Novel Schiff-base complexes of methyltrioxorhenium (VII) and their performances in epoxidation of cyclohexene

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ABSTRACT

Methyltrioxorhenium (MTO) forms complexes with Schiff-bases derived from 2-pyridinecarboxaldehyde and amines. These complexes were isolated and fully characterized by NMR, IR, UV–Vis, EA, MS. Two were analyzed by X-ray crystallography, which showed that the compounds display distorted octahedral geometry in the solid state with a *trans*-position of Schiff-base ligand. The characterized results indicated that the more Lewis basic the ligand is, the stronger the metal–ligand interaction between the rhenium atom and the ligand. The complexes displayed high catalytic activity and selectivity when applied to the epoxidation of cyclohexene with urea hydrogen peroxide adduct (UHP) as oxidant in methanol, but poor performances with hydrogen peroxide (30%) as oxidant due to their decomposition. Experimental results revealed that the MTO Schiff-base complexes are, in general, more sensitive to water than MTO itself. Moreover, large excess of ligand is detrimental to the catalytic performance as it leads to the decomposition of the complexes.

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1. Introduction

Methyltrioxorhenium (CH_3ReO_3, MTO) has outstanding catalytic properties in numerous oxy functionalization reactions [1–9,10]. Among all of them MTO-catalyzed epoxidation of olefins with hydrogen peroxide as oxidant has received particular attention since the process is environmentally friendly [4,11]. However, due to the Lewis acidity of the rhenium center, a major limitation of this system is the opening of the epoxide ring leading to the formation of diols in the presence of water during the reaction [2,3,12]. Several methods have been suggested to overcome this problem. An efficient procedure developed to avoid this side reaction requires the use of urea hydrogen peroxide adduct (UHP) as oxidant, which enables epoxidation to be carried out in non-aqueous media [13–15]. A second alternative is based on the tendency of organorhenium (VII) oxides to form Lewis acid–base adducts to increase their coordination numbers [16–19]. Some research revealed that the aromatic N-base ligands work by coordinating to the metal center, thereby reducing the Lewis acidity of the catalyst and accelerating the catalytic reactions additionally [17,18,20–26]. Lewis base adducts of MTO were first mentioned in 1989 by Herrmann et al. [27,28]. It was reported that MTO forms trigonal-bipyramidal adducts with aromatic N-donor bases and certain Schiff-bases [17,29–32]. Several bidentate Lewis base adducts of MTO have been synthesised and fully characterized too [33,34]. Results

showed that MTO forms (distorted) octahedral adducts with bidentate Lewis bases, e.g. 2,2-bipyridine and 1,10-phenanthroline [33]. The complexes showed high catalytic activity and selectivity in the epoxidation of olefins with H_2O_2 as oxidant (Scheme 1).

On the other hand, Schiff-bases are of great importance in homogeneous and heterogeneous reactions. They are easily synthesised by the condensation of primary amines and aldehydes or ketones and form complexes with transition metals via nitrogen lone pair electrons. The catalytic activity of metal complexes has been analyzed critically in various reactions such as polymerization, oxidation, epoxidation, reduction of ketones, allylic alkylation and Michael addition reactions [35]. The activity of these complexes varied with the type of ligands, coordination sites and metal ions.

Despite the large numbers of Lewis base adducts of MTO described in the literature, only a few examples of complexes with Schiff-bases have been reported [32,33]. Considering the outstanding catalytic properties of MTO and the excellent corresponding ability of Schiff-bases, it is very interesting to synthesize some Schiff-bases especially the bidentate ones and their complexes with MTO. To our knowledge, 2-pyridinecarboxaldehyde like other aldehydes is also able to condense with amines to form Schiff-bases. Combined with the nitrogen atom in the pyridine moiety the generated Schiff-bases can serve as bidentate ligands which can coordinate with metal atoms to form the corresponding complexes as shown in Scheme 2. Therefore, herein we first synthesize some Schiff-bases from 2-pyridinecarboxaldehyde and their corresponding MTO complexes. Then the complexes are applied to the
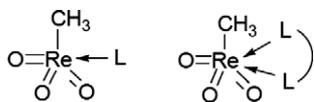
Scheme 1. Lewis base adducts of MTO.

