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METHYLTRIOXORHENIUM CATALYZED OXIDATIONS

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Abbreviations

bik	bis(1-methyl-2-yl)ketone
bmim	1-butyl-3-methyl-imidazolium
bmPy	1-butyl-3-methyl-pyridinium
Cp	cyclopentadienyl
CTAS	cetyltrimethylammonium hydrogensulfate
CTAT	cetyltrimethylammonium sulfate
DFT	density functional theory
DMF	dimethylformamide
DMC	dimethyl carbonate
ee	enantiomeric excess
HFIP	hexafluoroisopropanol
*m*CPBA	*meta*-chloroperbenzoic acid
MTO	methyltrioxorhenium
NHC	*N*-heterocyclic carbene
NMO	*N*-methylmorpholine *N*-oxide
PTC	phase transfer agent
r.t.	room temperature
salox	salicylaldoxime
SDS	sodium dodecyl sulfate
SPC	sodium percarbonate
TBHP	*tert*-butyl hydroperoxide
TFE	trifluoroethanol
TOF	turn-over-frequency
TON	turn-over-number
UHP	urea hydrogen peroxide

1. Introduction

1.1 Homogeneous catalytic epoxidation of olefins

The catalytic epoxidation of olefins is of great interest for science and industry. For industry, epoxides are one of the most used chemicals, especially propen oxide with a produced amount of 813,763 t only in Germany in 2010 [1]. Latest plants use titanium-based catalysts to transform propene into propene oxide with hydrogen peroxide as oxidant. A plethora of review articles deal with catalytic epoxidation of olefins, representing its importance to the scientific community [2-22].

The interest in olefin epoxidation, the development of new, more efficient and generally applicable catalysts is the driving force for persistent scientific developments and warrants a short summary of the most recent contributions in this field. Besides the most known complexes of Mo, Re, Ti and V, other metals, such as Fe, Ru and Co, which have so far not been in the focus of this research, have emerged as potential alternatives as homogeneous catalysts. The main aspect herein is the catalytic performance and the applicability not only to typical test substrates like cyclooctene, but also industrially interesting substrates, such as ethylene and propylene, as well as prochiral olefins for the synthesis of fine chemicals.

Vanadium

For the epoxidation of olefins, mostly oxovanadium (IV) complexes tethered by nitrogen or oxygen atoms have so far been applied. In 2008, Rayati et al. presented Schiff base complexes for the epoxidation of cyclooctene and styrene [23]. Compound **1** and **2** (Figure 1) were examined with TBHP as oxidant in different solvents and at different temperatures. Selected results are presented in Table 1. Although chiral complexes were used as catalysts no enantiomeric excess (ee) is given for the epoxidation of styrene. Complexes **3**-**5** (Figure 1) were used for the epoxidation of cyclohexene and cyclooctene (Table 1) [24].

