



# Methyltrioxorhenium catalysed epoxidations: A comparative study of different *N*-donor ligands

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## ABSTRACT

This report presents a comparative study on the influence of various *N*-donor ligands coordinated to methyltrioxorhenium (MTO) on the catalytic activity of olefin epoxidation. A monodentate (4-*tert*-butylpyridine), a bidentate (4,4'-dimethyl-2,2'-bipyridine) and a *Schiff*-base ligand were chosen for the coordination to MTO. This report is supposed to act as a benchmark for past and future results in this type of catalysis. Until now, unfortunately, the results are often difficult to compare due to varying sets of reaction conditions. In the present examination, identical reaction conditions were applied to find the optimum in performance. Accordingly, (i) ligand concentration, (ii) reaction temperature, (iii) catalyst concentration, (iv) olefin and (v) the solvent were varied. For labile olefins such as *trans*- $\beta$ -methylstyrene, both the monodentate and the bidentate pyridine derivatives show very good selectivities and activities with a MTO/ligand ratio of 1:5 at 25 °C. The *Schiff*-base is only a useful additive for the epoxidation of cyclooctene. Due to phase transfer effects it is difficult to compare two-phase systems (solvent dichloromethane (DCM)) to one-phase systems (solvent *tert*-butanol). A correlation between rotation speed of the stirrer and the turnover frequency was observed.

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## 1. Introduction

Since the discovery of the catalytic activity of methyltrioxorhenium (MTO) by Herrmann et al. in the late 1980s [1] this compound received a great deal of attention as a homogeneous catalyst for a variety of reactions, including olefin metathesis [2], aldehyde olefination, [3] and above all, olefin epoxidation [4–6]. In the latter reaction, hydrogen peroxide is often used as a cheap oxidant together with MTO, leading to a catalytically active mono- and bis(peroxo)complex [7,8]. Problems in this reaction system mostly occur in the form of ring opening reactions due to the strong Lewis-acidity of the rhenium centre, forming diols instead of epoxides. These undesired reactions can be suppressed by addition of Lewis-bases as shown by Sharpless and co-workers [9–11] and other groups [12–14]. In the past, a plethora of different ligands for MTO has been investigated [15–18] and pyridine and its derivatives were found to belong to the most efficient catalysts, increasing the catalytic performance in terms of activity and selectivity [4–6,8,9]. In 2007, Kühn and co-workers introduced *Schiff*-bases as a new group of additives with very good results in cyclooctene epoxidation [6]. This paper presents a direct comparison between three different types of *N*-donor ligands that were reported to display good results in previous papers [4–6]. As *N*-donor li-

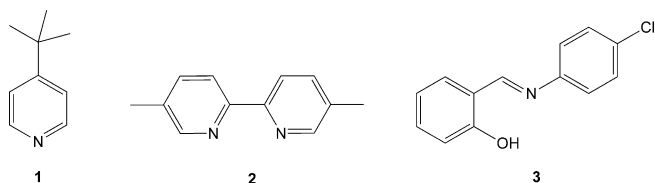
gands, a pyridine derivative, 4-*tert*-butylpyridine (**1**), a chelate ligand, 4,4'-dimethyl-2,2'-bipyridine (**2**) and a *Schiff*-base (**3**) were selected (Fig. 1). All these *N*-donors readily form complexes with MTO, which are catalytically active in the presence of H<sub>2</sub>O<sub>2</sub> (Fig. 2) [4–6]. Furthermore, all systems are well soluble in a variety of solvents. Previous papers already described the coordination of *N*-donors to MTO [4–6,11,13,19–22]. Herein, we report for the first time on a direct comparison between a monodentate, a bidentate and a *Schiff*-base ligand under identical conditions. The catalytic performance of these three systems at different ligand concentrations, catalyst concentrations, temperatures, and in different solvents is investigated. For an examination of the influence of the different *N*-donor ligands on the catalytic activity of MTO, the epoxidation of *trans*- $\beta$ -methylstyrene was selected, as it is known that this substrate forms a labile epoxide, which is easily converted to the corresponding diol. Hence, it is intricate to obtain good yields with this substrate if the catalyst is not highly selective. Differences between the catalyst selectivities should be particularly pronounced.