R=Aryl or Alkyl
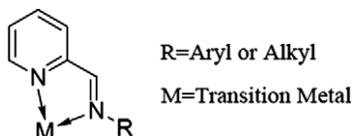
M=Transition Metal

Scheme 2. Complex of transition metal with Schiff-base.

epoxidation of cyclohexene with UHP and 30% hydrogen peroxide as oxidants, respectively.

2. Results and discussions

2.1. Synthesis and spectroscopy

The reaction of primary amine with 2-pyridinecarboxaldehyde to afford the corresponding pyridinecarboxaldimine ligand is a well-known route to obtain bidentate ligands of nitrogen [36,37]. By changing the amine it is allowed to receive ligands as needed and subsequently to prepare metal complexes with different physical and chemical properties. Herein, 2-pyridinecarboxaldehyde reacted with the primary amines smoothly to afford the Schiff-bases as described in literature [38]. Complexes I–IV (see Scheme 3) were synthesised by treating MTO with pyridinecarboxaldimine in methanol at room temperature. All complexes were isolated as yellow crystals in yields 75–80%. In comparison with other N-coordinated Lewis base adducts [33,35], compounds I–IV are slightly more sensitive to moisture and temperature. Their color changes from yellow to black green slowly when exposed to air, which can be avoided by storing under a water free nitrogen atmosphere.

In the IR spectra of compounds I–IV, the symmetric Re=O stretching vibrations appear within a narrow interval of 938–945 cm^{-1}, and the asymmetric stretching vibrations occur between 909 and 912 cm^{-1}. Compared to the vibrations of non-coordinated MTO, the Re=O bands of compounds I–IV are strongly red-shifted due to the pronounced donor capacity of the respective ligands in the solid state. The additional electron density donated from the ligand to the rhenium (VII) center generally reduces the bond order of the Re=O bonds. Besides, differences of 24–35 cm^{-1} between v_s (Re=O) and v_{as} (Re=O) are observed in the above complexes. It was reported that the size of the difference between the symmetric and asymmetric stretching is related to the geometry of the Schiff-bases-MTO adducts. In the literatures, the differences of vibrations of free MTO [33], monodentate and bidentate adducts of MTO [32,33] are 33 cm^{-1}, 60–80 cm^{-1} and 20–27 cm^{-1}, respectively, which correspond to the tetrahedral, trigonal-bipyramidal, octahedral coordination geometry, respectively. In some special cases, the

differences can become very large (167 cm^{-1}) due to the rather asymmetric coordination of the rhenium atom [31]. Therefore, we conclude that complexes I–IV have an octahedral geometry, which was confirmed by the crystal structure analysis late.

Generally, C=N has a medium or strong band around 1630 cm^{-1} for its stretching vibrations in an undisturbed situation in the FT-IR spectra [31,39]. For the synthesised Schiff-bases (a–d) strong bands between 1626 and 1650 cm^{-1} were observed and the corresponding bands were located between 1621 and 1650 cm^{-1} slightly lower than those of the Schiff-bases (shown in Table 1).

The UV–Vis absorption spectra of compounds a–d and I–IV in methanol at room temperature are shown in Table 2. The absorption bands between 228 and 236 nm are derived from the $\pi \rightarrow \pi^*$ transition of imine group in the Schiff-bases, and the bands between 271 and 283 nm are due to the $\pi \rightarrow \pi^*$ transition in the pyridine moiety [40]. The maximum absorptions at 325 and 341 nm are attributed to $\pi \rightarrow \pi^*$ transition of the phenyl moiety in the ligands of complexes III and IV, respectively. The above results indicate that the maximum absorption is proportional to the coordination capacity of the ligand, which is determined by the combined results of steric and electronic effects of the group R in the ligand as shown in Scheme 3. More detailed data are presented in Table 2. After complexation to MTO, all maximum absorption band exhibits a slight blue-shifted in all cases compared with that of a free ligand. This can be attributed to the addition of Re (VII) in the conjugated system.

Initially, the proton signals originating from the ReCH$_3$ group of non-coordinated MTO was observed at 2.67 ppm, but after complexation to Schiff-bases, the methyl signal was high-field shifted in all cases (see Table 3). It has been reported that the magnitude of these shifting is directly related to the electron donor character of the ligand. The higher the electron density given to the Re(VII) center by the donor ligand, the larger the high-field shift of the ^{1}H NMR signal in the ReCH$_3$ group [41]. Indeed, electron-rich pyridinecarboxaldimine derivatives induced the strong up-field shift of the methyl signal. It is noteworthy that compounds I and II show chemical shift changes of the methyl signal around 1.5 ppm relative to non-coordinated MTO, however, the corresponding magni-

Table 1
Selected IR spectroscopic data of Schiff-bases and MTO adducts.

