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# Synthesis, Structure, and Catalytic Application of a New (3-Methoxy-N-salicylidene)aniline—Derived Schiff Base Complex of Methyltrioxorhenium[1]

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**Abstract**—A new (3-methoxy-N-salicylidene)aniline—derived Schiff base complex of methyltrioxorhenium ($C_{14}H_{13}NO_2 \cdot CH_3ReO_3$) (**I**), displaying a *cis*-arrangement of the Schiff base ligand to the Re-bonded methyl group, has been synthesized and characterized by elemental analysis, IR, $^1$H NMR, and single-crystal X-ray diffraction. The X-ray diffraction analysis reveals that **I** crystallizes in the triclinic system, space group $P\bar{1}$, which displays a distorted trigonal-bipyramidal structure in the solid with the $O^-$ moiety binding to the Lewis acidic Re atom. The intermolecular hydrogen bands link the molecules of the complex into a two-dimensional layer structure. The presence of the π–π stacking interactions enhances the stability of the layers, which are further linked via π–π stacking interactions forming a three-dimensional supramolecular network. The unit cell parameters for **I**: $a = 7.0032(14)$, $b = 9.3762(19)$, $c = 11.649(2)$ Å, $\alpha = 84.60(3)°$, $\beta = 89.08(3)°$, $\gamma = 84.45(3)°$, $V = 757.9(3)$ Å$^3$, $Z = 2$, $F(000) = 456$, $R_1 = 0.0591$, $\omega R_2 = 0.1346$. In order to study the catalytic activity of complex **I**, *cis*-cyclooctene epoxidation in dichloromethane is examined. The result shows that the electron-donating $OCH_3$ group on the Schiff base influences the catalytic behavior significantly.

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## INTRODUCTION

Methyltrioxorhenium ($CH_3ReO_3$ abbreviated as **MTO**) has emerged in the last decade, and the discovery of its catalytic activity was made by Herrmann and coworkers [1]. Since a few years that have passed, MTO has drawn considerable attention due to its versatility as a catalyst [2, 3]. The main areas of its application are oxidation catalysis, especially epoxidation of olefins [4, 5]. Usually, the use of easily available, low cost, and environmentally friendly oxidants such as hydrogen peroxide ($H_2O_2$) is of particular interest [6, 7], It turned out already nearly two decades ago that MTO is one of the most active olefin epoxidation catalysts. However, Lewis acidity of MTO and the presence of water (formed as a byproduct from hydrogen peroxide) in organic solvent have a tendency to promote further ring-opening reactions of the epoxidation products to give diols, particularly, when more sensitive epoxides are formed [8, 9]. Further research of them revealed that the addition of an excess of nitrogenous bases, particularly, pyridine as the Lewis base mediator for the oxidation, is beneficial for both the product selectivity and catalyst lifetime [10, 11].

To date, many N-base complexes of MTO have been isolated, characterized, and applied for the epoxidation of olefins as catalysts [12]. However, only recently the papers have appeared dealing with Schiff base complexes of MTO [13–16]. Many of them are *trans*-coordination, and there are only few *cis*-complexes. All of them show comparatively good catalytic activities in cyclooctene epoxidation. An excess of the ligand is not necessary to achieve high yields in the process of catalysis. In this work we reported the synthesis and structure of the *cis*-MTO complex with the Schiff base ligand derived from *o*-vanillin and amine, as well as its catalytic application in cyclooctene epoxidation.