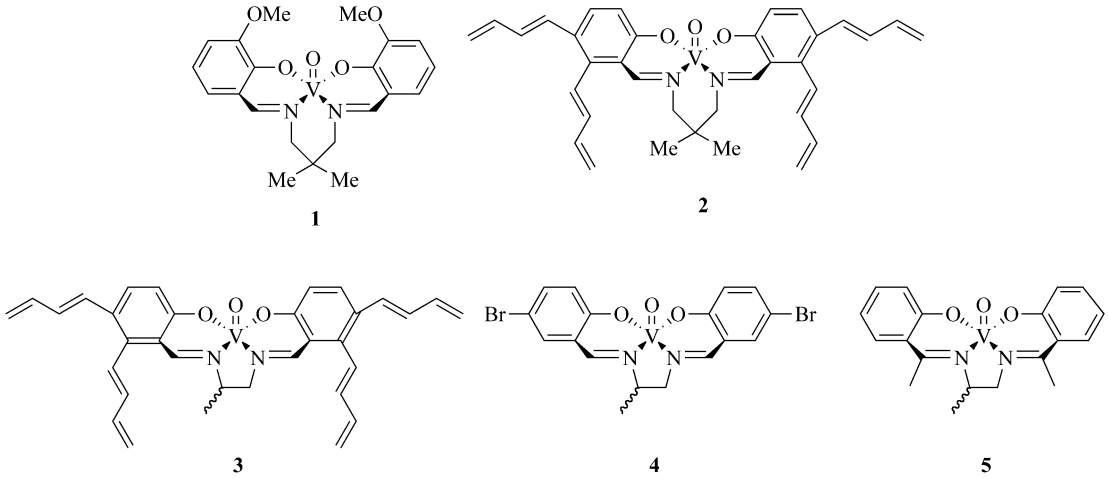


Figure 1. V-catalysts used by Rayati et al.

In 2009, the application of hydrogen peroxide as environmental friendly oxidant instead of TBHP lead to a more sustainable approach with vanadium-based catalysts [25]. The epoxidation of cyclooctene was performed in different ionic liquids as well as conventional solvents. The best results are presented in Table 1, the catalysts (**6**-**8**) are shown in Figure 2. Even taking the milder conditions into account, the results with vanadium catalysts and H_2O_2 were not satisfying with a maximum yield of 53 %.

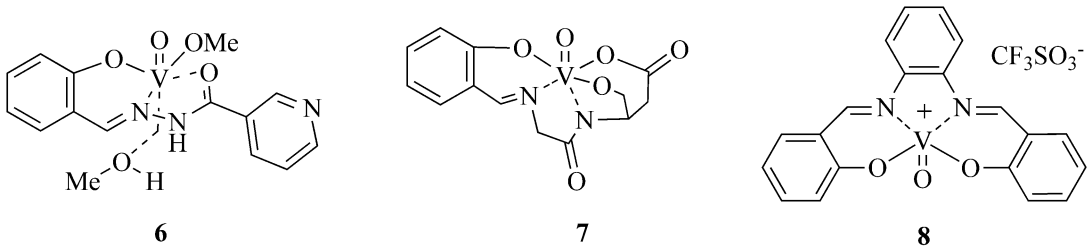


Figure 2. Vanadium catalysts used with hydrogen peroxide.

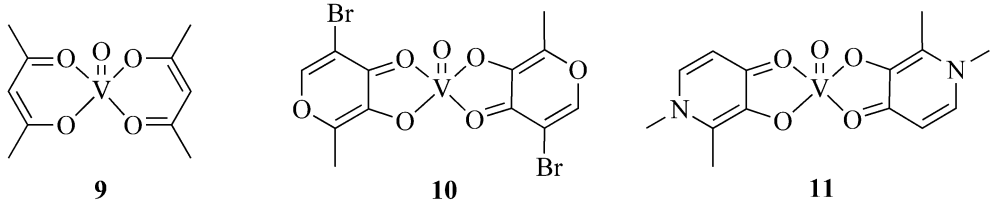
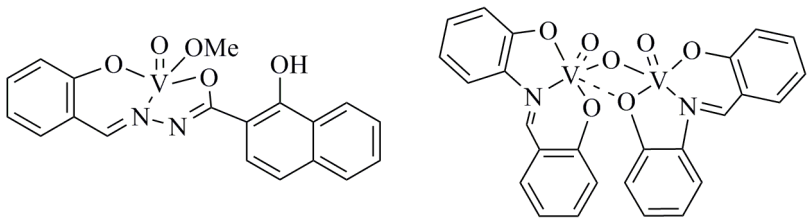


Figure 3. Catalysts for the epoxidation of geraniol.

The epoxidation of geraniol was done with acetylacetonate- (**9**), pyrone- (**10**) and pyridione- (**11**) complexes of vanadium (Figure 3) in 2010 [26]. The application of

vanadium-complexes resulted in quantitative yields for the most active ones (Table 1). The TOFs were relatively small, which might be a result of the long time interval of 15 min that was used for the calculation. Vanadium-Schiff base complexes were again part of examinations undertaken in 2010. The catalysts by Monfared et al. of which only **12** is shown as an example here (Figure 4), were examined under similar conditions as **6** and reached good activities for an vanadium/H_2O_2-system (Table 1) [27]. The dimeric Schiff base complex **13** was used in cyclooctene epoxidation with aqueous TBHP and H_2O_2 but worked only with the latter (Figure 4) [28]. Taking the high amount of catalyst and the high concentration of the reaction solution into account, the results were only medicore (Table 1). Other Schiff base complexes of oxovanadium species were part of studies in 2011 but only results for heterogeneous catalysis were stated, although homogeneous experiments were performed [29].



