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(N-Salicylidene)aniline Derived Schiff Base Complexes of Methyltrioxorhenium(VII): Ligand Influence and Catalytic Performance

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Abstract: Methyltrioxorhenium(VII) (MTO) readily forms 1:1 adducts with several N-(salicylidene)aniline derived Schiff bases. If the aromatic rings of the N-(salicylidene)aniline ligands display non-donating or electron withdrawing substituent groups, the resulting MTO adducts show good activities in olefin epoxidations. However, steric effects seem to play a major role, leading often to instable *o*- and *m*-Schiff base–MTO adducts, while *p*-substituted Schiff bases usually lead to more stable adducts. In catalysis, electron-withdrawing substituents on the aniline moiety lead to better catalysts than electron donating ones. The gap between good catalysts and instable or non-existing compounds, however, is small. The general tendency, however, that good donors on the Schiff base ligands lead to shorter Re–O(Schiff base) bridges and lower catalytic activity, while the opposite is true with acceptor ligands on the Schiff bases, seems to be quite clear.

Keywords: (N-salicylidene)aniline · catalysis · epoxidation · rhenium · Schiff bases

Introduction

From 1958 to the early 1960s, organometallic compounds with high metal oxidation states were looked upon more as laboratory curiosities than possible catalysts.[1] At that time many organic reactions were not catalysed and produced large amounts of waste—like in the synthesis of propene epoxide—an olefin epoxidation reaction.[2] At the end of the 1960s however, Halcon and Arco patented[3] a homogenous catalytic process that allowed for a much cleaner production of propene oxide and other oxiranes, using various alkyl hydroperoxides as oxidizing agents. Subsequently, in the following years, numerous efforts were dedicated to unravel the mechanism of the catalytic olefin epoxidation process and to the search for increasingly efficient catalysts.[4]

Although many of its congeners originally were considered to be mere curiosities,[5] methytrioxorhenium (MTO) soon came to be known as an important catalyst.[6] It has been shown that MTO is an extremely versatile catalyst or catalyst precursor for a broad variety of organic reactions.[7] Among the plethora of applications, olefin epoxidation is, so far, one of the best examined.[8] MTO utilizes hydrogen peroxide as an oxidizing agent thereby producing only water as the by-product, making such a reaction environmentally benign unlike others of this type.[9] MTO has the additional advantage of being stable in an aqueous medium.

The production of water combined with the pronounced Lewis acidity of MTO has a side effect which is sometimes unwanted: it furthers ring opening reactions of more sensitive epoxides via the formation of diols.[10] However, it was found that Lewis base adducts of MTO, such as adducts with nitrogen donor ligands, largely suppress the ring opening reaction.[11] Unfortunately the activity of the MTO Lewis base adducts originally examined was, at least in most

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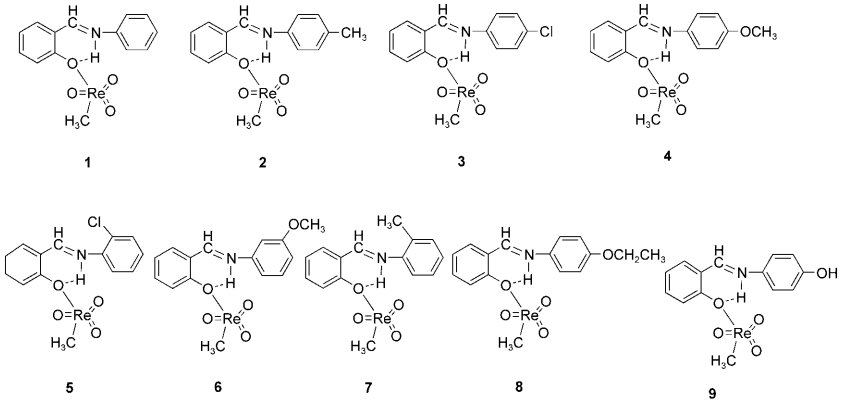
cases, found to be significantly lower than that of MTO itself.[12] Nevertheless, application of aromatic N-donor ligands in ten or twelve fold excesses together with MTO, leads to higher activities and selectivities in epoxidation catalysis than the application of MTO alone.[13] Both monodentate and bidentate aromatic Lewis bases with N-donor ligands display this behaviour.[14] To date, many N-base adducts of MTO have been isolated, characterized, and applied for the epoxidation of olefins as catalysts,[15] however, significant excess of N-base is essential for the selectivity of those reactions.

It is only recently that papers have appeared dealing with the title complexes of this work, (N-salicylidene)aniline based Schiff base adducts of MTO and their performances in catalytic olefin epoxidation.[16] It was found that some of these complexes display high catalytic activities in cyclooctene epoxidation, while others are highly unstable and decompose readily at room temperature within seconds. In the case of the highly active compounds, however, no excess of Schiff base in comparison to MTO is necessary to reach similar selectivities as the MTO/excess N-base systems. This work examines the influence of substituents on the aromatic ring of the aniline moiety on the stability and catalytic performance of Schiff base adducts of MTO and their performance in the epoxidation of a broader variety of substrates.

