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Synthesis of di-nitrogen Schiff base complexes of methyltrioxorhenium(VII) and their application in epoxidation with aqueous hydrogen peroxide as oxidant

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Several di-nitrogen Schiff bases were synthesized through the condensation of 2-pyridinecarboxaldehyde with primary amines. The Schiff bases as ligands coordinated with methyltrioxorhenium (MTO) smoothly to afford the correspondent complexes which were characterized by IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. One of the complexes was analyzed by X-ray crystallography as well. The results revealed that the complexes display distorted octahedral geometry in the solid state with a *trans*-position of Schiff base. Catalytic results indicated that the complexes as catalysts increased the selectivity of epoxides remarkably compared with MTO in the epoxidation of alkenes with 30% hydrogen peroxide as oxidant and the increasing rate depended on the structure of the Schiff base ligands of the complexes. The results indicated that the stronger the donating ability of the ligand, the higher selectivity of epoxides the complex gave in the epoxidation of alkenes with 30% hydrogen peroxide as oxidant.

Keywords: methyltrioxorhenium; di-nitrogen; Schiff bases; 2-pyridinecarboxaldehyde; cyclohexene; epoxidation; hydrogen peroxide

Introduction

Epoxides are versatile compounds that form building blocks of many pharmaceuticals and other chemicals.[1–6] Therefore, the development of more efficient and selective means of epoxidation is very important. In 1991 the group of Herrmann[7] discovered that methyltrioxorhenium(VII) ($MeReO_3$, MTO) acts as an efficient catalyst for the epoxidation of alkenes with hydrogen peroxide (H_2O_2) as oxidant. 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.[8] Such a side reaction can be circumvented by employing anhydrous source of H_2O_2 such as urea hydrogen peroxide adduct (UHP), instead of aqueous H_2O_2.[9,10] An alternative to suppress the above side reaction is the addition of Lewis base ligands to reduce the Lewis acidity of rhenium center.[11–20] In such a case, an excess of Lewis base ligand is needed to achieve excellent catalytic performance,[12,15,21] which is unfavorable from the viewpoints of cost and separation. Therefore, it is necessary to seek stable Lewis base–MTO complexes with good catalytic performance to avoid using excess of Lewis base in the epoxidation process with aqueous H_2O_2 as oxidant. Based upon this idea many MTO complexes of monodentate and bidentate N-donor ligands have been prepared and reported in the last few years.[22–29] Despite a large number of Lewis base adducts of MTO being described in the literature, only a few examples of complexes with Schiff bases have been reported,[30–33] whereas Schiff bases are very accessible from the condensation of carbonyl compounds and primary amines.

Recently, we reported the preparation of several bidentate Schiff base ligands from the condensation of 2-pyridinecarboxaldehyde with amines and the correspondent MTO complexes of the ligands.[34] Structure determination showed that the coordination features of the MTO complexes are related to both the electronic and steric properties of the Schiff bases. Catalytic results showed that the MTO complexes displayed very active and highly selective performances in the epoxidation of cyclohexene with UHP as oxidant in methanol, but poor performances in case of H_2O_2 (30%) as oxidant due to the decomposition of the complexes in the system. Primary results showed that the electronic and steric properties of the Schiff bases can also influence the catalytic performances of the complexes in the epoxidation of cyclohexene. To further elucidate how the electronic and steric properties of the ligands influence the structures and catalytic characteristics of the Schiff base–MTO complexes, we synthesized and characterized several more di-nitrogen Schiff bases and their MTO complexes. The complexes were applied to the epoxidation of several alkenes and the dependence of catalytic properties on the structures of the complexes was received.

Experimental

Reagents and Methods

Methyltrioxorhenium(VII) (MTO) and 2-pyridinecarboxaldehydes were purchased from Alfa Aesar. All other reagents were obtained from commercial sources and used as received except methanol. Methanol was dried by standard procedures, distilled under

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nitrogen and kept over 4 Å molecule sieves. All preparations and manipulations were carried out under an oxygen- and water-free nitrogen atmosphere using the standard Schlenk techniques.

