



Communication

A (salicylidene)aniline derived Schiff-base adduct of methyltrioxorhenium(VII) – *Cis*- and *trans*-coordination of the ligandMing-Dong Zhou^{a,b}, Shu-Liang Zang^b, Eberhardt Herdtweck^a, Fritz E. Kühn^{a,*}^a Molekulare Katalyse, Fakultät für Chemie der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany^b Department of Petroleum and Chemical Technology, Liaoning University of Petroleum and Chemical Technology, Dandong Road, No. 1, 113001 Fushun, PR China

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ABSTRACT

A (salicylidene)aniline derived Schiff-base adduct of methyltrioxorhenium(VII), displaying both a *cis*- and a *trans*-arrangement of the Schiff-base ligand to the Re bound methyl group has been synthesized and described. Despite displaying some significant differences in the solid state (e.g. Re–O (Schiff base) bond distance, Re–C bond distance and several bond angles), the two configurations are indistinguishable in solution, obviously interchanging quickly.

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1. Introduction

Organorhenium oxides, in particular methyltrioxorhenium(VII) (MTO) have received significant attention due to their versatility as catalysts [1]. The increasingly easy and straightforward synthetic access ways to MTO [2], combined with its extraordinary stability furthered a plethora of examinations. The main areas of its application are in the mean time oxidation catalysis, olefination reactions and metathesis reactions [3]. A field of particularly detailed examinations within the catalytic oxidation area are olefin epoxidations [4]. It turned out already nearly two decades ago that MTO is one of the most active olefin epoxidation catalysts in the presence of hydrogen peroxide as the oxidant [4,5]. However, due to the pronounced Lewis acidity of MTO and the presence of water (formed as by-product from hydrogen peroxide) ring opening of the epoxides to diols takes place, particularly when more sensitive epoxides are formed [5,6]. The presence of Lewis bases diminishes the likelihood of epoxide ring opening, but also reduces the catalytic activity of MTO [6]. It was quickly discovered that Lewis bases form 1:1 adducts with MTO and many of its derivatives [1–3,7]. The Lewis-base adducts are usually coordinated in *trans*-position to the Re bound methyl group. The electron-donating Lewis bases result in a lengthening of the Re=O and Re–CH₃ bonds after complexation. These bond lengths changes are due to

the reduced need of the Lewis acidic Re atom (formally being in the oxidation state +VII) to withdraw significant electron density from these ligands, since additional electron density is provided by the Lewis base.

This effect is reflected in the spectroscopic and crystallographic data of adducts and leads usually to a slightly reduced stability of these adducts, when compared to MTO itself. If 10–12-fold excesses of aromatic Lewis bases are added to MTO in situ, these reaction mixtures show very high catalytic activity (even surpassing MTO itself) and high selectivities towards the epoxides, the diol formation being completely or almost completely suppressed [8]. More detailed examinations, following closely this breakthrough revealed that some disadvantages still remain [9]. The weak coordination of the Lewis bases largely prevent a successful immobilization of the otherwise excellent catalytic system [10] and the attempt to transfer chirality by introducing it via the base ligand into the system also suffers from both the huge excess of (expensive) base ligand needed and the insufficient chirality transfer due to the weak ligand–metal interaction [11]. The application of Schiff-base ligands instead of N-donor ligands seemed to solve at least one problem: large ligand excesses were not necessary to achieve high activities and selectivities [12]. Nevertheless, Schiff bases are also weakly coordinated to the Re atom and the reasons behind the observation of a *cis* or a *trans* coordination (with respect to the Re–CH₃ bond) of the Schiff base to the MTO moiety remained unknown, although some influence of the substituents at the Schiff base was considered to be the driving force. It was noted that *cis* and *trans* coordination is dependent on the ligand employed. In

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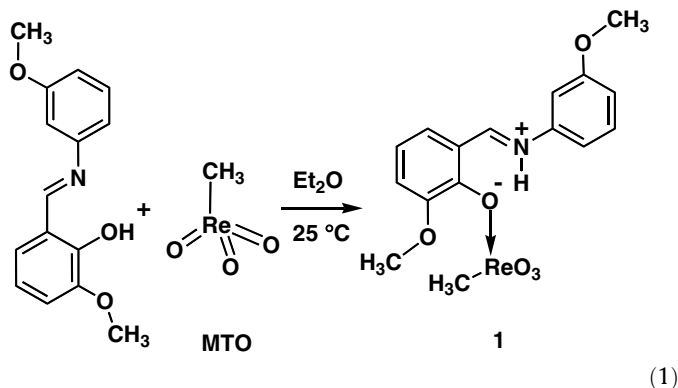
the case of N-donor ligands, *cis* coordination is very rare and has, to the best of our knowledge, been described only twice [7,12].