## 2. Experimental

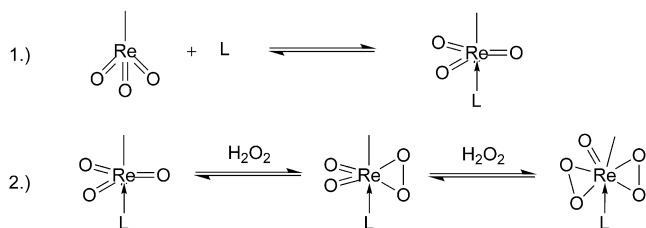
*Trans*- $\beta$ -methylstyrene, cyclohexene and cyclooctene were purchased from Aldrich and Acros. The solvents *tert*-butanol and DCM were used without further drying or purification. H<sub>2</sub>O<sub>2</sub> was used as the oxidising agent in a 35% aqueous solution for the epoxidation

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**Fig. 1.** Used additives to MTO: 4-*tert*-butylpyridine (**1**), 4,4'-dimethyl-2,2'-bipyridine (**2**) and the Schiff-base (**3**).



**Fig. 2.** (1) Reaction of MTO with L. (2) Reaction of MTO-Lewis-base complex with  $H_2O_2$ , forming the mono- and the bis(peroxo)complex, L = electron donor ligand.

catalysis. Mesitylene (5 ml) acted as an internal standard in all reactions performed.

In typical experiments, 2 mmol olefin were taken to perform the catalysis. The amounts of ligand and MTO taken for the different experiments are listed in Table 1. The catalytic experiments were carried out in water-cooled double walled glass vessels in order to keep the reaction temperatures constant during the experiments. Thus, the reaction temperatures could be kept constant during the experiments. For the one-phase experiments, 2 ml of a 10% mixture of hydrogen peroxide in *tert*-butanol were used, whereas the two-phase experiments were performed with a mixture of 0.34 ml aqueous  $H_2O_2$  solution (35%) and 1.66 ml DCM.

Solvent, oxidising agent, MTO and the ligands were separately mixed under ice cooling to suppress the oxidation of pyridine. The yellow catalytically active MTO-peroxo complex was formed instantaneously. Olefin and internal standard were placed in the reactor and the solution containing MTO was added to start the reaction. In each oxidation experiment, samples (2 ml) were taken from the reaction solution after 5 min, 30 min and 3 h. The remaining hydrogen peroxide was destroyed with  $MnO_2$ . After drying over  $MgSO_4$  and dilution with dry DCM, the samples were analysed with a calibrated VarianWS gas chromatograph.

### 3. Results and discussion

As mentioned above, the aim of this investigation was a comparison of different MTO-ligand systems in epoxidation catalysis under identical reaction conditions. One-phase conditions with *tert*-butanol as solvent to avoid any phase transfer influences were applied first.

**Table 1**  
Amounts of MTO and ligand.

Experiment	MTO	<b>1</b>	<b>2</b>	<b>3</b>
1:1	5 mg	2.9 mg	3.7 mg	4.6 mg
	0.02 mmol	0.02 mmol	0.02 mmol	0.02 mmol
1:5	5 mg	13.5 mg	18.4 mg	23.2 mg
	0.02 mmol	0.1 mmol	0.1 mmol	0.1 mmol
1:10	5 mg	27 mg	36.8 mg	46.3 mg
	0.02 mmol	0.2 mmol	0.2 mmol	0.2 mmol
0.5 mol% cat	2.5 mg	6.8 mg	9.2 mg	x
	0.01 mmol	0.05 mmol	0.05 mmol	x
0.1 mol% cat	0.5 mg	1.4 mg	1.8 mg	2.3 mg
	0.002 mmol	0.01 mol	0.01 mmol	0.01 mmol