## EXPERIMENTAL

**Materials and methods.** All reagents and solvents employed were commercially available. All preparations and experimentations were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures (*n*-hexane and $Et_2O$ over Na/benzophenone), distilled under argon, and used immediately or kept over 4 Å molecular sieves. Elemental analyses were performed with a Flash EA 1112 series elemental analyser. $^1$H NMR was measured in DMSO with a Mercury-Vx-300 spectrometer. IR spectra were recorded with a Nicolet 5700 FT-IR spectrometer using KBr pellets as

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**Table 1.** Crystallographic data and experimental details for structure **I**

| Parameter | Value |
|---|---|
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$, Å | 7.0032(14) |
| $b$, Å | 9.3762(19) |
| $c$, Å | 11.649(2) |
| α, deg | 84.60(3) |
| β, deg | 89.08(3) |
| γ, deg | 84.45(3) |
| Volume, Å$^3$ | 757.9(3) |
| $Z$ | 2 |
| $\rho_{calcd}$, mg/cm$^3$ | 2.088 |
| Absorption coefficient, mm$^{-1}$ | 8.039 |
| $F$(000) | 456 |
| Crystal size, mm | 0.10 × 0.08 × 0.04 |
| θ range of data collection, deg | 1.76 to 25.02 |
| Reflections collected | 4281 |
| Independent reflections ($R_{int}$) | 2614 (0.0506) |
| Max., min. transmission | 0.7392, 0.5003 |
| Goodness-of-fit on $F^2$ | 1.234 |
| Data/restraints/parameters | 2614/0/201 |
| Final $R$ indices ($I > 2\sigma(I)$)* | $R_1 = 0.0547$, $wR_2 = 0.1338$ |
| $R$ indices (all data)* | $R_1 = 0.0591$, $wR_2 = 0.1346$ |

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

**Table 2.** Selected bond lengths and angles for **I**

| Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|
| Re(2)–O(1) | 2.230(8) | Re(2)–O(3) | 1.722(8) |
| Re(2)–O(4) | 1.714(8) | Re(2)–O(5) | 1.718 (8) |
| Re(2)–C(15) | 2.119(12) | O(1)–C(1) | 1.330(13) |
| N(1)–C(7) | 1.317(14) | | |
| **Angle** | **ω, deg** | **Angle** | **ω, deg** |
| O(3)Re(2)O(1) | 85.5(3) | O(3)Re(2)O(4) | 116.4(4) |
| O(3)Re(2)O(5) | 103.9(4) | O(3)Re(2)C(15) | 120.1(4) |
| O(4)Re(2)O(1) | 79.8(4) | O(4)Re(2)O(5) | 104.1(4) |
| O(4)Re(2)C(15) | 115.6(5) | O(5)Re(2)O(1) | 166.3(4) |
| O(5)Re(2)C(15) | 90.2(5) | C(15)Re(2)O(1) | 76.3(4) |
| C(1)O(1)Re(2) | 131.9(7) | C(7)N(1)C(9) | 126.8(11) |

the IR matrix. Qualitative and quantitative analyses of organic products were conducted with gas chromatography on a SP 2100 instrument equipped with a FID and a capillary column (30 m × 320 μm × 0.25 μm) HJ SE-54. The Schiff base ligand was prepared according to the reference [17].

**Synthesis of $C_{14}H_{13}NO_2 \cdot CH_3ReO_3$ (I).** Complex **I** was prepared as follows: MTO (0.10 g, 0.4 mmol) was dissolved in diethyl ether (5 ml) and added dropwise to an equally concentrated solution of the ligand (0.4 mmol) in diethyl ether (5 ml), while stirring at 25°C. After 1.5–2.0 h the yellow-orange solution was concentrated under oil-pump vacuum to about 10 ml, and the precipitate was recrystallized under diethyl ether-hexane. The salmon-pink crystals of **I** were obtained in 30% yield.

For $C_{15}H_{16}NO_5Re$ ($M_r$ = 476.49)

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 37.92; | H, 3.33; | N, 3.04. |
| Found, %: | C, 38.06; | H, 3.36; | N, 3.20. |

IR (KBr; ν, cm$^{-1}$): 1638 (CH=N), 1092 $\nu_{as}$(Re=O), 934, 922 $\nu_s$(Re=O), 536 (Re–C). $^1$H NMR (300 MHz, DMSO, RT), δ: 13.212 (s., 1H, NH), 8.268–8.923 (s., 1H, CH=N), 6.861–7.480 (m., 8H, Ph), 3.829–3.847 (s., 3H, $OCH_3$), 1.859 (s., 3H, MTO–$CH_3$).