Compound	v/cm^{-1}				
	Imine	Pyridine	ReO$_3$		
	v (C=N)	v (C=N)	v_{as}	v_s	$v_s–v_{as}$
MTO	–	–	965	998	33
a	1650	1587	–	–	–
I	1650	1600	912	938	26
b	1647	1588	–	–	–
II	1643	1598	910	934	24
c	1623	1588	–	–	–
III	1621	1590	910	945	35
d	1626	1584	–	–	–
IV	1622	1599	909	944	33
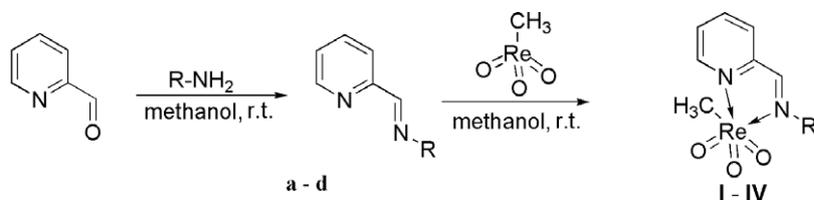
R= n-Propyl (a, I); R= iso-Propyl (b, II); R= Phenyl (c, III); R= p-Methoxyphenyl (d, IV).

Scheme 3. Route for the synthesis of Schiff-bases (a–d) and their MTO complexes (I–IV).

Table 2
The UV–Vis spectroscopic data of the Schiff-bases and the MTO complexes.

Compound	λ_{max}/nm[a]		
	Imine ($\pi \to \pi^*$)	Py ($\pi \to \pi^*$)	Ph ($\pi \to \pi^*$)
a	231	272	–
I	228	271	–
b	231	272	–
II	229	271	–
c	236	281	325
III	236	278	325
d	238	289	342
IV	238	283	341

[a] Tested in methanol.

Table 3
Selected ^{1}H NMR spectroscopic data of Schiff-base and MTO complexes **I–IV**.

Compound	δ (ReCH$_3$)	δ (C=NH)
MTO	2.67s	
a	–	8.38 s
I	1.36s	8.61 s
b	–	8.41 s
II	1.12s	8.76 s
c	–	8.60 s
III	1.88s	8.61 s
d	–	8.63s
IV	1.85s	8.66s

tudes of **III** and **IV** are only about 0.8 ppm in ^{1}H NMR spectra. The results indicate that alkyl groups have stronger electron donation capacity than aromatic ones in the synthesised bidentate ligands. The ^{1}H NMR signals of the imine group and pyridine moiety of compounds **I–IV** are shifted to lower field, in agreement with a changed coordination situation.

In the FAB mass spectra of compounds **III** and **IV**, only the peaks of the Schiff-base ligands can be observed. In contrast, less information could be obtained from FAB MS for compounds **I** and **II**. Whereas the ESI mass spectra of compounds **I–IV** show the peaks of the Schiff-base ligand and the MTO moiety separately, although no molecular peaks of the complete molecules can be observed.

2.2. Crystal structure examinations

The crystal structures of complexes **I** and **III** in the solid state were examined and they are shown in Figs. 1 and 2. In addition, the selected bond lengths and angles are listed in Table 5 and Table 6. Both complex **I** and **III** display an octahedral geometry with a pyramidal *facial* arrangement of the three oxygen atoms and a *trans*-position of the ligand. Two double-bonded oxygen atoms and the ligand occupy the equatorial positions, which can be defined as the plane of the five-membered metallacycle Re1–N1–C5–C6–N2, while the methyl group and the remaining oxygen atom reside in the apical sites. The same arrangement is found for the reported complexes derived from 2,2′-bipyridine and MTO [33]. The Re=O bond distances of 1.719(4) and 1.724(4) Å in the case of complex **I** are very similar to those of all known Re (VII) oxo complexes containing an Re=O double bond [33,42].