12 **13**

Figure 4. Oxovanadium-Schiff base complexes synthesized in 2010.

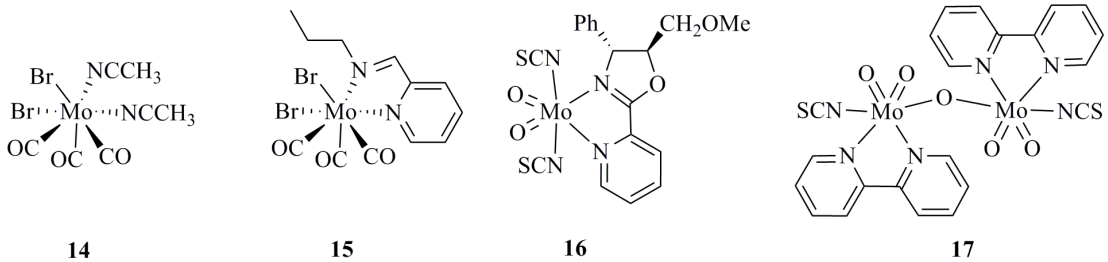
Table 1. Epoxidation with V-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TOF [h^{-1}]	TON	Yield [%]
[23]	**1** 0.32	60	$CHCl_3$	Cyclooctene	TBHP (3:1)	-	-	93 (6 h)
[23]	**1** 0.32	60	$CHCl_3$	Styrene	TBHP (3:1)	-	162	29 (6 h)
[23]	**2** 0.32	60	$CHCl_3$	Cyclooctene	TBHP (3:1)	-	312	100 (6 h)
[23]	**2** 0.32	60	$CHCl_3$	Styrene	TBHP (3:1)	-	231	23 (6 h)
[24]	**3** 0.13	80	CH_3CN	Cyclooctene	TBHP (-:-)	-	420	54 (6 h)
[24]	**4** 0.13	80	CH_3CN	Cyclooctene	TBHP (-:-)	-	348	41 (6 h)
[24]	**5** 0.13	80	CH_3CN	Cyclooctene	TBHP (-:-)	-	558	70 (6 h)
[25]	**6**	r.t.	$bmimPF_6$	Cyclooctene	H_2O_2	-	-	20

	1				(2:1)			(5 h)
[25]	**7**	r.t.	CH_3CN	Cyclooctene	H_2O_2	-	-	33
	1				(2:1)			(24 h)
[25]	**8**	r.t.	CH_3CN	Cyclooctene	H_2O_2	-	-	53
	1				(2:1)			(5 h)
[26]	**9**	r.t.	CH_2Cl_2	Geraniol	TBHP	200	-	100
	2				(1.5:1)			(0.25 h)
[26]	**10**	r.t.	CH_2Cl_2	Geraniol	TBHP	197	-	99
	2				(1.5:1)			(0.5 h)
[26]	**11**	r.t.	CH_2Cl_2	Geraniol	TBHP	24	-	94
	2				(1.5:1)			(2 h)
[27]	**12**	60	CH_3CN	Cyclooctene	H_2O_2	-	-	90
	2.5				(2:1)			(4 h)
[27]	**12**	60	CH_3CN	α-Methyl-	H_2O_2	-	-	24
	2.5			styrene	(2:1)			(4 h)
[28]	**13**	80	-	Cyclooctene	TBHP	-	-	78
	1				(2:1)			(5.5 h)

Molybdenum, Tungsten

Molybdenum. Molybdenum catalyzed homogeneous epoxidations are quantitatively the most examined over the last years. In 2008, complexes with two nitrogen donors were studied (Figure 5) [30, 31]. Carbonyl complexes **14** and **15** were studie in the epoxidation of cyclooctene and styrene with remarkable selectivities in the transformation of styrene to styrene oxide as no by-products occurred (Table 2) [30]. Brito et al. studied mono- and dimeric-dioxo complexes and applied them in cyclooctene and limonene oxidation with medicore success. (Figure 5 (**16**, **17**), Table 2) [31].