Results and Discussion

In a previous work,[16] some Schiff base adducts of MTO with *para*-substituents on the aniline moiety of the (N-salicylidene)aniline ligand, so as to avoid any steric interference of the adduct with the MTO, were described. In this work, various *ortho*- and *meta*-substituted aniline moieties are examined and the effects of such a substitution pattern of the Schiff base ligands on the catalytic activity of the MTO adducts are compared to the previously obtained results. Scheme 1 represents all synthesized complexes. The non-substituted compound **1**, also described previously,[16a] is used as the standard. The complexes **2**–**4** bearing trans-substituted aniline moieties have also been described before.[16a]



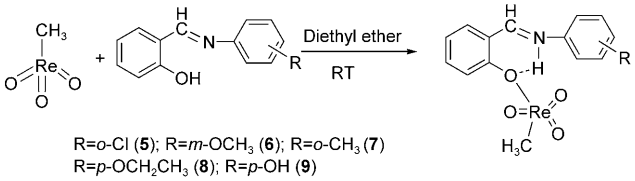
Scheme 1. Synthesized MTO Schiff base complexes.

This paper deals in particular with the synthesis and applications of complexes **5**–**9**.[10a] However, our attempt to synthesize other MTO adducts with *o*-, *m*-, and *p*-substituted aniline moieties to obtain a complete row of complexes was not successful. The Schiff base ligands either did not react with MTO or formed an instable product. The hypothetic formulae of the inaccessible compounds are shown in the Supporting Information.

Synthesis and Spectroscopic Characterization

Compounds **5**–**9** (Scheme 1) were synthesized by treatment of MTO with the respective Schiff bases in diethyl ether at room temperature (Scheme 2).

The compounds **5**–**9** are, as complexes **1**–**4**,[16a] stable at room temperature in solution as well as in the solid state and can be handled without decomposition. The asymmetric



Scheme 2. Synthesis of MTO compounds **5**–**9**.

Re=O stretching vibrations in the IR spectra of compounds **5**–**9** are found in the region 900–960 cm^{-1} on average. For compounds **5**–**7** and **9**, the ReO_3 stretching bands show a splitting of approximately 15 cm^{-1} (Table 1). It is seen that in comparison to the averaged symmetric and asymmetric stretching vibrations exhibited by non-coordinated MTO, the respective Re=O bands of compounds **5**–**9** are slightly red-shifted. This shift most likely originates from the moderate charge transfer from the ligand to the Lewis acidic MTO. Additional electron density donated from the ligand to the Rhenium(VII) center usually reduces the bond order of Re=O and this is observed for all the compounds **5**–**9**.

The differences between the averaged symmetric and asymmetric stretching vibrations as given in the last row of Table 1 deserve some attention. In our previous work we had ascribed the differences between the values mainly to the symmetry of the coordination around the Re atom.[16a] However, the larger quantity of data available now leads to a somewhat different hypothesis as an explanation. The values obtained for compounds **4** and **8** are most prominently different from the value of the "standard" compound **1**. Compounds

CHEMISTRY
AN ASIAN JOURNAL

Table 1. Characteristic IR vibrations of CH_3ReO_3 fragments (cm^{-1}) in **1–9**.

MTO	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	Assignment
1368	1376	1375	1375	1380	1369	–	1375	1385	1363	CH_3 asym def
1205	1216	1210	1215	–	1247	1245	1252	–	1217	CH_3 sym def
998	1005	1007	1012	1035	999	1000	1001	1011	1005	ReO_3 sym str
965	928	935	950	925	930	931	930	918	926	ReO_3 asym
	919	911	921	914	913	918	918		913	str
567	576	576	573	525	575	576	553	558	558	ReC str
976	950	951	961	958	947	950	950	965	948	ReO str. averaged
33	81.5	84	76.5	120.5	77.5	76	76.5	93	83.5	$(\nu_s-\nu_a)$ ReO_3

4 and **8** have donor ligands in the *para*-position of the aniline moiety. The weaker donors in compound **2** and **9** lead to a considerably less pronounced enlargement of the value, while the electron acceptor Cl leads to a slight reduction of the difference between the symmetric and asymmetric stretching vibrations. The *ortho*- and *meta*- substitutions lead only to smaller effects than those observed for the *para*-substituted compounds (comparable to the order of magnitude observed for compound **3**). It can be concluded that their electronic effects on the attached MTO moiety therefore is on average less pronounced than that of the substituents in the *para* position.

As has already been pointed out for complexes **1–4**,[16a] the absence of OH stretching bands of the Schiff bases in the region around 3400 cm^{-1} indicates the presence of a strong intramolecular hydrogen bond with the nitrogen atom of the imine group to form a six-membered ring. The broad band with a specific fine structure in the range 2900–2400 cm^{-1} is most likely from the phenolic OH stretching feature characteristic of a strong hydrogen bond. There are other low-frequency bands, which are characteristic for a phenolic OH group in the spectra of the pure Schiff base ligands. These bands, together with the OH stretching vibrations, are also conspicuously absent in the spectra of the newly synthesized compounds **5–9** (see Table 2), thereby supporting our original ideas about the coordination of the Schiff base ligands to MTO.