The Re–N bond distances are obviously governed by electronic effect. In complex **I**, the N(pyridine)–Re and N(imine)–Re length are 2.274(5) Å and 2.257(5) Å, respectively. In complex **III**, the corresponding Re–N lengths are respectively, 2.285(6) and 2.329(6) Å, longer than those in complex **III**, which indicates that the larger conjugated system of the ligand can lead to a weak N–Re bonding interaction by reducing electron density on nitrogen atom and, therefore, supporting the spectroscopic results given above. The
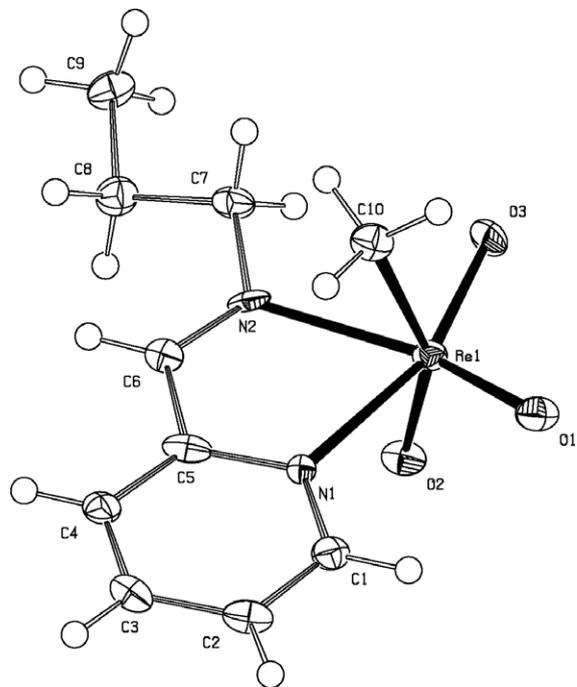

Fig. 1. PLATON drawing of complex **I** in the solid state. Thermal ellipsoids are at the 50% probability level.
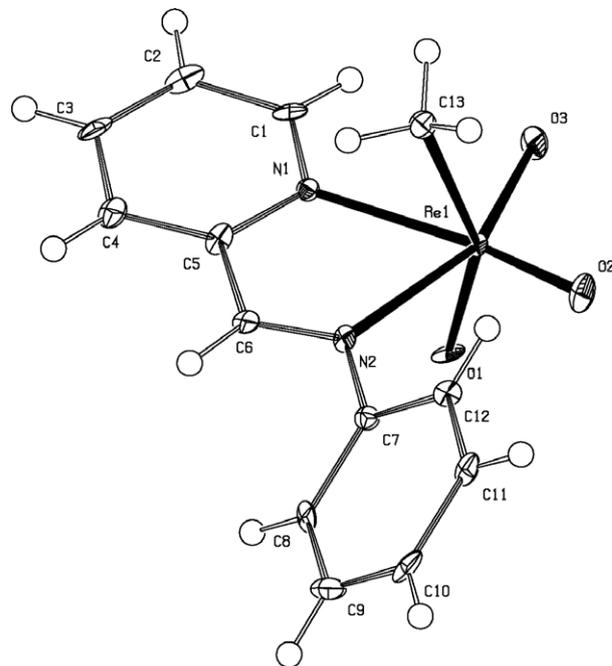

Fig. 2. PLATON drawing of complex **III** in the solid state. Thermal ellipsoids are at the 50% probability level.

imine C6–N2 distances in complex **I** and **III** are 1.280 (8) and 1.268(10) Å, respectively, which are in the range of accepted carbon–nitrogen double bonds [38].

The coordination of Schiff-base ligands to MTO is governed not only by electronic but also by steric effects. The phenyl group in the imine N-position of compound **III** generates even greater distortion with the neighboring oxygen atom (O2) spin as much as 42.7° away from the equatorial plane, comparing to the angle of 21.4° between the plane of N2–C7–C8–C9 and equatorial position in

Table 4
Crystal data and details of the structure determination.