In this work, we report on a Schiff-base ligand, being able to bind both in a *cis*- and a *trans*-mode to MTO. This uncommon feature allows a direct comparison of the structures and helps to gain insight in the MTO–ligand interactions, which are very important for the further choice of appropriate base ligands to fine tune the catalytic activities of MTO and its derivatives.

2. Results and discussion

2.1. Spectroscopy and catalysis

As many other Lewis-base adducts of organorhenium(VII) oxides, Schiff-base adducts are formed by mixing the reaction partner in a reaction vessel at room temperature in diethyl ether (Eq. (1)). The starting materials being white (MTO) and orange (ligand) solids, the product formation can be easily followed due to the appearance of a bright red colour. The red product complex of formula **1** (Chart 1) can be purified by recrystallization from Et₂O/*n*-hexane. It is stable in air at room temperature for several days but is slightly sensitive to moisture and elevated temperatures. For longer storage (weeks), it should be kept in a refrigerator to avoid partial decomposition.



IR spectroscopy (see Table 1) reveals the symmetric and asymmetric CH₃-deformation vibration (MTO) at 1371 and 1266 cm⁻¹, respectively. The symmetric and asymmetric ReO₃ vibrations are found at 1006, 931 and 917 cm⁻¹ and the Re–C stretching vibration is visible at 555 cm⁻¹. The value of ($\nu_s - \nu_{as}$) ReO₃ is 82 cm⁻¹ indicating a *cis*-arrangement of the Schiff-base ligand to the Re bound methyl group, however no significant split of the frequencies of Re=O vibrations can be observed for the *trans*-configuration. Compared to the average ReO₃ stretching vibration of MTO (976 cm⁻¹), a 25 cm⁻¹ frequency shift reduces the Re=O stretching force

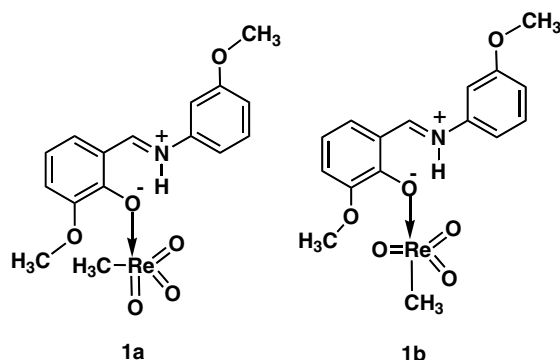


Table 1
Selected IR (KBr) data (cm⁻¹) for compound **1**

Compound 1	Assignment
1646 s	C=N ⁺ stretch
1500 s	CC stretch (aromatic)
1488 s	CC stretch (aromatic)
1371 m	CH ₃ asym deform (MTO)
1297 m	CH in-plane deform, CC stretch (aromatic)
1266 s	CH ₃ sym deform (MTO)
1142 m	CH ₃ rocking (methoxy); CH in-plane deformation (aromatic)
1006 m	ReO ₃ sym stretch
931 s; 917 vs	ReO ₃ asym stretch
742 s	CH ₃ rocking (MTO), CH out-of-plane deform (aromatic)
555 m	Re–C stretch (MTO)

constant from 8.31 N cm⁻¹ (MTO) to 7.83 N cm⁻¹ for complex **1** (951 cm⁻¹ in average), indicating a weaker Re=O interaction, due to the additional electron density given from the ligand to the Lewis acidic Re atom [13]. It is important to note that after complexation the imine group vibration shifts from 1617 to 1645 cm⁻¹ and the phenolic OH group and coupled ring vibrations disappear, but a broad and weak NH stretching band can be seen at 2580 cm⁻¹. This is in accord with the previously assumed transfer of the phenolic–OH proton to the imine nitrogen atom under formation of a zwitterion, the negatively charged oxygen coordinating as nucleophile to the electrophilic Re(VII) atom of MTO [12]. Proton and carbon NMR indicate only a weak interaction of the Re atom to the Schiff base, reflected only in a small chemical shift difference of the Re–CH₃ protons ($\Delta(\delta) = 0.05$ ppm) and carbon ($\Delta(\delta) = 0.1$ ppm) atom from non-coordinated to coordinated state of the MTO. This observation is supported by ¹⁷O NMR spectroscopy with Schiff-base adducts containing ¹⁷O-labelled MTO at 832 ppm. At room temperature, the Re bound oxygen atoms are seen as a single peak, which does not split up when lowering (to –50 °C) or increasing the temperature (to +50 °C). In the light of the X-ray structure (vide infra) this indicates significant fluctuancy within the system. If two distinct isomers would be present in solution without an easy transformation into each other, three different peaks should be observed in the ¹⁷O NMR spectrum (one for the *trans* isomer, two for the *cis* isomer). This fluctuancy behaviour is, however, not surprising, considering the previously observed structural lability of other MTO Lewis-base adducts [14].