Usually molecules of the type PhCH=NPh will display a medium strength IR band at about 1650 cm^{-1}, arising from the C=N stretching mode, if undisturbed. For the ligand complexes **5–9**, these bands are found between 1601–1619 cm^{-1} (Table 2). This lowering of 40–50 cm^{-1} is in a similar order of magnitude as the reduction observed in compounds **1–4**[16a] and also strengthens the assumption of the existence of an intramolecular hydrogen bond between the phenolic hydrogen and nitrogen atoms. After complexation, the proton is attached to the nitrogen atom, the C=N vibrations being observed at higher wave numbers ranging from 1633–1650 cm^{-1}.

In the ^{1}H NMR spectra of compounds **1–9** (Table 3), it is seen that the proton signals are only very slightly shifted to high field as compared to the value of MTO. It is observed that the new complexes with *ortho*- and *meta*- substituted derivatives show very similar properties with respect to the ^{1}H NMR spectra as the *para*-substituted derivatives. The values in the coordinating solvent DMSO are virtually identical with that of MTO. DMSO, being a coordinating solvent might be able to replace Schiff base ligands comparatively easily, particularly when used in large excess, as is the case here. These observations support the notion of a very weak MTO–Schiff base interaction. These results further indicate that Schiff bases are most likely even more weakly bonded to MTO than several of the N-donor adducts examined before.

Table 3. Selected ^{1}H NMR data (ppm) of MTO and compounds **1–9** in $CDCl_3$ or DMSO.

Compound	$\delta_{MTO-CH3}$ $CDCl_3$	DMSO	$\delta_{N(O)-H}$ $CDCl_3$	DMSO
MTO	2.67	1.91	–	–
1	2.62	–	13.25	–
2	2.63	–	13.49	–
3	2.62	–	13.02	–
4	2.61	–	13.45	–
5	2.63	–	13.07	–
6	2.60	–	13.22	–
7	2.61	1.91	13.49	13.37
8	2.60	1.90	13.52	13.30
9	–	1.90	–	13.41

The N (O) bonded hydrogen atom (proton) is in all cases observed between 13.02 and 13.52 ppm. The shift differences between the different compounds however, are too small to allow for a profound discussion of the influence of the varying Schiff base substituents.

Table 2. Selected IR (KBr) data (cm^{-1}) for compounds **5–9**. The respective pure ligand vibrations are given for sake of comparison.

Compound	Imine group	Phenolic OH group and coupled ring vibrations				
	ν(C=N)	β [OH]	ν(CX)	ν(CX)	N(CX)	γ(OH)
$C_{13}H_{10}Cl$ NO	1615 s	1367 m, sh	1281 s	1056 m, sh	818 m	755 vs
$C_{13}H_{10}Cl$ NO·CH_3ReO_3 (**5**)	1633 s					
$C_{14}H_{13}NO_2$	1601 s	1368 m	1287 s	1045 s	834 s	752 s
$C_{14}H_{13}NO_2$·CH_3ReO_3 (**6**)	1650 s					
$C_{14}H_{13}N$ O	1617 vs	1365 m	1280 s	1035 m	835 s	754 vs
$C_{14}H_{13}N$ O·CH_3ReO_3 (**7**)	1643 s					
$C_{15}H_{15}NO_2$	1617 vs	1367 m	1258 s	1107 m, sh	838 s	754 s
$C_{15}H_{15}NO_2$·CH_3ReO_3 (**8**)	1634 s					
$C_{13}H_{11}NO_2$	1619 s	1391 m, sh	1241vs	1047 s	841 m	741 s
$C_{13}H_{11}NO_2$·CH_3ReO_3 (**9**)	1645 s					

Notation of vibrational modes: υ(C=N), C=N stretching; β(OH), hydrogen bonded OH in-plane deformation; $\upsilon_{(CX)}$, substituent sensitive aromatic ring stretchings; γ(OH) phenolic out-of-plane vibrations.

These results help to realize that the border between stability, instability, and non-existence of these Schiff base adducts is seemingly quite narrow. The reasons whether or not a complex can be isolated or prepared seems to depend on both steric and electronic factors, and steric hindrance seems to be a good reason to account for the non-existence of some of the complexes.

X-ray Crystal Structures of Compounds 5–9

The solid-state structures of the examined compounds are shown in Figure 1–5, and selected bond distances and bond angles given in Tables 4–6.

It is observed that both trans (compounds **5**, **7–9**, Figures 1, 3–5) and cis (compound **6**, Figure 2) structures, with

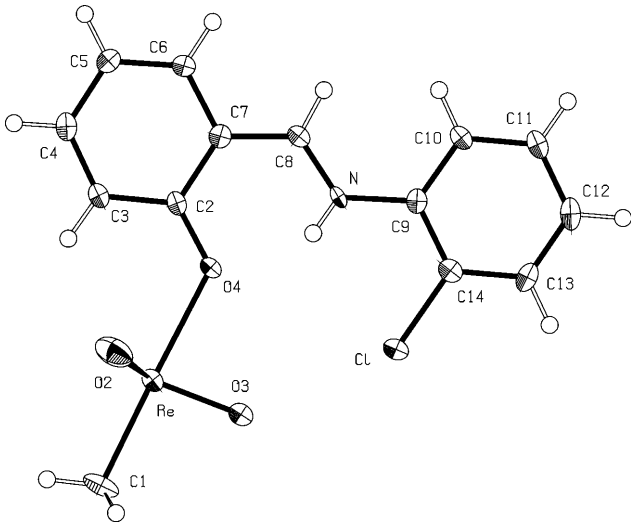


Figure 1. ORTEP style plot of compound **5** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. The molecule is located on a mirror plane.