Compound	I	III
Empirical formula	$C_{10}H_{15}N_2O_3Re$	$C_{13}H_{13}N_2O_3Re$
Formula weight (g/mol)	397.44	431.46
Temperature (K)	113(2)	113(2)
Wave length (Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
Crystal system	Orthorhombic	Triclinic
Space group	$Pbca$	$P\bar{1}$
Crystal size (mm)	$0.14 \times 0.18 \times 0.20$	$0.12 \times 0.18 \times 0.20$
Crystal color/shape	Yellow/needle	Yellow/plate
a (Å)	7.6641(15)	7.7319(15)
b (Å)	15.422(31)	7.9525(16)
c (Å)	19.275(39)	10.677(2)
α (°)	90.00	80.50(3)
β (°)	90.00	76.59(3)
γ (°)	90.00	80.03(3)
V (Å^3)	2278.21(8)	623.60(5)
Z	8	2
D_{calc} (g/cm^3)	2.31733	2.29763
Absorption coefficient (cm^{-1})	10.661	9.748
$F(0\,0\,0)$	1504.0	408.0
θ Range for data collection (°)	2.11–25.02	2.62–25.01
Limiting indices	$-9 < h < 9, -15 < k < 18, -22 < l < 21$	$-9 < h < 9, -9 < k < 9 -12 < l < 12$
Reflections collected	14193	5535
Independent reflections [R_{int}]	2007[R_{int}0.104]	2150[R_{int}0.0674]
Refinement method	Full-matrix least-squares technique against F^2	Full-matrix least-squares technique against F^2
Data/restraints/parameters	2007/6/148	2150/18/173
Goodness-of-fit (GOF)	0.997	1.091
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0320, wR_2 = 0.0632$	$R_1 = 0.0443, wR_2 = 0.1136$
R indices (all data)	$R_1 = 0.0397, wR_2 = 0.0654$	$R_1 = 0.0454, wR_2 = 0.1146$
Largest difference in peak/hole (e Å^{-3})	1.40 and −1.65	3.14 and −4.50

Table 5
Selected bond angles for complex **I** and **III**.

Compound	Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
I	O3–Re1–O1	107.00(19)	O3–Re1–N2	91.44(19)	O2–Re1–N1	81.38(18)
	O3–Re1–O2	105.6(2)	O1–Re1–N2	157.2(2)	C10–Re1–N1	77.3(2)
	O1–Re1–O2	105.91(19)	O2–Re1–N2	81.04(19)	N2–Re1–N1	71.67(17)
	O3–Re1–C10	89.9(2)	C10–Re1–N2	75.5(2)	C5–N1–Re1	116.9(4)
	O1–Re1–C10	90.9(2)	O3–Re1–N1	160.77(18)	N2–C6–C5	119.5(6)
	O2–Re1–C10	152.2(2)	O1–Re1–N1	87.67(18)	C6–N2–Re1	117.6(4)
III	O3–Re1–O2	106.3(2)	O3–Re1–N2	158.0(2)	O1–Re1–N1	80.8(2)
	O3–Re1–O1	105.7(3)	O2–Re1–N2	92.3(2)	C13–Re1–N1	75.2(2)
	O2–Re1–O1	105.4(2)	O1–Re1–N2	79.6(2)	N1–Re1–N2	71.0(2)
	O3–Re1–C13	92.0(3)	C13–Re1–N2	75.4(3)	C5–N1–Re1	117.3(4)
	O2–Re1–C13	92.5(3)	O3–Re1–N1	88.6(2)	N2–C6–C5	121.0(7)
	O1–Re1–C13	149.7(3)	O2–Re1–N1	161.2(2)	C6–N2–Re1	115.6(5)

Table 6
Selected bond lengths for **I** and **III**.

Compound	Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
I	Re1–O1	1.724(4)	Re1–C10	2.219(6)	N1–C5	1.357(7)
	Re1–O2	1.758(4)	Re1–N1	2.274(5)	C5–C6	1.461(9)
	Re1–O3	1.719(4)	Re1–N2	2.257(5)	C6–N2	1.280(8)
III	Re1–O1	1.758(5)	Re1–C13	2.227(8)	N1–C5	1.357(0)
	Re1–O2	1.713(5)	Re1–N1	2.285(6)	C5–C6	1.453(10)
	Re1–O3	1.713(5)	Re1–N2	2.329(6)	C6–N2	1.268(10)

complex **I**. Moreover, in the process of synthesizing Schiff-bases-MTO complexes, when a 6-methyl or *iso*-propyl are present in the pyridine moiety, no product was received, which indicates that the alkyl in C-6 of pyridine can lead to an excessively bulky ligand which cannot coordinate to MTO. Similar behavior was reported for the unsuccessful synthesis of a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline MTO adduct, only free ligand and MTO were obtained in this case [33].