As expected from the presence of two electron-donating OCH₃ groups in the Schiff-base ligand [12], the catalytic activity with respect to olefin epoxidation is only moderate. If cyclooctene is used as epoxide, 55% of cyclooctene epoxide is reached, after 24 h, the yield is approximately 65%. The turnover frequency (TOF) is ca. 100 mol/(mol h), if a oxidant:substrate:catalyst ratio of 200:100:1 is applied.

2.2. Structural implications

As outlined in Section 1, many *trans*-configured Lewis-base adducts of MTO are known, and only a few *cis* adducts. Compound **1**, however, displays both forms in one crystal, thus allowing a direct comparison of both forms. The related (anilin-*N*)methyl (trioxo)rhenium(VII) adduct [7] is one of the rare examples with the same 1:1 mixture of *cis* and *trans* configuration in the solid state. The structures of **1a** and **1b** are depicted in Fig. 1, selected bond lengths and angles are summarized in Table 2.

In the *cis*-configured molecule **1a** the C–Re–O angle is 76.2(1)°, while the *trans* arranged O=Re–O moiety displays an O–Re–O angle of 166.7(1)°. The *trans*-configured molecule **1b** displays an almost linearly arranged H₃C–Re–O (Schiff base) moiety, the C–Re–O angle being 177.4(1)°.