Physical Measurements

Melting points were determined on a Perkin XT-4 microscopic analyzer. ^{1}H NMR and ^{13}C NMR spectra were measured in DMSO-d_6 or $CDCl_3$ using a Bruker AC 400 spectrometer. IR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets as the IR matrix. Mass spectra were obtained 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.

Synthesis of Di-nitrogen Schiff Bases and MTO Complexes

In a general procedure for the synthesis of the MTO complexes, 0.4 mmol of MTO was added to 0.4 mmol of the corresponding di-nitrogen Schiff base in methanol (4 ml) at room temperature. A yellow precipitate was formed rapidly. The precipitate was isolated by filtration, washed with n-hexane and dried under reduced pressure.

c1: Yellow solid, yield 80%, m.p. 101 °C (decomposition); ^{1}H NMR (400 MHz, DMSO) δ: 1.89 (s, 3H, $ReCH_3$),7.26–7.30 (m, 2H, PhH), 7.42–7.45 (m, 2H, PhH), 7.53–7.56 (m, 1H, PyH), 7.95–7.99 (m, 1H, PyH), 8.14–8.16 (d, 1H, PyH), 8.61 (s, 1H, HC═N), 8.72–8.74 (m, 1H, PyH) ppm; ^{13}C NMR (100 MHz, DMSO) δ: 160.85 (HC═N), 153.42, 149.62, 146.47, 146.44, 137.42, 125.95, 123.34, 123.25, 122.16, 116.10, 115.88 (aryl-C), 25.10 ($ReCH_3$) ppm; IR (KBr) ν: 3114 3083 3012 2923 1954 1623 1594 1499 1242 1159 1022 944 932 908 849 785 644 551 cm^{-1}. MS (ESI): 201.1 [M^+ − MTO]; elemental analysis calcd (%) for $C_{13}H_{12}FN_2O_3Re$ (449.45): C, 34.74; H, 2.69; N, 6.23. Found: C, 34.92; H, 2.68 N, 6.24.

c2: Yellow solid, yield: 80%, m.p. 112 °C (decomposition); ^{1}H NMR (400 MHz, DMSO) δ: 1.89 (s, 3H, $ReCH_3$),7.37–7.40 (m, 2H, PhH), 7.48–7.52 (m, 2H, PhH), 7.54–7.57 (m, 1H, PyH), 7.95–8.00 (m, 1H, PyH), 8.15–8.17 (m, 1H, PyH), 8.61 (s, 1H, HC═N), 8.72–8.73 (m, 1H, PyH) ppm; ^{13}C NMR (100 MHz, DMSO) δ: 161.58 (HC═N), 153.58, 149.70, 149.14, 137.24, 131.11, 129.23, 125.92, 123.05, 121.72 (aryl-C), 25.01 ($ReCH_3$) ppm; IR (KBr) ν: 3074 3015 2953 1628 1592 1485 1293 1199 1093 945 933 915 859 780 643 557 cm^{-1}. MS (ESI): 217.0 [M^+ − MTO]; elemental analysis calcd (%) $C_{13}H_{12}ClN_2O_3Re$ (465.91): C, 33.51; H, 2.60 N, 6.01. Found: C, 33.34; H, 2.84; N, 6.07.

c3: yellow solid, yield 78%, m.p. 102 °C (decomposition); ^{1}H NMR (400 MHz, DMSO) δ: 1.89 (s, 3H, $ReCH_3$),7.30–7.34 (m, 2H, PhH), 7.54–7.57 (m, 1H, PyH), 7.61–7.65 (m, 2H, PhH), 7.95–8.00 (m, 1H, PyH), 8.15–8.17 (m, 1H, PyH), 8.61 (s, 1H, HC═N), 8.73–8.74 (m, 1H, PyH) ppm; ^{13}C NMR (100 MHz, DMSO) δ: 161.60 (HC═N), 153.68, 149.73, 149.62, 137.18, 132.16, 125.88, 123.38, 121.57, 119.41 (aryl-C), 24.99 ($ReCH_3$) ppm; IR (KBr) ν: 3090 3066 3026 2910 2775 1618 1591 1482 1307 1074 1011 938 912 852 786 647 557 cm^{-1}. MS (ESI): 261.0 [M^+ − MTO]; elemental analysis calcd (%) $C_{13}H_{12}BrN_2O_3Re$ (510.36): C, 30.59; H, 2.37 N, 5.49. Found: C, 30.42; H, 2.48; N, 5.53.