2.3. Application in epoxidation catalysis

Compounds **I–IV** were examined as catalysts for the epoxidation of cyclohexene with UHP and 30% hydrogen peroxide as oxidants, respectively. A catalyst: oxidant: substrate ratio of 1:200:100 was used in all experiments. The results are shown in Table 7. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst.

Table 7
Epoxidation of cyclohexene using calalyst **I–IV**.

Entry	Catalyst	Ligand (mmol)[a]	Oxidant	Time (h)	Conversion (%)[b]	Selectivity (%)[c]
1	**MTO**	–	UHP	2.5	>99	>99
2	**MTO**	–	H_2O_2	3.0	99	30
3	**I**	–	UHP	8.0	>99	>99
4	**I**	–	H_2O_2	1.5	25	99
5	**I**	**a** (0.01)	H_2O_2	0.5	2.5	39
6	**I**	**ab** (0.02)	H_2O_2	0.5	1.2	60
7	**II**	–	UHP	8.0	>99	>99
8	**II**	–	H_2O_2	3.0	23	99
9	**II**	**b** (0.01)	H_2O_2	0.5	6.4	44
10	**II**	**b** (0.02)	H_2O_2	0.5	6.0	60
11	**III**	–	UHP	2.0	>99	>99
12	**III**	–	H_2O_2	3.0	>99	30
13	**III**	**c** (0.01)	H_2O_2	2.0	30	47.5
14	**III**	**c** (0.02)	H_2O_2	2.0	16.2	30
15	**IV**	–	UHP	3.0	>99	>99
16	**IV**	–	H_2O_2	3.0	>99	2
17	**IV**	**d** (0.01)	H_2O_2	2.0	15	87.5
18	**IV**	**d** (0.02)	H_2O_2	2.0	9.5	77.5

[a] Reaction conditions: 2.5 mmol of cyclohexene; 5.0 mmol of oxidant; 0.025 mmol of catalyst; 3.5 ml of methanol; 25 °C; figures in bracket are the amount of ligand (mmol).
[b] Calculated by GC.
[c] Calculated by GC.

When UHP was used as oxidant for the epoxidation of cyclohexene, no significant amount of diol was observed. All catalytic reactions showed high reaction rate and completed within 3 h. Complexes **III** and **IV** showed similar catalytic activity for the epoxidation of cyclooctene, and the epoxide yield reached up to100% after 4 h. The catalytic activities of complexes **I** and **II**, both of which are prepared from the ligands derived from alkylamines, are relatively low, and the reaction time must be prolonged to 8.0 h for getting a 100% epoxide yield. These results match well with the spectroscopic data of the complexes presented above and show that the low electron donating ligand (complex **III** and **IV**) leads to a relatively weak Re–N bond, but to an active catalyst. Stronger electron donating ligand leads to a stronger Re–N bond (complex **I** and **II**), but a lower reactive catalyst. This can be explained by the fact that the ligands can exert their influence on the Lewis acidity of the Re atom and the adjacent terminal ligands. If the Lewis acidity of the metal is reduced, the formation of catalytically active mono and bisperoxo complexes is hampered. Additionally, a decrease in the electron deficiency of the peroxo-oxygen atoms makes the catalyst less prone to be nucleophiliclly attacked by an olefin [32,43]. In addition, the solvent remained yellow during the whole reaction time in all catalytic reactions. This is similar to the observations made with several aromatic N-ligated MTO complexes which are usually quite stable under oxidative conditions [31,32].

In the cases where complexes **I** and **II** were used as catalyst, use of 30% H_2O_2 as oxidant, without an excess of the ligand, resulted in only a 20% conversion, and after 0.5 h no further increase in conversion was observed. When a mixture of a complex and its corresponding ligand was applied to the epoxidation reaction, in contrast with the case of UHP as oxidant, the reaction mixture became colorless after 30 min, and a poor reaction conversion was noted. However, in the cases of complex **III** and **IV**, the catalytic reaction achieved 100% conversion after 3 h. Different from the case of UHP as catalyst, significant diol was observed, the selectivity for the epoxide is only 30% and 2% with **III** and **IV** as catalyst, respectively. The much lower catalytic activities of **I** and **II** than those of **III** and **IV** may be derived from the much easer hydrolysis of the pyridineimine moiety of the former two complexes than the later ones. It is obvious that the hydrolysis happened for **I** and **II** but not for III and IV is due to the greater steric hindrance present in the latter complexes. This deduction is confirmed by the fact

that n-propylamine and iso-propylamine were detected by GC in the reaction mixtures catalyzed by **I** and **II**, respectively.