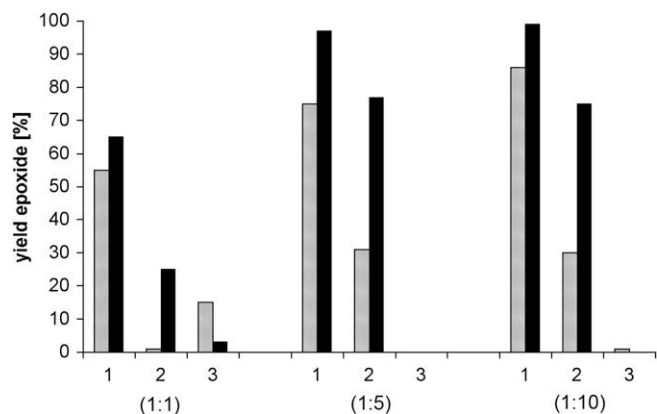
#### 3.1. Ligand concentration

The first step of the investigation was to determine the optimum of activity and selectivity that could be reached by varying the concentrations of the ligand in the reaction solution. The Re-N bond is rather weak; hence, the MTO-base adduct is in equilibrium with the dissociated molecules [4–6]. Accordingly, an excess of base shifts the equilibrium to the adduct complex [23]. Already at a MTO/ligand ratio of 1:5, the selectivities with the pyridine and the bipyridine systems were 100%. Previous reports do not describe the ligand effect on the catalytic selectivity for MTO/ligand ratios between 1:1 and 1:10 [4,5]. Hence, it can be shown from the results presented here that already with a 5-fold excess of ligand, 100% selectivity can be reached. The equation shown in Fig. 2 is sufficiently shifted to the MTO-Lewis-base complex. Fig. 3 shows that a further increase of ligand (1:10) results in an increased yield only during the first 30 min. However, after 3 h no yield difference between 1:5 and 1:10 ratios can be detected. The turnover frequencies (TOFs), summarised in Table 2, show the increase in activity from 1:5 to 1:10 for systems **1** and **2**. Using MTO and the ligand in a ratio of 1:1, especially for the bipyridine ligand, the epoxide further reacts to the corresponding diol, decreasing the selectivity significantly.

The Schiff-base, although it has good conversions of ca. 90% after 3 h, only produces undesired ring opening products. This indicates that these ligands are not able to decrease the Lewis-acidity at the rhenium centre significantly and therefore do not lead to a good epoxide selectivity, at least for sensitive epoxides such as those obtained from *trans*- $\beta$ -methylstyrene. As the ratio of 1:5 turned out to be sufficient in the catalysis it was applied for all following experiments. System MTO/**3** was no longer investigated, because the epoxide yields were too low to be competitive with the more selective Lewis-base adduct systems.

#### 3.2. Temperature effects

For the MTO/**1** system, the highest yields are reached between 25 °C and 45 °C. The yields obtained with MTO/**2** are generally lower compared to those obtained with the system MTO/**1**. Best yields are again reached somewhat above room temperature. From 55 °C onwards decomposition of the catalyst is observed leading to decreasing yields and TOFs (Table 2 and Fig. 4). This is in accordance with the reported decomposition of MTO adducts to methanol, pyridinium cations and perrhenate at elevated temperatures [8,24] and the comparatively weak interaction of MTO with the ligand [25]. Furthermore, ring opening reactions can be observed at