c4: See Qiu *et al*.[34]

c5: yellow solid, yield 76%, m.p. 104 °C (decomposition); ^{1}H NMR (400 MHz, DMSO) δ: 1.88 (s, 3H, $ReCH_3$), 2.34 (s, 3H, $PhCH_3$), 7.24–7.29 (m, 4H, PhH), 7.51–7.55 (m, 1H, PyH), 7.94–7.98 (m, 1H, PyH), 8.14–8.17 (m, 1H, PyH), 8.61 (s, 1H, HC═N), 8.71 (d, 1H, PyH) ppm; ^{13}C NMR (100 MHz, DMSO) δ: 159.10 (HC═N), 154.18, 149.58, 146.78, 137.07, 135.79, 131.84, 130.93, 127.35, 125.48, 121.16, 117.42 (aryl-C), 24.96 ($ReCH_3$), 20.52, 17.43 (Ph-CH_3) ppm; IR (KBr) ν: 3091 3036 2994 2892 1633 1598 1504 1301 1197 1027 941 924 912 849 777 640 561 cm^{-1}. MS (FAB): *m/z* (%) 197.0 (100) [M^+ − MTO]; elemental analysis calcd (%) $C_{14}H_{15}N_2O_3Re$ (445.49): C, 37.74; H, 3.39 N, 6.29. Found: C, 37.70; H, 3.59; N, 6.35.

c6: See Qiu *et al*.[34]

c7: See Qiu *et al*.[34]

c8: Yellow solid, yield 76%, m.p. 106 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88–0.91 (m, 3H, CH_3), 1.33–1.43 (m, 6H, $CH_2CH_2CH_2$), 1.59 (s, 3H, $ReCH_3$), 1.93–1.94 (m, 2H, CH_2), 3.93∼3.96 (m, 2H, NCH_2), 7.50–7.53 (m, 1H, PyH), 7.92–8.01 (m, 2H, PyH), 8.54 (s, 1H, HC═N), 8.91–8.92 (d, 1H, PyH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.98 (HC═N), 149.93, 149.64, 139.65, 127.71, 127.29 (Py-C), 62.21, 31.39, 28.85, 26.75 (*n*-hexyl-C), 26.02 ($ReCH_3$), 22.52, 14.02 (*n*-hexyl-C) ppm; IR (KBr) ν: 3094 3043 2962 2923 2857 1648 1599 1475 1300 1231 1022 936 911 855 785 645 517 cm^{-1}. MS (ESI): 191.2 [M^+ − MTO]; elemental analysis calcd (%) $C_{13}H_{21}N_2O_3Re$ (439.52): C, 35.52; H, 4.82; N, 6.37. Found: C, 35.24; H, 4.89; N, 6.42.

c9: yellow solid, yield 75%, m.p. 101 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.41–1.44 (m, 3H, cyclohexyl-H), 1.61 (s, 3H, $ReCH_3$), 1.70–1.80 (m, 3H, cyclohexyl-H), 1.87–1.91 (m, 2H, cyclohexyl-H), 2.01–2.04 (m, 2H, cyclohexyl-H), 3.69–3.74 (m, 1H, cyclohexyl-H), 7.46–7.47 (d, 1H, PyH), 7.92–7.96 (m, 2H, PyH), 8.54 (s, 1H, HC═N), 8.84–8.85 (d, 1H, PyH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.67 (HC═N), 149.80, 149.61, 138.79, 126.51, 126.19 (Py-C), 70.39, 33.12, 25.40, 25.16 (cyclohexyl-C), 25.13 ($ReCH_3$) ppm; IR (KBr) ν: 3069 3032 2977 2924 2851 1647 1601 1480 1451 1313 1057 937 916 844 772 646 519 cm^{-1}. MS (ESI): 189.2 [M^+ − MTO]; elemental analysis calcd (%) $C_{13}H_{19}N_2O_3Re$ (437.51): C, 35.69; H, 4.38; N, 6.40. Found: C, 35.43; H, 4.49; N, 6.51.