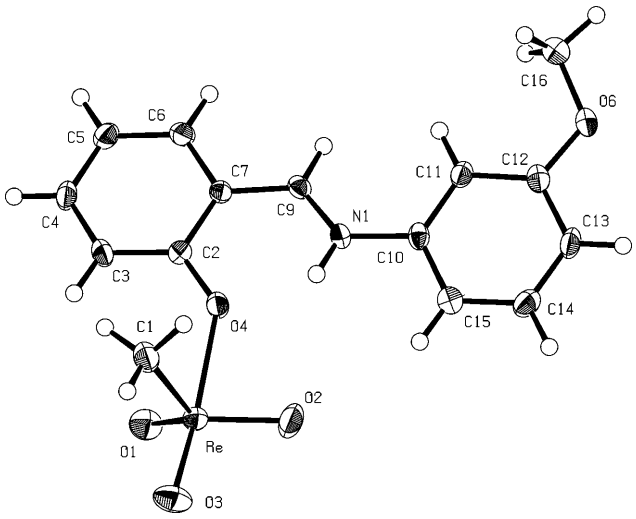


Figure 2. ORTEP style plot of compound **6** in the solid state. Thermal ellipsoids are drawn at the 50% probability level.

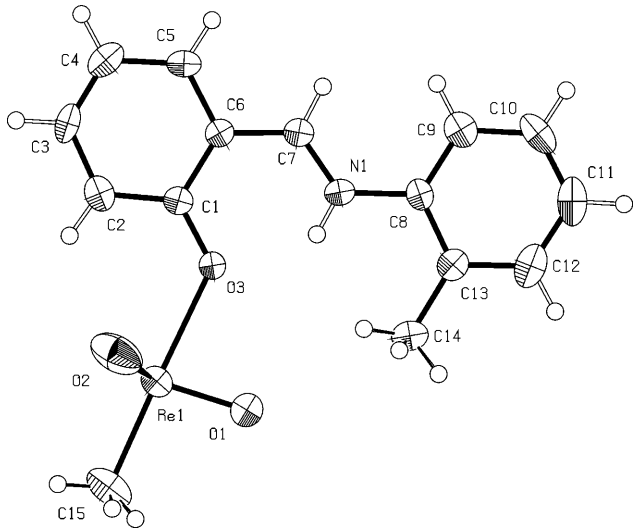


Figure 3. ORTEP style plot of compound **7** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. The molecule is located on a mirror plane.

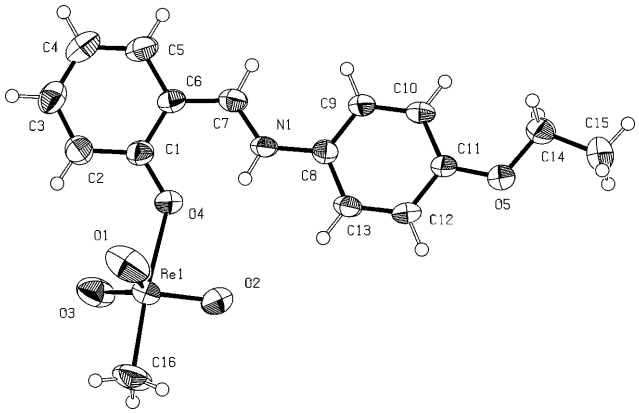


Figure 4. ORTEP style plot of compound **8** in the solid state. Thermal ellipsoids are drawn at the 50% probability level.

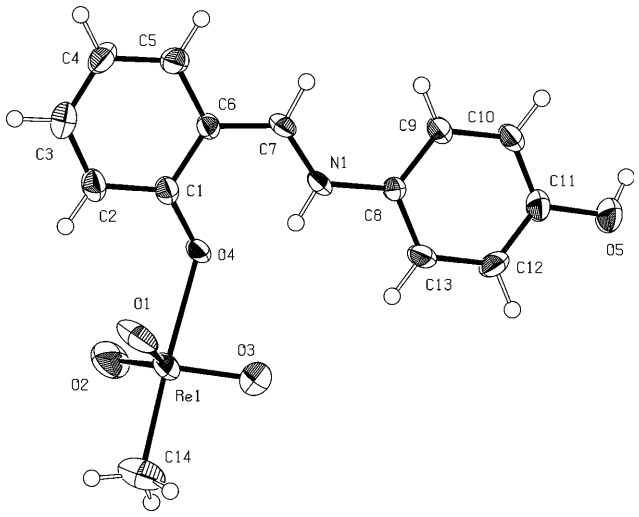


Figure 5. ORTEP style plot of compound **9** in the solid state. Thermal ellipsoids are drawn at the 50% probability level.