**X-ray structure determination.** Preliminary examination and data collection were performed with a Bruker Smart 1000 CCD diffractometer operating at 50 kV and 30 mA, which was equipped with a Mo$K_\alpha$ radiation source (λ = 0.71073 Å). A collection of the data of the complex was carried out at 113(2) K with the ω–φ diffraction measurement method, and reduction was performed using the SMART and SAINT software. An empirical absorption correction was implemented using the ADABS program. The structures were described by a combination of direct methods. All non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least squares on $F^2$ using the SHELXL-97 package. All hydrogen atoms were generated in ideal positions, appropriate sotropic thermal parameters were calculated and included in structure-factor calculations at the final stage of the $F^2$ refinement [18–22]. Crystallographic data are summed up in Table 1. Selected bond lengths and angles are listed in Table 2. Hydrogen-bonding geometric data are listed in Table 3. The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Centre (no. 751342; deposit@ccdc. cam.ac.uk or http://www.ccdc.cam. ac.uk).

**Catalytic cyclooctene epoxidation.** To a stirred solution of olefin (0.38 ml, 2.93 mmol), and $H_2O_2$ (0.60 ml, 19.59 mmol) in $CH_2Cl_2$ was added **I** (1.5 mol %, 43.97 μmol), and mixture was maintained at room temperature. The course of the reactions was monitored by quantitative GC analysis, while the samples were taken at regular time intervals and treated with a catalytic amount of $MgSO_4$ and $MnO_2$ to remove water and to destroy the unreacted peroxide. The resulting

**Table 3.** Geometric parameters of hydrogen bond for structure **I**

| Contact D–H···A | Distance, Å | | | Angle D–H···A, deg | Symmetry operations for A |
|---|---|---|---|---|---|
| | D–H | H···A | D···A | | |
| N(1)–H(1)···O(1) (intra) | 0.88 | 1.95 | 2.648 | 135 | $x, y, z,$ |
| N(1)–H(1)···O(4) (intra) | 0.88 | 2.40 | 3.164 | 145 | $x, y, z,$ |
| C(14)–H(14)···O(4) (intra) | 0.95 | 2.50 | 3.277 | 140 | $x, y, z,$ |
| C(15)–H(15B)···O(2) (intra) | 0.98 | 2.33 | 3.134 | 138 | $x, y, z,$ |
| C(4)–H(4)···O(4) (inter) | 0.95 | 2.53 | 3.205 | 128 | $x, -1 + y, z$ |
| C(7)–H(7)···O(3) (inter) | 0.95 | 2.57 | 3.398 | 146 | $-x, 1 - y, -z$ |
| C(11)–H(11)···O(5) (inter) | 0.95 | 2.58 | 3.474 | 157 | $x, y, -1 + z$ |

compound was filtered. The filtrate (0.1 ml), 8.6 mg of mesitylene (internal standard), and $CH_2Cl_2$ were added in 10-ml flask. A 1-μl sample was injected into a GC column. The conversion of *cis*-cyclooctene and the formation of cyclooctene oxide were calculated from calibration curves ($r = 0.99$) recorded prior to the reaction.