X-ray Structure Determination

Suitable crystal was obtained by slow solvent diffusion techniques from methanol at room temperature. Diffraction data for complex **c5** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 113 (2) K using graphite-monochromated Mo K_α radiation (λ = 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.[35]

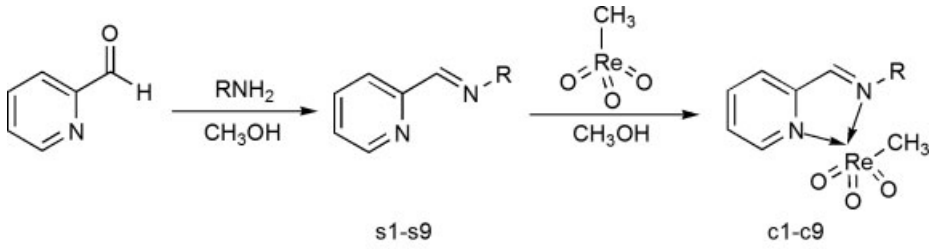
Catalytic Reaction

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, 5 mmol of substrate, 7 ml of methanol and 0.05 mmol of the catalyst were mixed in the flask. Aqueous H_2O_2 (30 wt%, 10 mmol) was added to start the reaction. Samples were taken out at regular time intervals. The products were analyzed by gas chromatography in a capillary column using an FID detector.

Results and Discussion

Synthesis and Characterization

The route for the synthesis of the di-nitrogen Schiff bases and their MTO complexes is shown in Scheme 1. The di-nitrogen Schiff bases were prepared smoothly according to the procedure described in



R=p-Fluorophenyl(s1,c1); p-Chlorophenyl(s2,c2); p-Bromophenyl(s3,c3); Phenyl(s4,c4); p-Methylphenyl(s5,c5); p-Methoxyphenyl(s6,c6); n-Propyl(s7,c7); n-Hexyl(s8,c8); Cyclohexyl(s9,c9).

Scheme 1. Synthesis of Schiff bases (**s1**–**s9**) and their MTO complexes (**c1**–**c9**).

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

	ν (cm^{-1})				
			ReO_3		
Compound	Imine $\nu_{(C=N)}$	Pyridine $\nu_{(C=N)}$	ν_{as}	ν_s	$\nu_s - \nu_{as}$
MTO	–	–	965	998	33
s1	1627	1582	–	–	–
c1	1623	1594	920	944	24
s2	1625	1587	–	–	–
c2	1628	1592	924	945	21
s3	1624	1588	–	–	–
c3	1618	1591	912	938	26
s5	1627	1582	–	–	–
c5	1633	1597	918	941	23
s8	1650	1587	–	–	–
c8	1648	1599	911	936	25
s9	1648	1584	–	–	–
c9	1647	1601	916	937	21

the literature.[34,36] By changing the amine it is possible to obtain the ligand as needed.

The addition of one equivalent of MTO to the di-nitrogen Schiff base in methanol at room temperature immediately leads to the formation of the corresponding complex which can be easily isolated as a yellow solid in good yield. In the solid state, all the complexes obtained are stable in air for several days, but slightly sensitive to moisture. Therefore, a water-free nitrogen atmosphere is needed to preserve the complexes.