CHEMISTRY
AN ASIAN JOURNAL

Table 4. Selected bond lengths (Å) of compounds **5–9**.

	5	6	7	8	9
Re–$O_{terminal}$	1.708(4)	1.714(3)	1.693(6)	1.697(6)	1.690(6)
	1.717(3)	1.721(2)	1.697(5)	1.701(6)	1.714(5)
	1.717(3)	1.724(2)	1.697(5)	1.703(6)	1.719(6)
Re–O_{bridge}	2.286(3)	2.166(3)	2.309(5)	2.234(6)	2.271(4)
Re–CH_3	2.116(5)	2.116(3)	2.089(10)	2.073(9)	2.098(8)
C–O_{bridge}	1.316(5)	1.320(4)	1.315(9)	1.324(9)	1.311(7)
$C_{methylene}$–N	1.310(6)	1.301(4)	1.301(9)	1.295(9)	1.305(7)
C_{aryl}–N	1.416(6)	1.419(4)	1.438(10)	1.416(9)	1.418(8)

Table 5. Comparison of Re–CH_3 and Re–O_{bridge} bond lengths (Å) for MTO and compounds **1–9**.

	Re–CH_3	Re–O_{bridge}
MTO[10]	2.063(2)	
4	2.119(7)	2.153(5)
6	2.116(3)	2.166(3)
8	2.073(9)	2.234(6)
2	2.084(8)	2.243(4)
1	2.112(12)	2.269(7)
9	2.098(8)	2.271(4)
5	2.116(5)	2.286(3)
3	2.095(11)	2.286(5)
7	2.089(10)	2.309(5)

Table 6. Selected bond angles (°) of compounds **5–9**.

	5	6	7	8	9
$O_{terminal}$–Re–$O_{terminal}$	119.04(10)	103.77(13)	117.7(4)	118.3(4)	118.1(3)
	119.04(10)	103.49(13)	119.6(2)	119.1(4)	119.2(3)
	119.63(14)	119.34(12)	119.6(2)	119.9(4)	120.4(3)
$O_{terminal}$–Re–CH_3	94.9(2)	89.15(13)	95.4(2)	94.6(5)	94.5(3)
	95.08(12)	116.87(12)	95.4(2)	95.6(4)	94.5(3)
	95.08(12)	116.63(12)	96.6(4)	96.0(4)	96.2(4)
$O_{terminal}$–Re–O_{bridge}	83.81(15)	80.04(11)	82.0(3)	79.5(3)	81.3(2)
	85.54(10)	85.51(10)	85.3(2)	86.8(3)	86.3(2)
	85.54(10)	166.23(11)	85.3(2)	87.6(3)	87.2(2)
O_{bridge}–Re–CH_3	178.75(17)	77.48(12)	178.6(3)	175.4(3)	177.5(3)

respect to the orientation of the methyl groups and the Schiff base ligand, can be seen. This is largely attributed to packing effects in the crystals. It is noteworthy, however, that the $-OCH_3$ substituted Schiff bases form the only cis-oriented MTO complexes, all others display trans configuration of the Re-bound CH_3 group to the Re-bound Schiff base oxygen atom. However, we have recently described a related compound, displaying both cis- and trans-arrangements in the solid state.[16b] This is a strong indication that packing forces are the main reasons for a certain configuration rather than any ligand or substituent influences.

Table 4 gives selected bond distances for the compounds **5–9**. The Re–C bond distances in Å for the compounds **5–9** are 2.116(5), 2.116(3), 2.089(10), 2.073(9), and 2.098(8) Å, respectively, which are on average slightly longer than in free MTO (2.063(2) Å). This effect is already known from Lewis base adducts of MTO. It contributes to the higher lability of the Re–CH_3 bond and accordingly, adducts of MTO are generally somewhat less stable than the non-coordinated organometallic compound alone. The Re=O bond distances for all compounds are around 1.713(3) Å on average. The Re–O_{bridge} distances in the compounds are between 2.166(3) (compound **6**) and 2.271(4) Å (compound **9**), which are in agreement with the IR results and consistent with what was found in our previous work.[16] It should be noted that the cis-configured adducts **4** and **6** display the shortest Re–O_{bridge} bond distances. They are 2.153(5) Å and 2.166(3) Å, while all other compounds exhibit Re–O_{bridge} bond distances above 2.23 Å. The cis configuration obviously allows a closer proximity of the Schiff base ligand to the Re center, as has previously been noted.[16b] The Re–O_{bridge} increases in the order **4**<**6**<**8**<**2**<**1**<**9**<**5**<**3**<**7**. The Re–C bond distances seem to (inversely) correlate very roughly with this pattern, but the bond distance differences are even less pronounced and are largely within the error margins (see Table 5), which makes a well-founded discussion of the Re–C distances impossible. However, it is noteworthy that only Schiff base ligands substituted with good electron donor groups tend to form cis adducts with MTO.[16]Within the group of the trans adducts the general tendency towards longer Re–O bonds with decreasing donor ability of the Schiff base ligand is clearly seen. However, the particularly long Re–O bond in **7** might arise from a steric effect.

