde, BzAC – benzoic acid, PhAA – phenylacetaldehyde, PhED – 1-phenylethane-1,2-diol.

the case of all the molybdenum(VI) complexes are rather similar and they are generally distinctly more selective toward styrene oxide (73–85%) than benzaldehyde (13–24%). Furthermore, their selectivity against 1-phenylethane-1,2-diol is relatively low (1–4%). Judmaier et al. [23] described some new dioxidomolybdenum(VI) Schiff base complexes with pendant OMe donor arms where two ligands coordinate in a bidentate manner to the metal center, and these were used as catalysts in similar reactions but in chloroform at 50 °C. In this case, 71–75% conversions were obtained in 5 h of reaction time with 97–98% styrene oxide selectivity after 24 h. When a one-pot synthesis by reductive amination was employed, dimeric dioxidomolybdenum(VI) complexes with one Schiff base in a tridentate manner were obtained. Catalytic reactions with these complexes under the same reaction conditions gave only 35% conversion of styrene in 5 h and 44% in 24 h of reaction time [31]. On the other hand, the catalytic properties of dioxidomolybdenum(VI) complexes with naphtholate-oxazoline ligands for the epoxidation of styrene in DCE at 80 °C have been also reported [32]. At low catalyst loadings of 0.05 mol% with TBHP after 6 h of reaction time, 76–83% conversion with 90–92% styrene oxide selectivity resulted.

The catalytic oxidation of styrene has also been performed by us under the same reaction conditions, but with aqueous 30% H_2O_2 acting as an oxidizing agent. Distinctly lower conversion in the same contact time was found (17–30%). Moreover, much lower selectivity against styrene oxide has been observed (51–68%) than in the case of TBHP. Also, with H_2O_2 the catalysts are much more selective toward benzaldehyde (28–42%) and 1-phenylethane-1,2-diol (4–11%).

For a comparison of catalysts **1**–**7** to chiral tridentate oxidovanadium(V) complexes with the same Schiff base ligands, reported by us earlier [25], we have also tested the catalytic activity for the oxidation of styrene using 1 mol% of the catalysts in an optimized 5 h of reaction time, 3:1 oxidant:styrene molar ratio at 80 °C, but in acetonitrile as the solvent. Generally, the conversion is slightly better in MeCN, using both H_2O_2 and TBHP as oxidizing agents, and comparable with vanadium(V) complexes. On the other hand, the selectivity, in the case of molybdenum(VI) and vanadium(V) complexes, is very similar and both complexes with both metals are generally distinctly more selective toward benzaldehyde (*ca.* 60%) than styrene oxide (20–30%) using TBHP. The selectivity of the other oxidation products is also comparable and varies in the order: benzoic acid > 1-phenylethane-1,2-diol > phenylacetaldehyde. When aqueous 30% H_2O_2 was used as an oxidant under the same styrene oxidation conditions, distinctly lower conversions (below 30%) for all of the catalysts have been noticed. As can be also seen, the conversion of styrene is distinctly lower than with TBHP, but the selectivity against benzaldehyde is very impressive (over 78%) in all cases. The selectivity for the other oxidation product is below 10%. In the presence of H_2O_2, a strong oxidizing agent, oxidation of styrene results in styrene oxide in the first step, but further reaction, via nucleophilic attack of the oxidant to styrene oxide followed by the cleavage of the intermediate hydroperoxystyrene, is very fast, converting the product into benzaldehyde [33]. Moreover, the formation of benzaldehyde is probably facilitated via a radical mechanism by direct oxidative cleavage of the styrene side-chain double bond. A significant amount of water in aqueous 30% H_2O_2 can be blamed for the decomposition of the catalyst and thus the very low conversion of styrene. Formation of 1-phenylethane-1,2-diol by the hydrolysis of styrene oxide is also caused by the presence of water. The other processes, although surely much slower, can be responsible for the formation of benzoic acid in the further oxidation of benzaldehyde or isomerisation of styrene oxide to phenylacetaldehyde.

3.2.3. Oxidation of cyclohexene

The catalytic activity of complexes **1–7** has been tested for the oxidation of cyclohexene in the presence of *tert*-butyl hydroperoxide (TBHP) in decane or aqueous 30% H_2O_2 as an oxidant, giving four products, *i.e.* cyclohexene oxide, cyclohexane-1,2-diol, 2-

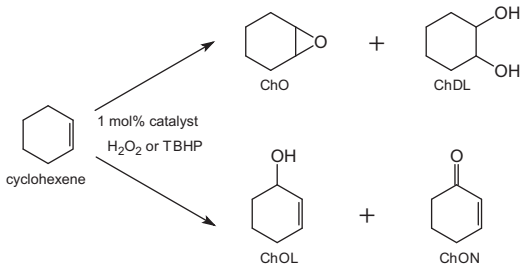

Fig. 4. Various oxidation products of cyclohexene catalyzed by the molybdenum (VI) complexes.