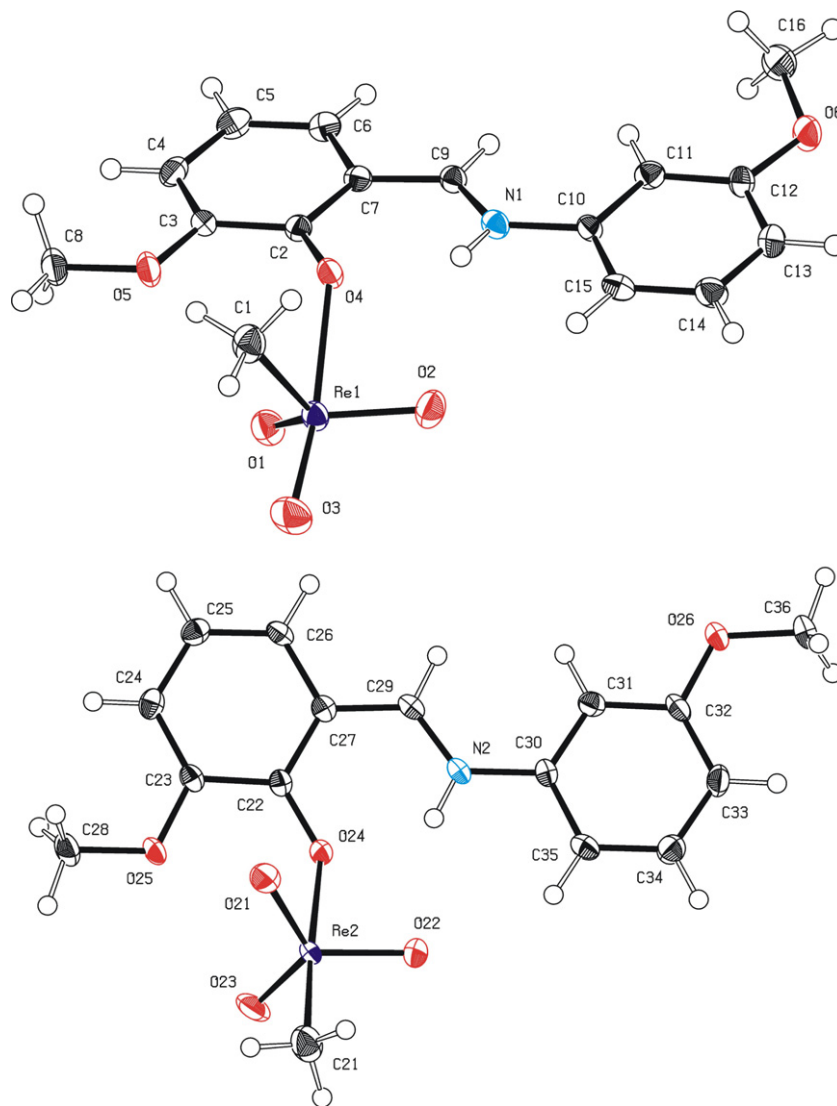


Fig. 1. ORTEP style plot of molecules **1a** (top) and **1b** (bottom) in the solid state. Thermal ellipsoids are drawn at the 50% probability level.

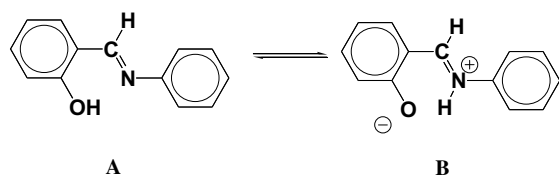
Table 2

Selected bond lengths (Å) and bond angles (°) for **1a** and **1b**

1a (<i>cis</i>)				1b (<i>trans</i>)			
<i>Bond lengths</i> (Å)							
Re1–O1	1.717(2)	Re1–O4	2.218(2)	Re2–O21	1.719(2)	Re2–O24	2.295(2)
Re1–O2	1.710(3)	Re1–C1	2.121(5)	Re2–O22	1.706(3)	Re2–C21	2.093(4)
Re1–O3	1.714(3)	C7–C9	1.419(5)	Re2–O23	1.702(3)	C27–C29	1.415(5)
<i>Bond angles</i> (°)							
O1–Re1–O2	117.0(1)	O2–Re1–C1	113.3(2)	O21–Re2–O22	119.1(1)	O22–Re2–C21	95.9(2)
O1–Re1–O3	104.2(2)	O3–Re1–O4	166.7(1)	O21–Re2–O23	120.7(1)	O23–Re2–O24	87.1(1)
O1–Re1–O4	83.7(1)	O3–Re1–C1	90.5(2)	O21–Re2–O24	86.3(1)	O23–Re2–C21	94.5(2)
O1–Re1–C1	121.8(2)	O4–Re1–C1	76.2(1)	O21–Re2–C21	94.6(2)	O24–Re2–C21	177.4(1)
O2–Re1–O3	103.6(2)	Re1–O4–C2	131.7(2)	O22–Re2–O23	117.9(1)	Re2–O24–C22	130.3(2)
O2–Re1–O4	81.7(1)	C9–N1–C10	127.6(3)	O22–Re2–O24	81.6(1)	C29–N2–C30	126.9(3)

In **1a** the Re–O (Schiff base) distance is 2.218(2) Å, while it is 2.295(2) Å in **1b**. The difference in length is almost 0.08 Å and therefore significant. It is interesting to note that all so far examined *cis* adducts display shorter Re–L bond distances than the *trans* adducts [7,12]. In (anilin-*N*)methyl(trioxo)rhenium(VII), where a non-zwitter ionic ligand coordinates via the N-atom to MTO, the Re–N bond distances are longer, namely 2.333(5) Å (*cis*-derivative)

and 2.469(4) Å (*trans*-derivative) [7]. In the other known *trans*-configured MTO-Schiff-base adducts—C₁₃H₁₁NO · (CH₃)ReO₃, C₁₄H₁₃NO · (CH₃)ReO₃ and C₁₃H₁₀CINO · (CH₃)ReO₃, The Re–O (Schiff base) bond distances are 2.269(7) Å, 2.243(4) Å, and 2.286(5) Å, respectively. However in the *cis*-arranged compounds C₁₄H₁₃NO₂ · (CH₃)ReO₃ and C₁₅H₁₅NO₂ · (CH₃)ReO₃, the Re–ligand bonds are 2.153(5) Å and 2.210(7) Å [12]. The observation that in



Scheme 1. Tautomerism in (salicylidene)aniline.

the *cis* coordinated derivatives the Re–ligand bond is generally shorter might be due to the fact that *cis* adducts have an electro-negative oxygen atom in *trans*-position to the donor ligand L, employing its *trans*-effect on the ligand standing at the opposite side of the molecule. The *trans*-adducts have a methyl group in *trans*-position, which, being a donor, does not allow such a close proximity of the donor atom of the base in *trans* position to another donor group. The closer the Schiff-base donor ligand comes, the more the Re–C bond is weakened, as reflected in the 2.121(5) and 2.093(4) Å Re–C bond distance in **1a** and **1b**, respectively. Usually a widening of the Re–C bond distance leads to an easier complex decomposition, which also explains the lower temperature stability of the Lewis- and Schiff-base adduct complexes in comparison to MTO.