Table 1 presents the selected IR spectroscopic data of the Schiff bases and the MTO complexes. In the IR spectra of the complexes, the symmetric Re=O stretching vibrations occur within an interval of 936–945 cm^{-1}, and the asymmetric stretching vibrations are found in the region of 911–924 cm^{-1}. The Re=O bands of the complexes are red-shifted compared with the vibrations (ν_{sym} = 998 cm^{-1}, ν_{asym} = 965 cm^{-1}) of non-coordinated MTO.[37] The vibration differences reflect the donating capacity of the di-nitrogen Schiff base ligands because the additional electron from the ligand to the Lewis acidic Re(VII) atom significantly reduces the bond order of the Re=O bonds. The stretching vibrations of the pyridine moiety in the ligands locate at an interval of 1591–1601 cm^{-1}. Compared with the vibrations between 1582 and 1588 cm^{-1} of the free Schiff base ligands, the corresponding vibration bands of the complexes are blue-shifted due to electron delocalization. The same situation was also observed by others in the literature.[24,38] However, the stretching vibrations of iminic bonds in the complexes occur between 1618 and 1648 cm^{-1}, with a deviation of about 4 cm^{-1}, which is within the error range of the measurement (4 cm^{-1}) in comparison to that of the free ligands (1624–1650 cm^{-1}).

In addition, differences of 21–26 cm^{-1} between ν_{sym}(Re=O) and ν_{asym}(Re=O) are observed in the above complexes. Generally the difference between the symmetric and asymmetric stretching of ReO_3 moiety is related to the geometry of the MTO complexes. The differences of 20–27 and 60–80 cm^{-1} between ν_{sym}(Re=O) and ν_{asym}(Re=O) correspond to the octahedral and trigonal–bipyramidal coordination geometry, respectively.[25,30,32] For the free MTO, the difference is 33 cm^{-1}, which corresponds to a tetrahedral coordination geometry.[39] Therefore, it can be deduced that the structures of the title complexes are closer to an octahedral geometry, in which the Schiff bases act as bidentate ligands to coordinate to MTO through the two nitrogen atoms.

The selected ^{1}H NMR spectroscopic data of the Schiff bases and the MTO complexes are shown in Table 2. Compared with the spectra of the non-coordinated MTO, the proton signals originating from the Re–CH_3 of the Schiff base MTO complexes shifted clearly to high magnetic field. As reported in the literature,[22,25] the magnitude of the shift is directly related to the electron-donating capability of the ligands. Our experimental results confirmed that, the better the electron donating ability of the ligand, the larger high-field shift is of the ^{1}H NMR signal of the Re–CH_3 group. For example, relative to non-coordinated MTO, complexes **c1, c1** and **c3** which bear an electron-withdrawing halogen atom in the phenyl moiety show chemical shift changes of the methyl signal around 0.78 ppm; however, the corresponding magnitude of complex **c5**, which has a methyl group in the phenyl moiety, is about 0.79 ppm in ^{1}H NMR spectra. In cases of complexes **c8** and **c9** in which the ligands are derived from aliphatic amines with the nature of higher electron donation than aromatic ones, the chemical shift changes relative to noncoordinated MTO are 1.08 and 1.06 ppm, respectively. Furthermore, the ^{1}H NMR signals of the imine group of these complexes are slightly shifted to a lower field with regard to those of the free Schiff bases. The observed chemical shifts match the characters of the Schiff base ligands in the complexes very well.

The ^{1}H NMR spectroscopic data are also in agreement with the structure characters of the MTO complexes.

Table 2. Selected ^{1}H NMR spectroscopic data of Schiff base and MTO complexes

Compound	δ ($ReCH_3$)	δ (C=NH)
MTO	2.67s	–
s1	–	8.61s
c1	1.89s	8.61s
s2	–	8.60s
c2	1.89s	8.61s
s3	–	8.60s
c3	1.89s	8.61s
s5	–	8.60s
c5	1.88s	8.61s
s8	–	8.36s
c8	1.59s	8.54s
s9	–	8.38s
c9	1.61s	8.54s