The X-ray crystal structures reveal that the proton is bound to the C=N group and not to the oxygen atom.

Applications as Epoxidation Catalysts

Compounds **5–9** were examined as catalysts for the epoxidation of cyclooctene, 1-octene, and styrene with hydrogen peroxide and compared to the results obtained for the previously described complexes **1–4**. Details of the catalytic reaction are given in the Experimental Section. Blank reactions showed that there is no significant formation of epoxide in absence of the catalyst. A catalyst/oxidant/substrate ratio of 1:200:100 was used in all cases. All catalytic reactions followed first-order kinetics in which the reaction conversion increases steadily for the first two hours and then slows down.

Complexes **3** and **5**, which have electron withdrawing Schiff base ligands, show the highest activity (turnover frequency, determined after 5 min reaction time) and conversions of cyclooctene of above 70% after 2 h and of 90% after 4 h are reached. The Schiff base with the Cl-substituent in the *p*-position leads to a slightly less active complex (compound **3**) than the *ortho* derivative (compound **5**). Compounds **2** and **7**, having donor substituents at the Schiff base, display an opposite effect. The reasonably good activity (350 mol/(mol×h)) and conversion (ca. 70 after 4 h) exhibited by compound **2** compares to a TOF of approximately 200 mol/(mol×h) and a conversion of approximately 65%

after 4 h in the case of compound **7**, in which the methyl group is now at the *ortho* position. However, it is seen that the compounds **4** (ca. 50% after 4 h), **6** (ca. 45% after 4 h) and **8** (50% after 4 h) do not show a very high conversion nor a high activity in the cases of **6** and **8** (TOF = 150 (**6**) and 200 (**8**) mol/(mol×h)). It is interesting to note that these compounds have electron donating −OR ligands on the Schiff base ligand. Compound **9**, containing a *p*-substituted Schiff base ligand displays a moderately good conversion of ca. 70% after 4 h reaction time and a medium activity of ca. 250 mol/(mol×h). An overview of the catalytic performance of the compounds synthesized is given in Figure 6 and the turnover frequencies of the compounds for cyclooctene epoxidation are shown in Table 7.

While the good result obtained for compound **3** might be ascribed to the better electron accepting capability of the Cl-ligand at the *para*-position, in compound **5**, a combination of steric and electronic effects may contribute to the comparatively good results. In the case of compound **2** the donor ability of the methyl ligand reduces the activity somewhat, when compared to compound **3**. For compounds **6** and **7**, displaying a combination of donor abilities and steric hindrance, the activities are lower than in the case of the unsubstituted, standard compound **1**. In general, with the sole exception of compound **5**, steric hindrance seems to be negative for the catalytic activity of any of the examined complexes, in accord to what would be naively expected. The particularly good electron donating effects of the −OR groups also cause a reduced activity (compounds **4** and **8**) in comparison to compound **1**, having no additional substituents residing on the Schiff base ligand.

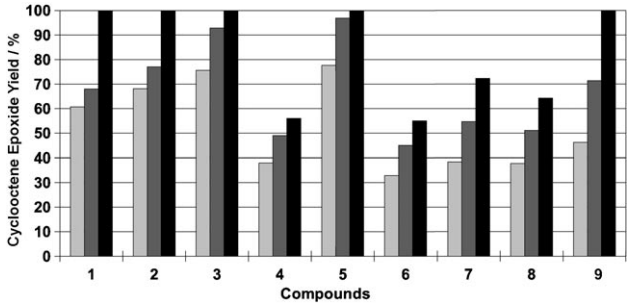


Figure 6. Conversions of the substrate cyclooctene to cyclooctene epoxide after 2 h (hatched bars), 4 h (gray bars) and after 24 h (black bars) in the presence of the compounds **1**–**9** as catalysts and H_2O_2 as oxidant (catalyst/substrate/oxidant = 1:100:200; reaction temperature: 20 °C).

Table 7. TOF (h^{-1}) for cyclooctene epoxidation after 5 min for compounds **1**–**9**.

Compound	TOF	Compound	TOF
1	300	**5**	400
2	350	**6**	150
3	375	**7**	200
4	325	**8**	200
		9	250

While cyclooctene is epoxidized fast and selectively, the epoxidation of 1-octene is slower, but still highly selective (no diols are formed). With the more sensitive substrate styrene, however, epoxides are the predominant products only during the first 2 h of the reaction (epoxide yields are between 30 and 40% after 2 h, diols are formed usually in smaller amounts). However, after 4 h and particularly after 24 h reaction time, this picture has changed drastically and diols are either predominant or the only products present (see also the Supporting Information).