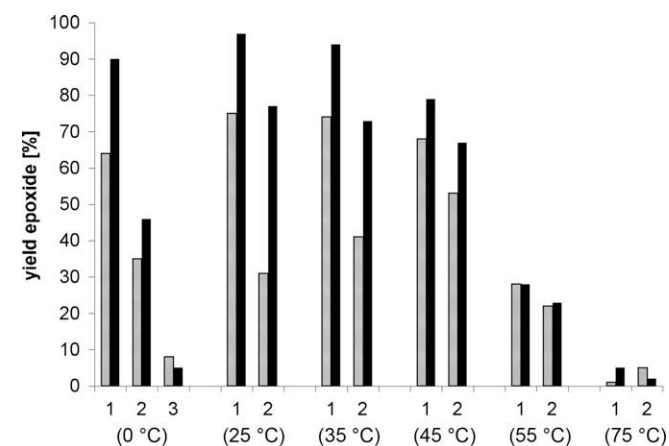
**Fig. 3.** Epoxide yield with different MTO/ligand ratios (1:1, 1:5, 1:10), 25 °C, catalyst/substrate/oxidant 1/100/300, *trans*- $\beta$ -methylstyrene, after 30 min (hatched bars) and after 180 min (filled bars).

**Table 2**

TOFs (mol(epoxide) mol(cat)<sup>-1</sup> h<sup>-1</sup>) measured after 5 min, solvent: *tert*-butanol, substrate: *trans*- $\beta$ -methylstyrene.

Experiment	1	2	3
1:1	450	100	0
1:5	590	380	0
1:10	700	430	0
0 °C	490	260	130
25 °C	590	380	0
35 °C	740	330	<sup>a</sup>
45 °C	740	410	<sup>a</sup>
55 °C	270	170	<sup>a</sup>
75 °C	200	230	<sup>a</sup>
1 mol% cat	590	380	0
0.5 mol% cat	690	190	<sup>a</sup>
0.1 mol% cat	3160	2500	<sup>a</sup>

<sup>a</sup> Not determined.



**Fig. 4.** Epoxide yields at different temperatures, MTO/ligand 1:5, catalyst/substrate/oxidant 1/100/300, *trans*- $\beta$ -methylstyrene, after 30 min (hatched bars) and after 180 min (filled bars).

45 °C and higher temperatures, pointing at decreasing ligand influence due to the increased ligand fluctuonality at high temperatures [25]. At 45 °C and above, diol formation cannot be suppressed with a MTO/ligand ratio of 1:5. In general, the use of the pyridine ligand gives higher epoxide yields than the bipyridine/MTO system (Fig. 4). Whereas epoxidation catalysed by the MTO-pyridine complex leads to a yield of 75% already after 30 min, with the MTO-bipyridine catalyst even after 3 h a yield of 75% is not reached.

### 3.3. Catalyst concentration

In an additional set of experiments, the catalyst concentration was reduced from 1 mol% to 0.5 mol% and 0.1 mol%. The turnover frequencies (Table 2) are significantly higher at lower catalyst concentration. The corresponding yields at lower catalyst concentrations are higher than they should be if all catalyst molecules would be fully utilised at high catalyst concentrations as these epoxidation reactions follow a first order kinetics with respect to catalyst and substrate concentration [8]. A reason for that might be that at high catalyst concentrations not every catalyst molecule is used to capacity. At a catalyst concentration of 0.1 mol% the epoxide yield of catalyst MTO/1 drops to the value reached by catalyst MTO/2. The 30 min value of MTO/2 remains nearly constant for all tested catalyst concentrations, fluctuating between 30% and 20% yield. Presumably, the bipyridine, which has two possible coordination sites, can hinder the formation of the catalytically active species up to a certain extent by chelating effects (Fig. 2). Fur-

**Table 3**

Yields and TOFs (after 5 min) of **3** in different solvents, catalyst/substrate/oxidant 1/100/300, substrate: cyclooctene, 25 °C.