14 **15** **16** **17**

Figure 5. Selected Mo-catalysts applied in 2008.

In 2009 the group of Kühn studied halide- and Cp-substituted molybdenum complexes (Figure 6) [32-35]. The use of ionic liquids turned out to be not very promising as solvent-free conditions were superior (Table 2). A new class of ansa-

Mo-complex (**20**) turned out to be a versatile catalyst for cyclooctene epoxidation with a remarkable activity [34]. The combination of ionic liquids as solvents together with complex **20** resulted in a highly active recyclable system (Table 2) [36]. As these kind of complexes are likely to react with oxidants like TBHP just as **21** would, the kinetics and active species were therefore examined for **21** to reveal the nature of the real catalytic species [35]. Later, a large variety of different substituted bipyridine ligands was examined in complexes similar to **18** but the results did not exceed the ones of catalyst **18** [37].

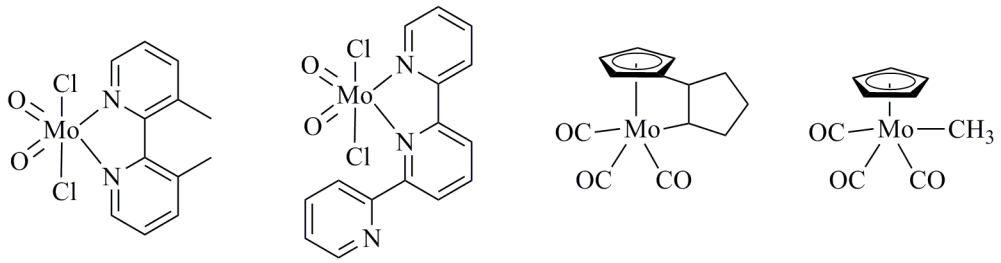


Figure 6. Selected Mo-catalyst studied in 2009 by Kühn and co-workers.

Catalyst **22** was originally meant to be a precursor for heterogenisation but it showed also good performance under homogeneous conditions (Figure 7, Table 2) [38]. An attempt to oxidize styrene to styrene oxide with the ferrocenyl-functionalized catalyst **23** was performed by Chai et al. [39]. Only 0.1 mol% of catalyst lead to 79 % yield after 12 h. The combination of ansa-Cp-complexes like **20** with carbenes resulted in the synthesis of complex **24** (Figure 7) [40]. The catalytic performance of this catalyst did not match the good results of **20** (Table 2). The use of ionic liquids as solvents in catalytic reactions was part of the studies by Monteiro et al. [41]. The best catalyst was **25** in combination with the ionic liquid bmPyBF$_4$ (Table 2). The best catalytic performance so far was reached with the bisperoxo-species **26** (Figure 7) [42]. The reaction mixture contained, despite the catalyst and the substrate, H_2O_2, $NaHCO_3$ and acetone, which was also able to epoxidize cyclooctene up to 50 % without catalyst. Very good catalytic performance was reached with catalyst **27** [43]. Nevertheless, the best activities were obtained at elevated temperatures up to 80 °C (Table 2).