Table 3. Crystal data and details of the structure determination

Compound	**c5**
Empirical formula	$C_{14}H_{15}N_2O_3Re$
Formula weight (g mol^{-1})	445.48
Temperature (K)	113(2)
Wavelength (Å)	Mo K_α (0.71073)
Crystal system	Monoclinic
Space group	P21/c
Crystal size (mm)	$0.18 \times 0.14 \times 0.06$
a (Å)	6.2896(13)
b (Å)	13.186(3)
c (Å)	16.815(3)
β (deg)	96.68(3)
V (Å^3)	1385.1(5)
Z	4
D_{calc} (g cm^{-3})	2.136
Absorption coefficient (cm^{-1})	8.781
F(000)	848.0
θ range for data collection (deg)	1.97 to 25.02
Limiting indices	$-7 < h < 7$, $-15 < k < 15$, $-20 < l < 12$
Reflections collected	7852
Independent reflections [$R_{(int)}$)]	2414(R_{int} = 0.1224)
Reflections observed[$I > 2\sigma(I)$]	2193
Data/restraints/parameters	2414/24/184
Goodness-of-fit (GOF)	1.076
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0574$, $wR_2 = 0.1372$
R indices (all data)	$R_1 = 0.0619$, $wR_2 = 0.1419$
Largest difference peak/hole (e Å^{-3})	2.591 and −2.742

X-ray Crystal Structures of Complex c5

As an example for the prepared di-nitrogen Schiff base complexes of MTO, the crystal structure of **c5** was examined by means of X-ray structure determination. Details of the X-ray experiment, crystal parameters, data collections and refinements are summarized in Table 3. The crystal structure of **c5** is shown in Figure 1. The selected bond lengths and bond angles are listed in Tables 4 and 5.

The crystal structure determination indicates that the Re(VII) atom is coordinated with both nitrogen atoms from Schiff base in the complex and the complex exhibit a distorted octahedral geometry in accordance with the deduction from the spectroscopic results given above. The results are same as those of complexes **c4** and **c7** reported by us recently.[34] As is known for most structurally characterized bidentate Lewis base complexes of MTO,[24,25] the three oxygen atoms display a pyramidal facial arrangement. The two nitrogen atoms from di-nitrogen Schiff base and two double-bonded oxygen atoms occupy the equatorial position, while the methyl group and the remaining oxygen atom reside in the apical sites in a *trans* position. The Re–C bond distance in **c5** is 2.201(6) Å, prolongated in comparison to that of 2.063(2) Å in the free MTO[40]. The Re—C bond distance here is close to the average Re—C bond distance found in other N-donor complexes of MTO.[30,39–41] On the other hand, the Re=O bond distance in **c5** is about 1.7 Å, which is comparable to those in the other trioxorhenium complexes described in the literature.[8,11,25,34,39,42–50]

Application in Epoxidation Catalysis

Cyclohexene, styrene and 1-octene were employed as substrates to evaluate the efficiency of the complexes as catalysts for the epoxidation of olefins with 30% H_2O_2 as oxidant and the results are summarized in Table 6.

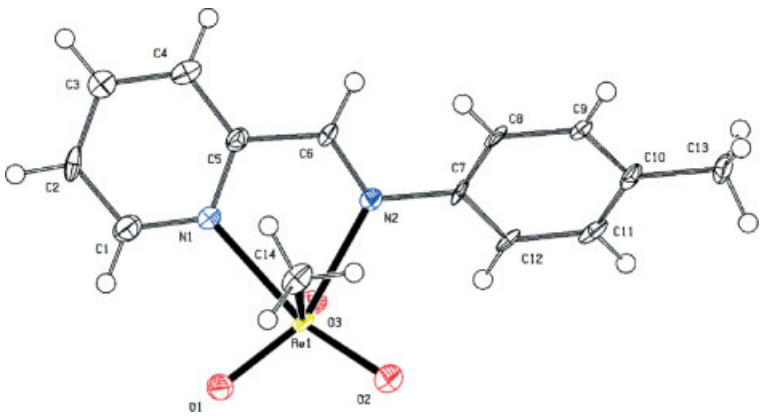


Figure 1. PLATON drawing of complex **c5** in solid state. Thermal ellipsoids are at the 50% probability level.