Conclusions

Several Schiff bases readily form stable complexes with MTO and have distorted trigonal-bipyramidal structures. Others, however, lead to unstable complexes or prevent, seemingly dependent on their steric demand, a reaction with MTO. The electronic differences leading to stable complexes and/or good catalysts seem to be quite small since they are not clearly reflected from the gathered data. However, it seems that Schiff bases with *para* substituents at the aniline moiety lead in general to more stable complexes with MTO than their more sterically hindered *o*- and *m*- derivatives. Furthermore, the Re−O(Schiff base ligand) bond distance was found to roughly correspond to the donor ability of the ligand. Stronger donors seem to have the tendency to crystallize as cis-derivatives with MTO (i.e., the Re−CH_3 group in the cis-position to the bridging oxygen) since this configuration allows a shorter Re−O bond distance. If a reaction of a Schiff base and MTO takes place, the phenolic proton of the ligand is transferred to a ligand imine group upon coordination to Re, which means that the Lewis acidic Rhenium(VII) is coordinated to O^- and forms a comparatively short Re−O bond. In solution, the molecules seem to be flexible with respect to their structures. Nevertheless, different Schiff base ligands have a pronounced influence on the catalytic performance of the complexes. Thus, whilst particularly −OCH_3 groups (good donors) on the aniline moiety of the Schiff bases lead to reduced catalytic activities of the stable adducts, other Schiff bases, namely those with electron withdrawing Cl-ligands (acceptors), lead to active and selective epoxidation catalysts. An excess of ligand, however, always leads to rapid decomposition of the catalyst. Given the ready availability and room temperature stability of several of the title complexes, together with the good catalytic activity and high selectivity of some of them, they appear to be good alternatives to the, on average, more temperature sensitive MTO N-donor complexes as epoxidation catalysts. The Schiff base adducts of the latter can also be prepared and applied in situ. In contrast to N-donor adducts, no pronounced ligand excess is necessary to achieve high yields and selectivities in olefin epoxidation catalysis for substrates like cyclooctene and 1-octene. However, sensitive products such as styrene epoxide are quantitatively transformed to diols after prolonged reaction times.

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Experimental Section

Methods and Instrumentation

All preparations and manipulations were initially performed using standard Schlenk techniques in an Argon atmosphere. However, it was found that the syntheses can also be performed under (dry) air without problems. Solvents were dried by standard procedures (*n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately (as in the case of THF) or kept over 4 Å molecular sieves. Elemental analyses were performed with a Flash EA 1112 series elemental analyser. ^{1}H NMR were measured in $CDCl_3$ with a mercury-VX 300 spectrometer and a 400 MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer using KBr pellets as IR matrix. CI-MS spectra (isobutene as CI gas) were obtained using a Finnigan MAT 90 mass spectrometer. Catalytic runs were monitored by GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II. The Schiff base ligands were prepared as described previously.[17]

Synthesis

Compounds **5–9** were prepared as follows:

MTO (0.2 g, 0.8 mmol) was dissolved in diethyl ether (5 mL) and an equally concentrated solution of ligand (0.8 mmol) in diethyl ether (5 mL) was added to the stirred solution at room temperature. After 20–30 min the yellow solution was concentrated in an oil pump vacuum to ca. 3 mL and the orange or red precipitate was obtained by filtration, washed with *n*-hexane (10 mL) and dried under reduced pressure.

Compound **5:** (colour: red) Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta = 13.07$ (s, 1H; NH), 8.70 (s, 1H; CH=N), 7.51–7.34 (m, 6H; Ph), 7.11–6.94 (m, 2H; Ph), 2.63 ppm (s, 3H; MTO−CH_3); IR (KBr): see Tables 1 and 2; MS (70 eV, CI): *m*/*z* (%): 232.00 (100) $[C_{13}H_{10}ClNO+H^+]^+$, 336.0 (13.53), 463.0 (3.19); elemental analysis: calcd (%) for $C_{14}H_{13}ClNO_4Re$ (480.92): C 34.96, H 2.72, N 2.91; found: C 35.07, H 2.77, N 2.95.

Compound **6**: (colour: orange) Yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 13.25$ (s, 1H; NH), 8.60 (s, 1H; CH=N), 7.40–7.25 (m, 3H; Ph), 7.03–6.82 (m, 5H; Ph), 3.84 (3H, s, OCH_3), 2.60 ppm(3H, s, MTO−CH_3); IR(KBr): see Tables 1 and 2; MS (70 eV, CI): *m*/*z* (%): 228.1 (100) $[C_{14}H_{13}NO_2+H^+]^+$, 251.0 (48.15) $[CH_3ReO_3+H^+]^+$; elemental analysis: calcd (%) for $C_{15}H_{16}NO_5Re$ (476.50): C 37.82, H 3.36, N 2.94; found: C 37.99, H 3.24, N 2.88.

Compound **7:** (colour: red) Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta = 13.49$ (s, 1H; NH), 8.61 (s, 1H; CH=N), 7.45–7.28 (m, 3H; Ph), 7.23–7.10 (m, 4H; Ph), 6.97–6.94 m, 1H; Ph), 2.61 (s, 3H; MTO−CH_3), 2.40 ppm (s, 3H; CH_3); IR (KBr): see Tables 1 and 2; MS (70 eV, CI): *m*/*z* (%): 212.10 (100) $[C_{14}H_{13}NO+H^+]^+$, 250.1 (1.52) $[CH_3ReO_3]^+$; elemental analysis: calcd (%) for $C_{15}H_{16}O_4NRe$ (461.06): C 39.12, H 3.50, N 3.04; found: C 39.17, H 3.57, N 3.09.