## RESULTS AND DISCUSSION

The crystal structure of **I** has been characterized by single-crystal X-ray analysis, which reveals that **I** displays a distorted trigonal-bipyramidal geometry, whose fundamental unit is shown in Fig. 1. The Re center is a five-coordinate structure and surrounded by four oxygen atoms and one carbon atom. For **I**, the two oxo ligands and one methyl group occupy the equatorial positions, while the remaining oxo ligand and the donating phenol group occupy the axial positions. It is noteworthy that the compound forms a *cis*-complex with MTO. To the best of our knowledge, a lot of *trans*-configured complexes of MTO are known, but very few *cis* complexes have been reported to date [13, 14], More recently, however, one of the Schiff bases of MTO that displays both *cis*- and *trans*-arrangement in the solid state is described [15]. This is a strong indication that packing effects have been thought to be responsible for the coordination modes, as has previously been noted [13, 14, 16]. The Re–C distance of I is 2.119(12) Å, which is slightly longer than that in free MTO (2.063(2) Å). This also explains that the Re–C bond is weakened and the complexes of MTO are generally somewhat less stable than the non-coordinated MTO alone. The Re=O bond distances are 1.722(8), 1.714(8), and 1.718(8) Å, respectively, which are similar to those in other MTO complexes. The Re–$O_{bridge}$ distance is 2.230(8) Å, which is shorter than the Re–O distance or the Re–N distance in some organorhenium(VII) complexes [23, 24]. The shorter Re–O bond in **I** indicates the movement of the originally O-bound proton to the –N=C– moiety to create a zwitterionic structure with the negatively charged oxygen atom binding to the Lewis acidic rhenium center [13]. The O=Re=O angles of the $ReO_3$ fragment in **I** vary from 103.9(4)° to 116.4(4)°. In addition, the phenol ring and the phenyl ring lie in the same plane (the C(6)–C(7)–N(1)–C(9) torsion angle is 179.82°). The presence of an intramolecular hydrogen bond between the donating oxygen atom and the hydrogen atom riding on the imine nitrogen atom as well as some weaker intramolecular hydrogen bonds can be seen (Table 3). The intermolecular hydrogen bonds link the molecules of the complex into a 2D layer structure (Fig. 2). The presence of the π–π-stacking interactions enhances the stability of the layers [25]. The layers are further linked via π–π-stacking interactions forming a three-dimensional supramolecular network (Fig. 3). The distance between Cg(I) and Cg(II) is 3.705(7) Å, in which Cg(I) is the ring center of C(1)–C(6) and Cg(II) is the ring center of C(9)–C(14).

A comparison between the FT-IR spectra of the ligand and **I** reveals considerable changes due to the coordination reaction of the Re atom and Schiff base ligand. IR spectroscopy reveals the symmetric and asymmetric $ReO_3$ vibrations at 1092, 934, and 922 $cm^{-1}$. Compared to the vibrations of non-coordinated MTO