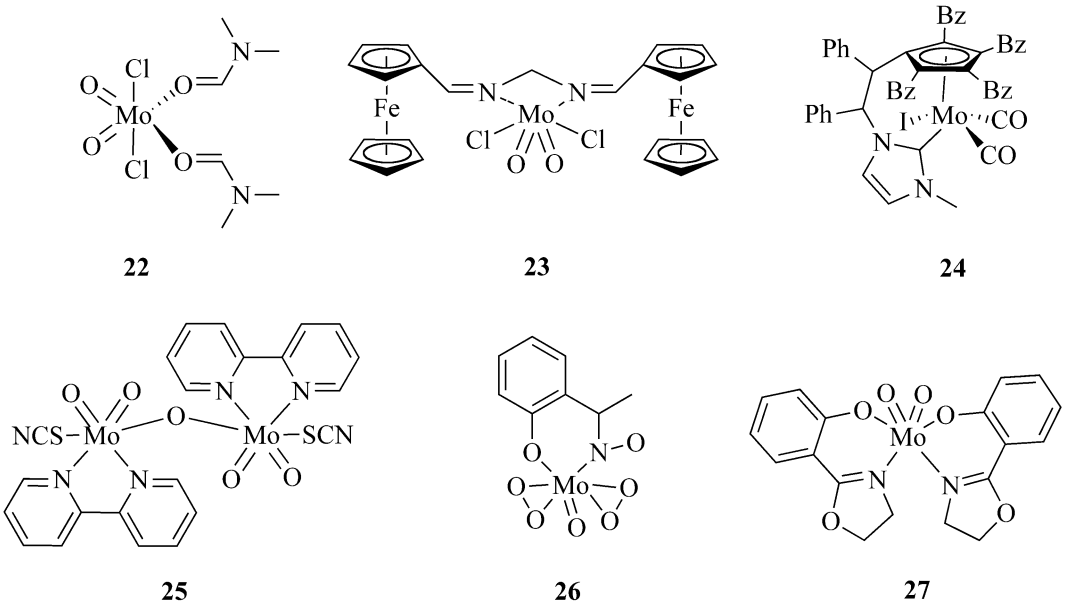


Figure 7. Molybdenum catalysts for olefin epoxidation in 2009.

The application of *N*-heterocyclic-carbenes (NHCs) remained a topic of interest in science, especially with environmental friendly oxidant hydrogen peroxide (Figure 8 (**28**)) [44]. A clear induction period of 2 h during the catalysis appeared. This indicates the high stability of complex **28**. The results are shown in Table 2. Other carbene-approaches were made with cationic compounds like **29** [45]. The counter-ion had a substantial influence on the catalytic performance. The most active chlorine derivative is included in Table 2. Ionic molybdenum complexes like **30** were also applied by Gago et al. in conventional solvents and ionic liquids [46]. The common $C_2H_4Cl_2$ turned out to provide the most active media for the reaction (Table 2). Wong et al. examined *N,N,O,O*-capped molybdenum complexes (**31**) in epoxidation catalysis [47]. The reaction of styrene could only be achieved in medium yields under harsh conditions and relatively high catalyst loadings (Table 2). Rezaeifard et al. studied epoxidation of cyclooctene with tridentate molybdenum Schiff base complexes [48]. Compound **32** turned out to have better catalytic characteristics than its phenyl-substituted derivatives (Figure 8, Table 2). To overcome the low solubility of complex **33** and congeners in conventional organic solvents, it was investigated in ionic liquids with remarkable success (Table 2) [49]. In 2010, Amarante et al. wanted to study the different catalytic behavior of compound **34** and its dioxo derivative [50]. The microwave assisted catalysis revealed no difference, like an induction period or

similar, at elevated temperatures. The diiodide-complex **35** was originally reacted with an amino acid to create a new, bio-inspired catalyst [51]. During the catalytic runs precursor compound **35** turned out to be even more active (Table 2).

A practical approach in epoxidation was made by functionalization of soybean oil [52]. The amount of all double bonds in the oil was referred to as substrate, catalyst was $[MoO_2(acac)_2]$ (**36**) with TBHP as oxidant. Although the TOF and TON were low, this is one rare example were a molybdenum catalyst is used to oxidize a substrate from a sustainable and biological source (Table 2).