A search in the Cambridge data base with the basic (salicylidene)aniline skeletal structure as a searching motif [15] revealed 330 hits out of 423 752 entries including both compounds with the phenol tautomer **A** and the zwitter ion tautomer **B** (Scheme 1). An accurate examination of the geometry of the central C_{ph}–C–N–C_{ph} moiety shows small but significant differences. For type **A** compounds the C_{ph}–C distances range around 1.43 Å whereas type **B** compounds show shortened distances of about 1.41 Å. For both the C–N and the N–C_{ph} distances are equal within 3 esd's and no trend is obvious. More pronounced and therefore significant are the bond angles C–N–C_{ph}. Type **A** compounds range around 121°. In type **B** compounds, this bond angle is widened up to 127°. Within this results, both molecules **1a** and **1b** fulfil the requirements for type **B** structures (**1a**): C7–C9 1.419(5) Å and C9–N1–C10 127.6(3)°; **1b**: C27–C29 1.415(5) Å and C29–N2–C30 126.9(3)°. Additional sophisticated refinements of the X-ray data confirmed the hydrogen position [16].

It is interesting to note, however, that in solution (*vide supra*) these different coordination modes are not reflected in the spectra. Even at low temperatures only one signal is present in ¹⁷O NMR spectroscopy. This indicates the weakness of the MTO Schiff-base interaction and the ease to interchange *cis*- and *trans*-configuration in solution phase.

3. Summary

A MTO Schiff-base adduct is described that displays both *cis*- and *trans*-coordination with respect to the ligand coordination mode to MTO. Both isomers must be very close in energy, since in solution no hint for different coordination modes can be found. The appearance of both isomers in one crystal also indicates that packing effects largely determine the coordination mode. It was not excluded prior to this work, that the donor- or acceptor-ability of the base ligand influences the coordination mode strongly. This is seemingly not the case since both isomers can obviously be present with the same base ligand attached to MTO. The structures described here also demonstrate that *cis* or *trans*-positioning of a donor ligand to MTO influences both the ligand–Re and the Re–C bond distance, but has no detectable impact on the Re=O bond length. The two electron-donating OCH₃ groups on the Schiff base lead to moderate catalytic activity with respect to olefin epoxidation.

4. Experimental

4.1. Synthesis and characterisation

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures (*n*-hexane and Et₂O over Na/benzophenone; CH₂Cl₂ over CaH₂), distilled under argon and kept over molecular sieves. Elemental analyses were performed with a Flash EA 1112 series elemental analyser. ¹H, ¹³C NMR and ¹⁷O NMR were measured in CDCl₃ with a Mercury-VX 300 spectrometer, a Varian 270 and 400 MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded with a Nicolet 5700 FT-IR spectrometer using KBr pellets as the IR matrix. CI mass spectra (isobutene as CI gas) were obtained with a Finnigan MAT 90 mass spectrometer. Catalytic runs were monitored by GC methods on a Varian CP-3800 instrument equipped with a FID and a VF-5ms column. The Schiff-base ligands were prepared as described in the literature [17]. Compound **1** was prepared as follows: a solution of [(CH₃)ReO₃] (0.15 g, 0.6 mmol) in diethyl ether (5 mL) was added drop wise to an equally concentrated solution of ligand (0.6 mmol) in diethyl ether (5 mL) while stirring at room temperature. After 30 min the orange solution-mixture was concentrated to about 3 mL under oil pump vacuum and the red precipitate recrystallized from CH₂Cl₂/*n*-hexane. Yield: 0.24 g, 79%. Anal. Calc. for C₁₆H₁₈NO₆Re (506.52): C, 37.94; H, 3.58; N, 2.77. Found: C, 38.49; H, 3.47; N, 2.70%.