Compound **8**: (colour: orange) Yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 13.43$ (s, 1H; NH), 8.60 (s, 1H; CH=N), 7.38–7.26 (m, 4H; Ph), 7.03–6.90 (m, 4H; Ph), 4.08–4.03 (q, 2H; CH_2), 2.60 (s, 3H; MTO−CH_3), 1.45–1.42 (t, 3H; CH_3); IR (KBr): see Tables 1 and 2; MS (70 eV, CI): *m*/*z* (%): 242.1 (100) $[C_{15}H_{15}NO_2+H^+]^+$, 298.1 (25.54), 483.0 (11.78); elemental analysis: calcd (%) for $C_{16}H_{18}O_5NRe$ (490.52): C 39.18, H 3.70, N 2.86; found: C 39.19, H 3.74, N 2.94.

Compound **9**: (colour: red) Yield: 82%; ^{1}H NMR (400 MHz, DMSO, RT): $\delta = 13.41$ (s, 1H; NH), 9.66 (s, 1H; OH), 8.90 (s, 1H; CH=N), 7.60–7.57 (m, 1H; Ph), 7.38–7.30 (m, 3H; Ph), 6.97–6.82 (m, 4H; Ph), 1.90 ppm (s, 3H, MTO-CH_3); IR (KBr): see Tables 1 and 2; MS (70 eV, CI): *m*/*z* (%): 212.1 (68.32) $[C_{13}H_{11}NO_2-H]^+$, 251.0 (60.02) $[CH_3ReO_3+H^+]^+$; elemental analysis: calcd (%) for $C_{14}H_{14}O_5NRe$ (462.47): C 36.36, H 3.05, N 3.03; found: C 36.41, H 3.09, N 3.05.

*X-ray Crystal Determination of Compounds **5** and **6***

General: Preliminary examination and data collection were carried out on an area detecting system (**5**: STOE IPDS 2T; **6**: NONIUS κ-CCD device) at the window of a rotating anode (NONIUS FR591) and graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data collections were performed at 173 K (OXFORD CRYOSYSTEMS). Reflections were integrated, corrected for Lorentz, polarization, absorption effects, and arising from the scaling procedure for latent decay. The structures were 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 (**5**: riding model, $d_{C-H} = 0.95$ and 0.98 Å **6**: riding model, $d_{N-H} = 0.88$ Å and $d_{C-H} = 0.95$ and 0.98 Å). Isotropic displacement parameters were calculated from the parent carbon/nitrogen atom ($U_{iso(H)} = 1.2/1.5 U_{eq(C)}$). Full-matrix least-squares refinements were carried out by minimizing $w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. The final residual electron density maps show no remarkable features. *Specials* **5**: Small extinction effects were corrected with the SHELXL-97 procedure [$\varepsilon = 0.0105(5)$]. The hydrogen atom located at the nitrogen atom was found in the final difference Fourier maps and was allowed to refine freely ($d_{N-H} = 0.80(7)$ Å). CCDC 702104 (**5**), CCDC 702105 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.[18a–g]

*X-ray Crystal Determination of Compounds **7–9***

The diffraction data were obtained with a Bruker Smart 1000 CCD diffractometer operating at 50 kV and 30 mA using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data collection was performed at 293 K with a diffraction measurement method and reduction was performed using the SMART and SAINT software with frames of 0.3° oscillation in the range $1.5 < \theta < 26.2°$. An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and included in structure factor calculations in the final stage of F^2 refinement. CCDC 648768 (**7**), CCDC 648766 (**8**), CCDC 648767 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.[18h–k]

Catalytic Reactions

Method A: cis cyclooctene (800 mg, 7.3 mmol), 1.00 g mesitylene (internal standard), H_2O_2 (30% aqueous solution; 1.62 mL, 14.6 mmol) (0.64 mL, 6.24 mmol,) and 1 mol% (73 μmol) of the catalyst (**5–9**) were mixed.

Method B: 1-octene (343.2 mg, 3.12 mmol), 429 mg mesitylene (internal standard), H_2O_2 (30% aqueous solution) (0.64 mL, 6.24 mmol,) and 1 mol% (31.3 μmol) of catalyst (**5–9**) were mixed.

Method C: Styrene (250 mg, 2.39 mmol), 100 mg mesitylene (internal standard), H_2O_2 (30% aqueous solution) (0.53 mL, 4.78 mmol,) and 1 mol% (24 μmol) of catalyst (**5–9**) were mixed.

Olefins, mesitylene (internal standard) and compounds **5–9** as catalysts were added to the reaction vessel under standard conditions. The reaction began with the addition of H_2O_2. The course of the reaction was monitored by quantitative GC analysis (cyclooctene and styrene) and GC-MS analysis (1-octene). Samples were taken in regular time intervals, diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of cyclooctene, 1-octene, styrene and the formation of the corresponding oxides were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

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