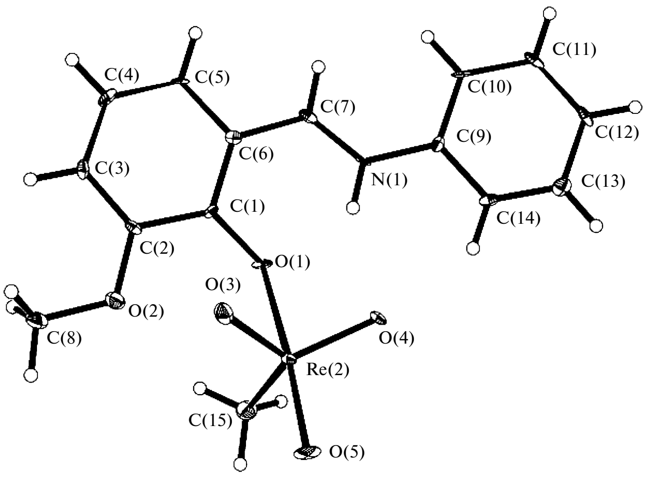

**Fig. 1.** Coordination environment of the Re atom in **I** with thermal ellipsoids at 30% probability.

**Fig. 2.** The 2D layer formed by intermolecular hydrogen bands.

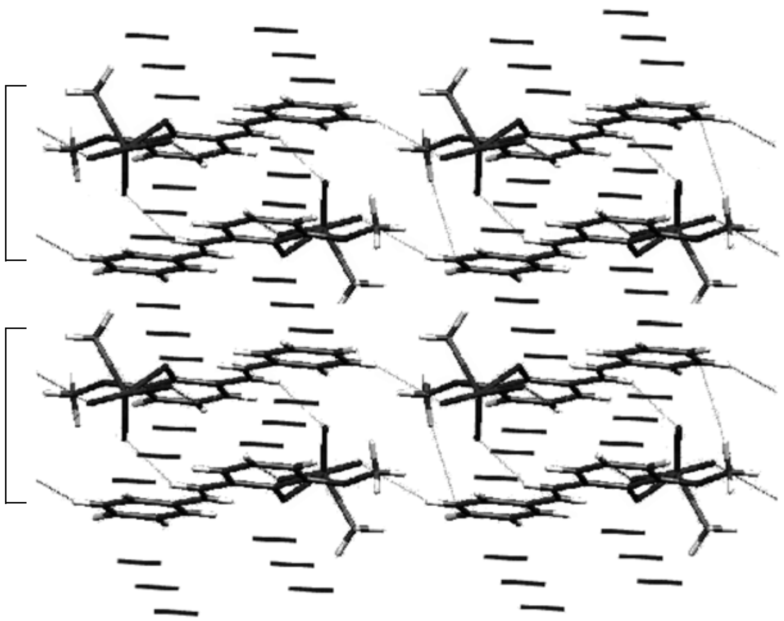

**Fig. 3.** View of the 3D supramolecular network along the *y* axis showing the presence of π–π-stacking interactions.

(998, 965 $cm^{-1}$), the Re=O bands of **I** are strongly red-shifted due to the pronounced donor capacity of the ligand in the solid state, which indicates that the oxygen atom of the Schiff base coordinates to the Re atom. For **I** and the free ligand, the C=N stretchings are visible at 1638 and 1615 $cm^{-1}$. As pointed out in our previous work [13], the displacement can be explained by the presence of an intramolecular hydrogen bond between the donating oxygen atom and the hydrogen atom riding on the imine nitrogen atom. The formation of the six-membered ring [C(1)O(1)H(1)N(1)C(7)C(6)] results in the absence of OH stretching bonds in the region about 3400 $cm^{-1}$.

It is observed from the $^1H$ NMR spectra that the proton signals are only very slightly shifted unfilled ($\Delta(\delta) = 0.052$ ppm) from the non-coordinated MTO to Schiff base-coordinated MTO. $^1H$ NMR data indicate only a weak interaction of the Re atom to the Schiff base. The $^1H$ signals of the imine group of **I** are shifted downfield slightly, in agreement with a changed coordination situation. The chemical shift change is about 0.038 ppm. The proton signals of the NH groups appear at about $\delta = 13.212$ ppm for **I**. The chemical shift change is about 0.007 ppm. The $^1H$ signals of the aromatic group both the ligand and **I** about $\delta = 6.861–7.480$ ppm. The observed chemical shifts match the ligand pattern very well.

The catalytic activity of **I**, which possesses the $OCH_3$ moiety on the phenolic ring with respect to olefin epoxidation is moderate. After further 24 h, the epoxide yield (70%) does not increase significantly compared to the yield (65%) after 4 h. This shows a similar high catalytic activity with the complex, which possesses the $OCH_3$ moiety on the phenolic ring and the phenyl ring, respectively [15]. These results match well with the spectroscopic data of the complex and show that a stronger donating ligand leads to a more stable catalyst, which is, however, less active.

Thus, the MTO Schiff base complex that displays *cis*-coordination about the ligand coordination mode to MTO is described. The complex displays distorted a trigonal-bipyramidal structure, as shown by X-ray crystallography, with the $O^-$ moiety binding to the Lewis acidic Re atom. The catalytic behavior is influenced significantly by the Schiff base coordinated to the MTO moiety, and the electron-donating $OCH_3$ group on the Schiff base leads to moderate catalytic activity with respect to olefin epoxidation.