Table 3
Catalytic oxidation of cyclohexene by aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) in the presence of 1 mol% molybdenum(VI) complexes in DCE.

Entry	Catalyst	TON	Oxidant	Conv. (%)	Product selectivity[a] (%)			
					ChO	ChOL	ChON	ChDL
1	**1**	60	H_2O_2	60	55	18	23	4
2	**2**	56	H_2O_2	56	42	16	33	10
3	**3**	51	H_2O_2	51	50	12	31	7
4	**4**	61	H_2O_2	61	46	10	37	6
5	**5**	57	H_2O_2	57	38	26	33	3
6	**6**	60	H_2O_2	60	46	12	40	2
7	**7**	63	H_2O_2	63	56	10	29	5
8	**1**	72	TBHP	72	74	26	–	–
9	**2**	83	TBHP	83	82	18	–	–
10	**3**	81	TBHP	81	85	15	–	–
11	**4**	85	TBHP	85	71	29	–	–
12	**5**	80	TBHP	80	69	31	–	–
13	**6**	77	TBHP	77	72	28	–	–
14	**7**	79	TBHP	79	76	24	–	–

[a] ChO – cyclohexene oxide, ChOL – 2-cyclohexen-1-ol, ChON – 2-cyclohexen-1-one, ChDL – cyclohexane-1,2-diol.

cyclohexene-1-ol and 2-cyclohexene-1-one (Fig. 4). The formation of all these products, conversion and selectivity are presented in Table 3.

Optimization of the reaction conditions has been performed with complex **2** as a representative catalyst, as in the case for the oxidation of styrene. Different amounts of the catalyst (0.5, 1 and 2 mol%) and both oxidants (1:1, 2:1 and 3:1 M ratios to cyclohexene), different solvents and temperature of the reaction mixture have been also employed.

The best results were found when 1,2-dichloroethane (DCE) and 80 °C were chosen to run the catalytic reactions. Three different molar ratios of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) to cyclohexene, *i.e.* 1:1, 2:1 and 3:1, have been studied. Cyclohexene (1.00 mmol) and catalyst (0.010 mmol) were taken in DCE (10 ml), and the reaction was carried out for 1 h of contact time at 80 °C. At a 1:1 H_2O_2 to styrene molar ratio, a maximum of 27% conversion was achieved. Increasing the ratio to 2:1 improved the conversion to 56%, while a 3:1 ratio showed a maximum of 57% conversion. Further increment of H_2O_2 improved the conversion only marginally, therefore a 2:1 ratio was considered as adequate. In the case using TBHP as an oxidizing agent, increasing the TBHP: cyclohexene molar ratio from 1:1 to 2:1 and 3:1 improved the conversion from 46 to 83 and 85%, respectively. As in the previous case, there was no significant conversion improvement upon further addition of the oxidant.

Similarly, for different amounts of catalyst (0.5, 1 and 2 mol%) with a 2:1 M ratio of oxidant to cyclohexene and under the above reaction conditions, 0.5 mol% gave only 18% (H_2O_2) and 34% (TBHP) oxidative conversion, while 1 mol% and 2 mol% of the catalyst showed a maximum conversion of 56% for H_2O_2 and 83% for TBHP. Thus, 1 mol% of catalyst may be considered sufficient to run the reaction under the above conditions. A blank reaction under the above reaction conditions gave *ca.* 4–5% conversion with both oxidants.

For the oxidation reactions with **1**–**7** as catalysts and aqueous 30% H_2O_2 as an oxidant, 51–63% conversion in 5 h of contact time was found. On the other hand, the conversion of styrene under the same reaction conditions is distinctly lower. The selectivity against cyclohexene oxide (38–56%) is slightly more noticeable than against 2-cyclohexen-1-one (23–40%), 2-cyclohexen-1-ol (10–26%) and cyclohexane-1,2-diol (2–10%). The preferential attack of the activated C—H bond over the C=C bond may be responsible for the formation of the allylic oxidation products (2-cyclohexen-1-ol and 2-cyclohexen-1-one) with higher selectivity [34].

Using the same optimized reaction conditions for the catalytic oxidation of cyclohexene, but with *tert*-butyl hydroperoxide (TBHP) in decane as the oxidant, catalysts **1**–**7** gave 85% conversion. In contrast to the catalytic reactions with H_2O_2, complexes **1**–**7** are distinctly more selective toward cyclohexene oxide (69–85%). The remaining amounts of 2-cyclohexene-1-ol found in the reaction mixture are by-products. Very similar results were reported by Rayati et al. [24] with MoO_2{hnaphnptn} – a dioxidomolybdenum(VI) complex with a symmetrical tetradentate Schiff base.