Spectroscopic data: IR(KBr, ν[cm⁻¹]): 1646s, 1500s, 1488s, 1371m, 1297m, 1266s, 1142m, 1006m ν_s (Re=O), 931s, 917vs ν_{as} (Re=O), 742s, 555m; ¹H NMR (CDCl₃, 300 MHz, 25 °C, ppm): 13.63 (C–OH, s, 1H), 8.62 (CH=N, s, 1H), 7.32–6.83 (aryl-H, m, 7H), 3.94 (Ph–OCH₃, s, 3H), 3.85 (Ph–OCH₃, s, 3H), 2.62 (Re–CH₃, s, 3H); ¹³C NMR (CDCl₃, 100.28 MHz, 25°C, ppm): δ = 196.59 (C–OH), 162.73, 160.49 (CH=N), 151.51, 149.48, 130.14, 123.83, 118.51, 114.86, 113.27, 112.62, 107.01 (C–aryl), 56.20, 55.38 (O–CH₃), 19.11 (Re–CH₃); CI-MS (70 eV): *m/z* = 258.1 [M⁺–MTO], 251.0 [M⁺–L].

4.2. Single crystal X-ray structure determination

General: Crystallographic data are presented in Table 3. Preliminary examination and data collection was carried out on an area detecting system (Nonius κ-CCD device) at the window of a rotat-

Table 3
Summary of the crystallographic data

Formula	C ₁₆ H ₁₈ NO ₆ Re
M _w	506.52
Crystal system	Triclinic
Space group	P1 (no. 2)
Crystal size (mm ³)	0.25 × 0.48 × 0.66
Crystal colour/shape	Red/needle
<i>a</i> (Å)	11.4383(1)
<i>b</i> (Å)	11.9898(1)
<i>c</i> (Å)	12.8468(2)
α (°)	94.4663(4)
β (°)	102.1709(4)
γ (°)	106.9578(5)
<i>V</i> (Å ³)	1628.96(3)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	2.065
μ (mm ⁻¹)	7.492
θ-Range (°)	1.64/25.42
Reflections collected	35 534
Reflections independent [<i>I</i> ₀ > 2σ(<i>I</i> ₀)/all data/ <i>R</i> _{int}]	5524/6004/0.057
Data/restraints/parameters	6004/0/440
<i>R</i> ₁ [<i>I</i> ₀ > 2σ(<i>I</i> ₀)/all data]	0.0214/0.0244
<i>wR</i> ₂ [<i>I</i> ₀ > 2σ(<i>I</i> ₀)/all data]	0.0544/0.0557
Goodness-of-fit	1.108
(Δρ) _{max/min} (e Å ⁻³)	0.98/–0.94

ing anode (Nonius, Fr591) and graphite monochromated Mo α radiation ($\lambda = 0.71073 \text{ \AA}$) [18]. Data collection were performed at 173 K (Oxford Cryosystems). The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions (riding model, $d_{\text{N-H}} = 88 \text{ pm}$ and $d_{\text{C-H}} = 95, 98 \text{ pm}$). Isotropic displacement parameters were calculated from the parent carbon/nitrogen atom ($U_{\text{H}} = 1.2/1.5U_{\text{C/N}}$). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. The final residual electron density maps show no remarkable features. Programs used: SIR92 [19], SHELXL-97 [20], and PLATON [21]. Raw data were corrected for Lorentz, polarization, and absorption effects. A numerical absorption correction was applied after crystal shape optimization with the programs XSHAPE and XRED ($\mu = 7.492 \text{ mm}^{-1}$, $T_{\text{min}} = 0.1304$, $T_{\text{max}} = 0.3735$) [22]. Small extinction effects were corrected with the SHELXL-97 procedure and $\varepsilon = 0.00223(9)$. The asymmetric unit cell contains two crystallographically independent molecules representing the possible *cis*- (**1a**) and *trans*- (**1b**) isomers.

4.3. Catalytic cyclooctene epoxidation

Cis-cyclooctene (800 mg, 7.3 mmol), 1.00 g of mesitylene (internal standard), H_2O_2 (30% aqueous solution; 1.62 mL, 14.6 mmol) and 1 mol% (73 μmol) of compounds **1** were mixed, diluted in 30 mL of CH_2Cl_2 , added to the reaction vessel under air at room temperature and the reaction was started by adding H_2O_2 . The course of the reactions was monitored by quantitative GC analysis. 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 slurry was filtered and the filtrate injected onto a GC column. The conversion of cyclooctene and the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction.

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Appendix A. Supplementary material

CCDC 688262 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.05.003](https://doi.org/10.1016/j.jorganchem.2008.05.003).

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