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## REFERENCES

1. Herrmann, W.A., Fischer, R.W., and Marz, D.W., *Angew. Chem.,* 1991, vol. 103, no. 12, p. 1706.
2. Kühn, F.E., Zhao, J., and Herrmann, W.A., *Tetrahedron: Asymmetry*, 2005, vol. 16, no. 21, p. 3469.
3. Kühn, F.E., Scherbaum, A., and Herrmann, W.A., *J. Organomet. Chem.*, 2004, vol. 689, no. 24, p. 4149.
4. Kühn, F.E., Santos, A.M., and Herrmann, W.A., *Dalton, Trans.,* 2005, vol. 7, no. 15, p. 2483.
5. Adam, W., Saha-Möller, C.R., and Weichold, O., *J. Org. Chem.*, 2000, vol. 65, no. 16, p. 5001.
6. Adam, W. and Mitchell, C.M., *Angew. Chem. Int. Ed.,* 1996, vol. 35, no. 5, p. 533.
7. Huston, P., Espenson, J.H., and Bakac, A., *Inorg. Chem.*, 1993, vol. 32, no. 21, p. 4517.
8. Owens, G.S., Arias, J., and Abu-Omar, M.M., *Catal. Today*, 2000, vol. 55, no. 4, p. 317.
9. Herrmann, W.A., Fischer, R.W., Rauch, M.U., and Scherer, W., *J. Mol. Catal., A*, 1994, vol. 86, p. 243.
10. Carreiro, E., Burke, A.J., Curto, M.J.M., and Teixeira, A.J.R., *J. Mol. Catal., A*, 2004, vol. 217, nos. 1–2, p. 69.
11. Saladino, R., Andreoni, A., Neri, V., and Crestini, C., *Tetrahedron*, 2005, vol. 61, no. 5, p. 1069.
12. Haider, J.J., Kratzer, R.M., Herrmann, W.A., et al., *J. Organomet. Chem.,* 2004, vol. 689, no. 23, p. 3735.
13. Zhou, M.D., Zhao, J., Li, J., et al., *Chem. Eur. J.*, 2007, vol. 13, no. 1, p. 158.
14. Zhou, M.D., Yu, Y., Capape, A., et al., *Chem. Asian J.*, 2009, vol. 4, no. 3, p. 411.
15. Zhou, M.D., Zang, S.L., Herdtweck, E., and Kühn, F.E., *J. Organomet. Chem.,* 2008, vol. 693, no. 15, p. 2473.
16. Capapé, A., Zhou, M.D., Zang, S.L., and Kühn, F.E., *J. Organomet. Chem.*, 2008, vol. 693, p. 3240.
17. Maurya, R.C., Mishra, D.D., Rathore, R., and Jain, S., *Synth. React. Inorg. Met. Org. Chem.*, 1994, vol. 24, no. 3, p. 427.
18. Sheldrick, G.M., *SHELXTL-97, Program for Crystal Structure Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.
19. Sheldrick, G.M., *SHELXS-97, Program for Crystal Structure Solution,* Göttingen (Germany): Univ. of Göttingen, 1997.
20. *SMART, Version 5.618, A Software for the CCD Detector System*, Madison (WI, USA): Bruker Analytical X-Ray Systems, Inc., 1998.
21. *SAINTPLUS, Version 6.45, A Software for the CCD Detector System*, Madison (WI, USA): Bruker Analytical X-Ray System, Inc., 1998.
22. Blessing, R.H., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, vol. 51, p. 33.
23. Herrmann, W.A., Correia, J.D.G., Rauch, M.U., et al., *J. Mol. Catal., A*, 1997, vol. 118, no. 1, p. 33.
24. Herrmann, W.A. and Kühn, F.E., *Acc. Chem. Res.*, 1997, vol. 30, no. 4, p. 169.
25. Chen, X.M. and Liu, G.F., *Chem. Eur. J.*, 2002, vol. 8, no. 20, p. 4811.