Table 4. Selected bond lengths for complex **c5**

Compound	Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
c5	Re1–O1	1.704(5)	Re1–C14	2.201(6)	N1–C5	1.343(9)
	Re1–O2	1.702(6)	Re1–N1	2.271(6)	N2–C6	1.256(9)
	Re1–O3	1.755(5)	Re1–N2	2.275(5)	C5–C6	1.466(9)

When the epoxidation was kept at the same progress and a comparison was made between the epoxide selectivities of the reactions with non-coordinated MTO and the complexes as catalysts, respectively, it was found that all the complexes gave higher epoxide selectivity than non-coordinated MTO (entries 3 and 5, 7, 9; 25 and 27, 28, 29; etc.). It was also found that the increasing degree of the selectivity of the epoxides depended on the structures of the di-nitrogen Schiff base ligands employed. For example, when the epoxidation of cyclohexene was run for 1.5 h with **c1**–**c3, c4**–**c6** and **c7**–**c9** as catalysts, respectively, the selectivity of the epoxide was around 75, 80–86 and 98–99%, respectively, compared with only 46% in the case of MTO as catalyst. When **c7, c8** and **c9**, in which the ligands are derived from alkylamines, were used as catalysts, high selectivities of the epoxides were obtained compared with other complexes in which the ligands are derived from aromatic amines. A slightly higher selectivity was obtained with **c5** as catalyst, in which an electron-donating methyl group is present in the phenyl moiety of the ligand, than with **c1**–**c3**, in which the ligands bear an electron-withdrawing group in the same position. Experimental results revealed that, the stronger the donating ability of the ligand, the higher epoxide selectivities the complex gave in the epoxidation of alkenes with 30% H_2O_2 as oxidant. This can be explained by the formation of 1,2-diols through ring-opening in the presence of water being accelerated by the acidity of rhenium center,[8,49] whereas the di-nitrogen Schiff base ligand can decrease the Lewis acidity of the Re atom, which suppresses the epoxide ring-opening process. At the same time, the formation of catalytically active mono and bisperoxo complexes in epoxide opening is hampered if the Lewis acidity of the rhenium center is reduced.

On the other hand, the trends of the conversion changes are contrary to those of the selectivity that the catalysts showed. When MTO itself was used as a catalyst for the epoxidation of cyclohexene, a quantitative conversion of cyclohexene was obtained within 1.5 h. However, the magnitudes of the conversion of cyclohexene were about 92, 85 and 30% when **c1**–**c3, c4**–**c6** and **c7**–**c9** were used as catalysts in the same reaction time, respectively. In other words, the stronger the donor ability of the ligand, the lower conversion the catalyst gave in the epoxidation reaction. The same results were also observed in epoxidation of styrene and 1-octene catalyzed by the complexes. These results match well with the spectroscopic data of the complexes presented above, that is, the stronger electron donating ligands can lead to higher strength of Re–N bond, which slows down the epoxidation reaction. The conversion decrease can be explained by the fact that the coordination of di-nitrogen Schiff bases increases the electron density of Re, which leads to it being less prone to being nucleophilically attacked by an olefin. The steric hindrance of the coordinated di-nitrogen Schiff bases hampering the approach of the olefin substrate to the Re atom is another reason to slow down the reaction. In brief, the strong coordination capacity of the di-nitrogen Schiff base is in favor of the augmentation of the selectivity of epoxide but reduces the conversion of alkenes in the epoxidation reaction. A similar situation is also observed in the literature.[8,51,52]

In addition we can also observed from the table that extending reaction time can cause an increase in conversion and decrease in epoxide selectivity due to ring opening reaction in cases of complexes as catalysts in which the ligands are derived from aromatic amines (entries 6, 8, 10, 12, 15 and 17). It is worth noting that high temperature is greatly disadvantageous to the epoxide selectivity (entries 13 and 18), which may be because the high temperature can accelerate the ring opening reaction of epoxide or facilitate the decomposition of the complex to species which enhance the ring opening reaction of epoxide. It was also noted that high reaction temperature can decrease the conversion due to high temperature, leading to fast decomposition of the complex with an aliphatic amine derived ligand (entry 21).

Conclusions

Several di-nitrogen Schiff base complexes of MTO were synthesized and fully characterized by IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. Besides, one of the complexes was also determined by X-ray diffraction. The results indicated that the crystal structure of the complex exhibit a distorted octahedral structure. In general the complexes were highly efficient and significant for achieving high selectivity of epoxides in the catalytic epoxidation of several alkenes. It is interesting that the selectivity of epoxides depended on the structure of the ligands employed. The continuous exploration of various di-nitrogen Schiff base as ligands will open perspectives for MTO-catalyzed epoxidation.