When Schiff-base **c** or **d** was used as an additive in the case with **III** or **IV** as catalyst, the selectivity for epoxide increased, however, the catalytic activity decreased obviously and no further increase of conversion was observed after 2.0 h. In addition, the color of the reaction mixture changed from yellow to colorless in the first 1 h as noted in the cases of **I** and **II**. Thus it can be concluded that this type complex of MTO is more sensitive to water than MTO itself [31], and furthermore, an excess of Schiff-base ligand can accelerate the decomposition of the complex. These can explain why more Schiff-base addition led to catalytic systems with very low activity of compounds **I–IV**. This result is in contrast to the behavior of bipyridine-MTO adducts, which can significantly accelerate the catalytic reactions when applied in large excess [16–19].

In conclusion, 4 MTO Schiff-base complexes were prepared and characterized thoroughly. The complexes displayed high catalytic activity and selectivity in the epoxidation of cyclohexene with urea hydrogen peroxide adduct (UHP) as oxidant in methanol, but poor performances in the case of hydrogen peroxide (30%) as oxidant due to the decomposition of them. The results showed that the complexes are more sensitive to water than MTO itself. Moreover, large excess of ligand is detrimental to the catalytic performance as it leads to the decomposition of the complexes.

3. Experimental

3.1. Reagent and methods

Methyltrioxorhenium (MTO) was purchased from Alfa Aesar. 2-Pyridinecarboxaldehydes were prepared according to literature methods. All other reagents were obtained from commercial sources. Methanol was dried by standard procedures, distilled under nitrogen and kept over 4 Å molecule sieves. Other reagents were used as received. All preparations and manipulations were carried out under an oxygen and water free nitrogen atmosphere using the standard Schlenk techniques.

3.2. Physical measurements

^{1}H NMR spectra were obtained in DMSO or CDCl$_3$ using a Bruker AC 400 spectrometer. IR spectra in KBr pellets were

recorded on a Bruker Vector-22 spectrophotometer. Melting points were determined on a Perkin XT-4 microscopic analyzer. ESI and FAB mass spectrometry was performed on a VG ZAB-HS mass spectrometer. Elemental analyses were performed on an Elementar Vario E1. Reaction products were analyzed on a Shandong Lunan Ruihong gas chromatograph, SP-6800A, equipped with an FID detector.

3.3. X-ray diffraction studies

Diffraction data for complex **I** and **III** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 113(2) K using graphite-monochromated Mo Kα radiation ($k = 0.71073$ Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F2 using SHELXL-97 with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms [44]. A summary of the most important crystallographic data is given in Table 4.

3.4. Synthesis of Schiff-base-MTO complexes **I–IV**

Schiff-base ligand was prepared according to the previously described method [34]. In a typical procedure, 0.5 mmol of MTO was added to a stirred solution of 0.5 mmol of corresponding Schiff-base in 5 ml of methanol at room temperatures. A few seconds later, a yellow precipitate was formed. The yellow precipitate was collected by filtration, washed with 1×3 ml of methanol, and dried under reduced pressure.

3.4.1. Complex I

Yellow solid, Yield: 75%, M. p. 94 °C (decomposition); UV–Vis: (see Table 1); ^{1}H NMR (CDCl$_3$) 1.04(t, $J = 8.0$ Hz, CH$_2$CH$_2$CH$_3$, 3H), 1.36(s, ReCH$_3$, 1H), 1.98–2.07(m, CH$_2$CH$_2$CH$_3$, 2H), 3.99(t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_3$, 3H), 7.58(t, $J = 6.4$ Hz, PyH, 1H), 7.95(d, $J = 7.6$ Hz, PyH, 1H), 8.07(t, $J = 7.6$ Hz, PyH, 1H), 8.61(s, HC = N, 1H), 8.98(d, $J = 4.8$ Hz, PyH, 1H) ppm; IR: 2966 m, 1650 m, 1600s, 1304s, 938vs, 912vs, 843vs, 786s, 753 m, 646 m, 517 m cm^{-1}; MS(ESI) m/z: 106.0[M^+−MTO-propyl] 149.1[M^+−MTO], 251.0[M^+−L]; Anal. Calc. for C$_{10}$H$_{15}$N$_2$O$_3$Re (397.44): C, 30.22; H, 3.80 N, 7.05. Found: C, 30.11; H, 3.97; N, 7.09%.