Experiment	Yield	Yield	TOF (mol(epoxide) mol(cat) <sup>-1</sup> h <sup>-1</sup> )
	30 min (%)	180 min (%)	
<i>Tert</i> -butanol	78	99	430
DCM	25	85	180
DCM doubled stirring frequency	55	98	350

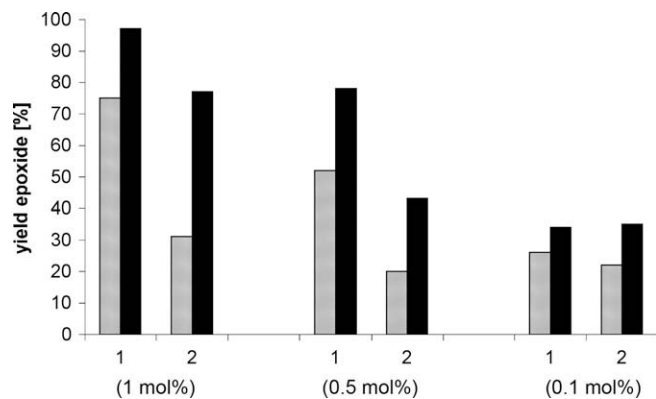
thermore, after a fast start, the reactions with low catalyst concentrations get diffusion limited after a short period of time. This assumption is also supported by the observed influence of the stirring velocity on the catalyst performance, which is particularly pronounced in two-phase systems.

### 3.4. Solvent effects

The effect of solvents has already been reported [4,23a,26,27]. In this study the difficulties of a comparison of one-phase with two-phase reactions in this catalytic system were additionally considered. Not only *trans*- $\beta$ -methylstyrene was used, but also cyclooctene, which is known to give very good results in the case of epoxidation reactions [4–6]. As expected, with cyclooctene the one-phase catalysis led to epoxide yields of about 98% in all cases, i.e. using the monodentate, the bidentate and the *Schiff*-base. However, for the two-phase system a very strong dependency of the TOFs on the stirring frequency could be observed as described already before [13]. Doubling the stirring speed from 400 to 800 rotations per minute leads to almost doubled TOFs (Table 3). Hence, it is obvious that an exact comparison between different examinations published previously is particularly problematic for two-phase systems. Even varying the drop size in dispersions has an influence on phase transfer phenomena and the size of the drops depends very strong on the stirring speed [28]. Generally, the bidentate base system is superior to the monodentate in two-phase systems in DCM solution.

## 4. Conclusions

In this comparative study, the differences between three kinds of donor ligands in the MTO catalysed olefin epoxidation were examined under consistent reaction conditions. The investigations included changes in temperature, ligand concentration, catalyst concentration, solvent and olefin. Generally, the *Schiff*-base ligand only gave good results in the epoxidation of cyclooctene (Table 3). Using *trans*- $\beta$ -methylstyrene leads to poor results in all examined cases (Table 2). This indicates the low ability of the *Schiff*-base to decrease the *Lewis*-acidity at the rhenium centre. In one-phase reactions in *tert*-butanol, 4-*tert*-butylpyridine as additive is superior to 4,4'-dimethyl-2,2'-bipyridine (Figs. 3–5). For both of them a MTO/ligand ratio of 1:5 is sufficient to suppress diol production completely and a temperature somewhat above room temperature leads to the highest yields in both cases. With a catalyst concentration of 0.1 mol%, good TOFs of 3160 h<sup>-1</sup> for MTO/1 and 2500 h<sup>-1</sup> for MTO/2 are achieved (Table 2). Under these conditions the number of active sites seems to be closer to the number of catalyst molecules in solution, so that more “realistic” TOFs are obtained. Both catalyst excess (not all active sites used) and catalyst decomposition lead to the impression of low activity. In two-phase systems with DCM, the bipyridine system shows the best performance. However, particularly two-phase experiments highlight the difficulties in comparing systems with different rotational speeds of



**Fig. 5.** Epoxide yield with different catalyst concentrations, MTO/ligand 1:5, 25 °C, *trans*- $\beta$ -methylstyrene, after 30 min (hatched bars) and after 180 min (filled bars).

the stirrer (Table 3). A correlation between the rotational speed and the TOF was found.

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