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Table 5. Selected bond angles for complex **c5**

Compound	Bond	Angle (deg)	Bond	Angle (deg)	Bond	Angle (deg)
c5	O1–Re1–O2	106.8(3)	O1–Re1–N1	86.4(3)	O3–Re1–N2	78.7(2)
	O1–Re1–O3	105.7(3)	O2–Re1–N1	161.6(2)	C14–Re1–N2	75.0(2)
	O2–Re1–O3	105.7(3)	O3–Re1–N1	82.2(2)	N1–Re1–N2	70.8(2)
	O1–Re1–C14	93.8(3)	C14–Re1–N1	77.6(3)	C5–N1–Re1	118.1(5)
	O2–Re1–C14	88.6(3)	O1–Re1–N2	156.2(3)	C6–N2–Re1	117.3(5)
	O3–Re1–C14	150.9(2)	O2–Re1–N2	94.1(2)	N2–C6–C5	120.4(6)

Table 6. Epoxidation of alkenes by complex **c1**–**c9**

Entry	Substrate	Catalyst	Time (h)	Conversion (%)	Selectivity (%)
1	Cyclohexene	MTO	0.25	35	>99
2	Cyclohexene	MTO	0.5	72	78
3	Cyclohexene	MTO	1	92	63
4	Cyclohexene	MTO	1.5	99	46
5	Cyclohexene	**c1**	1.5	92	75
6	Cyclohexene	**c1**	2	99	52
7	Cyclohexene	**c2**	1.5	91	76
8	Cyclohexene	**c2**	2	99	53
9	Cyclohexene	**c3**	1.5	94	75
10	Cyclohexene	**c3**	2	99	55
11	Cyclohexene	**c4**	1.5	87	80
12	Cyclohexene	**c4**	2	96	60
13[a]	Cyclohexene	**c4**	3	99	30
14	Cyclohexene	**c5**	1.5	85	82
15	Cyclohexene	**c5**	2	92	61
16	Cyclohexene	**c6**	1.5	77	85
17	Cyclohexene	**c6**	2	86	64
18[a]	Cyclohexene	**c6**	3	99	2
19	Cyclohexene	**c7**	1.5	29	98
20	Cyclohexene	**c7**	3	29	93
21[a]	Cyclohexene	**c7**	1.5	25	99
22	Cyclohexene	**c8**	1.5	30	99
23	Cyclohexene	**c9**	1.5	30	98
24	Styrene	MTO	1	18	43
25	Styrene	MTO	1.5	30	27
26	Styrene	MTO	2	43	13
27	Styrene	**c1**	2	33	34
28	Styrene	**c2**	2	33	32
29	Styrene	**c3**	2	34	35
30	Styrene	**c4**	2	29	40
31	Styrene	**c5**	2	28	44
32	Styrene	**c6**	2	25	46
33	Styrene	**c7**	2	8	89
34	Styrene	**c8**	2	10	84
35	Styrene	**c9**	2	11	85
36	1-Octene	MTO	2	15	99
37	1-Octene	MTO	8	63	90
38	1-Octene	MTO	10	74	79
39	1-Octene	MTO	12	81	70
40	1-Octene	**c1**	12	70	82
41	1-Octene	**c2**	12	72	82
42	1-Octene	**c3**	12	70	84
43	1-Octene	**c4**	12	67	89
44	1-Octene	**c5**	12	66	90
45	1-Octene	**c6**	12	64	90
46	1-Octene	**c7**	12	15	99
47	1-Octene	**c8**	12	21	99
48	1-Octene	**c9**	12	19	99

Reaction conditions: substrate 5 mmol, 30% H_2O_2 10 mmol, catalyst 0.05 mmol, methanol 7 ml, reaction temperature 20 °C.
[a] The reaction temperature is 25 °C and the data is from Qiu *et al.*[34]

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