3.4.2. Complex II

Yellow solid, Yield: 76%, M. p. 90 °C (decomposition); UV–Vis: (see Table 1); ^{1}H NMR (DMSO-d6):1.12(s, ReCH$_3$, 3H), 1.35–1.37(d, $J = 6.4$ Hz, CH(CH$_3$)$_2$, 6H), 4.03(s, CH(CH$_3$)$_2$, 1H), 7.69(s, pyH, 1H), 8.14(s, pyH,1H), 8.76(s, HC=N, 1H), 8.87(s, pyH, 1H) ppm; IR: 2973s, 1643 m, 1598s, 1390s, 1293s, 1115 m, 934vs, 910vs, 848vs, 774s, 749 m, 644 m, 512 m cm^{-1}; MS(ESI) m/z: 106.1 [M^+-MTO-iso-propyl], 149.1[M^+−MTO], 251.0[M^+−L]; Anal. Calc. for C$_{10}$H$_{15}$N$_2$O$_3$Re (397.44): C, 30.22; H, 3.80 N, 7.05. Found: C, 30.13; H, 4.08; N, 7.18%.

3.4.3. Complex III

Yellow solid, Yield: 80%, M. p.101 °C (decomposition); UV–Vis: (see Table 1); ^{1}H NMR (DMSO): 1.88(s, ReCH$_3$, 3H), 7.31–7.36(m, PhH, 3H), 7.44–7.48(m, PhH, 2H), 7.96–8.00(t, $J = 7.6$ Hz, pyH, 1H), 8.16–8.18(d, $J = 8.0$ Hz, pyH, 1H), 8.61(s, HC=N, 1H), 8.73–8.74(d, J=4.8 Hz, pyH, 1H); IR: 3077w, 3013 m, 2964w, 2919w, 1621s, 1590 m, 1562 m, 1486s, 945vs, 910vs, 899s, 851vs, 933s, 787s, 688s, 557 m cm^{-1}; MS (FAB): m/z=183.0(100)[M^{+-}MTO], MS(ESI): 183.4 [M^{+-}MTO], 251.1[M^+−L]; Anal. Calc. for C$_{13}$H$_{13}$N$_2$O$_3$Re (431.46): C, 36.19; H, 3.04 N, 6.49. Found: C, 36.22; H, 3.14; N, 6.56%.

3.4.4. Complex IV

Yellow solid, Yield: 81%, M.p.100 °C (decomposition); UV–Vis: (see Table 1); ^{1}H NMR (DMSO): 1.85(s, ReCH$_3$, 1H), 3.80(s, OCH$_3$, 1H), 7.02(d, $J = 6.8$ Hz, PhH, 2H), 7.41(d, $J = 6.8$ Hz, PhH, 2H), 7.51–7.54(m, pyH,1H), 7.96(t, $J = 7.6$ Hz, pyH, 1H), 8.15(d, $J = 7.6$ Hz, pyH, 1H), 8.66(s, HC=N, 1H), 8.71 (d, $J = 8.0$ Hz, pyH, 1H); IR: 3086w, 2972w, 2930w, 2838w, 1622 m, 1599s, 1511vs, 1296s, 1262s, 1025s, 944s, 909vs, 851vs, 831s, 541w cm^{-1}; MS (FAB) m/z: 213.0(100)[M^{+-}MTO], MS (ESI) m/z: 213.5(M^+−MTO), 251.1[M^+−L]; Anal. Calc. for C$_{14}$H$_{15}$N$_2$O$_4$Re (461.49): C, 36.44; H, 3.28 N, 6.07. Found: C, 36.55; H, 3.32; N, 6.08%.

3.5. Catalytic experiments

The catalytic reactions were carried out under continuous stirring in a glass flask immersed in a water bath with temperature control. In a typical experiment, 0.025 mmol of the catalyst, 3.5 ml of methanol, and a given amount (5 mmol) of UHP or diluted hydrogen peroxide (solution, 30 wt% in water) were mixed in the flask under agitation until the reaction temperature was reached. At this time, 2.5 mmol of the substrate was added (time zero). Small aliquots were taken at selected reactions times. The products were analyzed by gas chromatography in a capillary column using a FID detector.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.034.

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