3.2.4. Reactivity of the catalysts with H_2O_2

A variety of molybdenum(VI) complexes have been found to react with H_2O_2 to form the corresponding oxidoperoxido complexes. Although the isolation of $[MoO(O_2)]^{2+}$ Schiff base compounds was unsuccessful, the stepwise addition of a DMSO solution of H_2O_2 to the dioxidomolybdenum(VI) complex solutions and monitoring any UV–Vis spectral changes allowed us to establish the generation of such oxidoperoxido species and shed some light on the mechanism of these catalytic reactions. In an example procedure, the spectra were recorded after successive addition of one drop portions of aqueous 30% H_2O_2 (1.70 g, 13 mmol) dissolved in 5 ml of DMSO to 15 ml of an 8.1×10^{-5} M solution of catalyst **3** in DMSO and the resultant spectroscopic changes are presented in Fig. 5. Such a titration with a dilute solution of complex **3** caused a decrease with only a marginal change in intensity of the 375 nm band, which belongs to a weak ligand-to-metal charge transfer (LMCT) transition. On the other hand, the strong intraligand π–π^* transition, with a 276 nm band, increases its intensity considerably with a small shift to 265 nm, and then it finally disappears. In our opinion these changes indicate the inter-

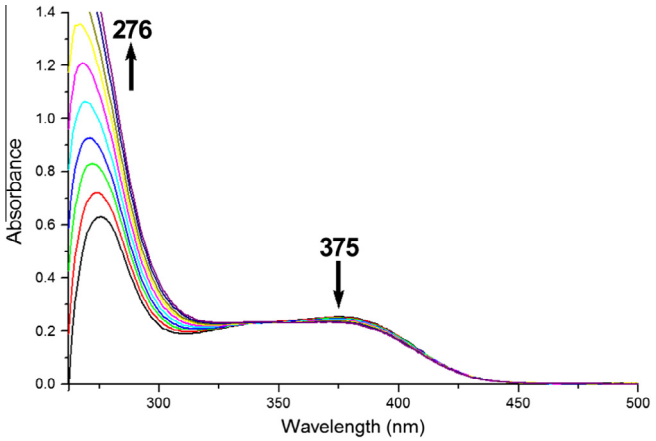

Fig. 5. Spectral changes observed during titration of catalyst **3**. The spectra recorded after successive addition of one drop portions of aqueous 30% H_2O_2 (1.70 g, 15 mmol) dissolved in 5 ml of DMSO to 15 ml of an 8.1×10^{-5} M solution of **3** in DMSO.

action of complex **3** with hydrogen peroxide and the plausible formation of the oxidoperoxidomolybdenum(VI) complex in DMSO, which in the catalytic reaction finally transfers oxygen to an appropriate organic substrate to give the various oxidation products.

4. Conclusion

New chiral dioxidomolybdenum(VI) complexes derived from Schiff bases, products of a single condensation of salicylaldehyde and its derivatives with *S*(+)-1-amino-2-propanol, were synthesized and characterized by UV–Vis, CD, IR, one- (^{1}H, ^{13}C) and two-dimensional (COSY, NOESY, gHSQC) NMR spectroscopy. Moreover, the catalytic properties of the chiral catalysts for the oxidation of organic sulfides (thioanisole and benzyl phenyl sulfide) and olefins (styrene and cyclohexene) have been studied.

The results of sulfoxidation studies showed that the overall yield and enantiomeric excess distinctly depend on the nature of the catalyst, *i.e.* the electron density at the metal center. Moreover, when a bulky substituent was involved in the structure of the sulfide, with large steric demand, both the activity and enantioselectivity dropped sharply. Finally, the sulfoxidation reactions carried out at much lower temperatures result in both better yields and enantioselectivities.

The catalytic potential of the dioxidomolybdenum(VI) complexes for the oxidation of olefins was investigated, and a comparison to similar oxidovanadium(V) catalysts was also studied, choosing the oxidation of styrene and cyclohexene as model reactions. These complexes are able to catalyze the oxidative conversion of styrene to styrene oxide and benzaldehyde as the main products, and cyclohexene to cyclohexene oxide and its successive by-products in the presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide in decane. The oxidation of styrene after 5 h of reaction time in DCE at 80 °C with H_2O_2 can give five different products, usually with a bigger excess of styrene oxide and benzaldehyde, but low conversion. On the contrary, *tert*-butyl hydroperoxide proved to be an excellent oxidant giving even 85% conversion of styrene, with styrene oxide as the main product. Moreover, oxidation of styrene in acetonitrile gave similar results as for oxidovanadium(V) complexes with the same Schiff base ligand. In the oxidation of cyclohexene, even significantly higher conversions were found than for styrene, especially when H_2O_2 was employed as the oxidant. However, when TBHP was employed, the selectivity against cyclohexene oxide achieved 85% with small amounts of 2-cyclohexene-1-ol as the by-product.

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