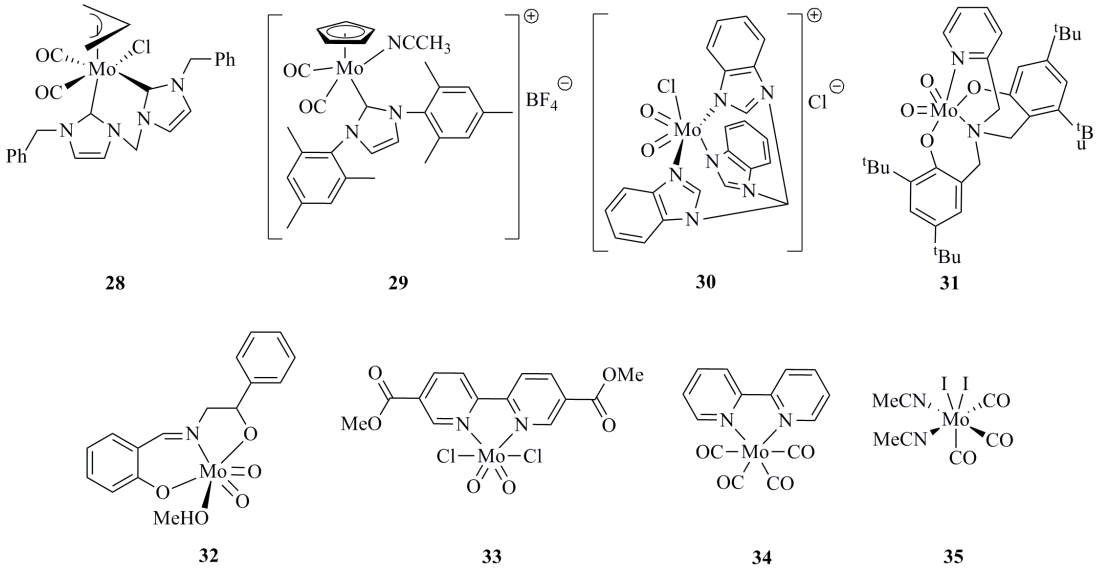
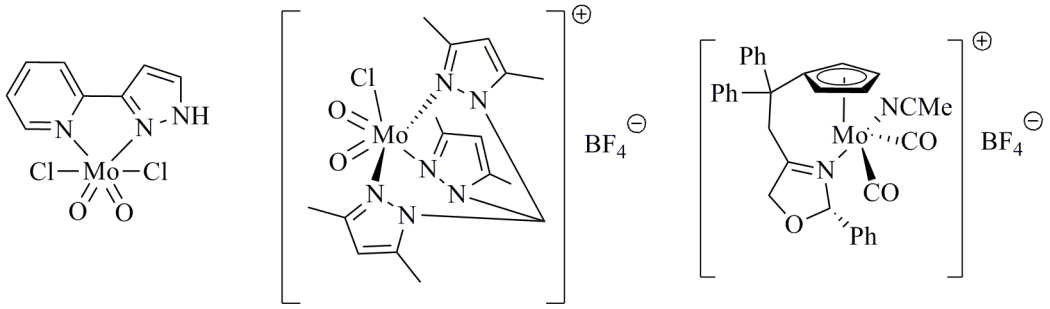


Figure 8. NHC- and nitrogen-ligated molybdenum complexes.

Later, pyrazole derivatives were used as ligands in neutral and ionic molybdenum complexes (**37**, **38**) [53, 54]. For **38,** catalysis did only work under absolute dry conditions and application of ionic liquids had no benefit for the reaction (Table 2). Ionic complex **39** was synthesized as combination of a cyclopentadienyl-ansa- and an ionic-complex, which worked well in catalysis (Table 2) [55]. The epoxidation of cyclooctene did even work with hydrogen peroxide as oxidant.



37 **38** **39**

Figure 9. Molybdenum catalysts by Coelho et al., Neves et al. and Reis et al.

Table 2. Epoxidation with Mo-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TOF [h^{-1}]	TON	ee	Yield [%]
[30]	**14** 1	55	CH_2Cl_2	Cyclooctene	TBHP (2:1)	272	-	-	100 (24 h)
[30]	**14** 1	55	CH_2Cl_2	Styrene	TBHP (2:1)	226	-	-	74 (24 h)
[30]	**15** 1	55	CH_2Cl_2	Cyclooctene	TBHP (2:1)	215	-	-	88 (24 h)
[30]	**15** 1	55	CH_2Cl_2	Styrene	TBHP (2:1)	214	-	-	66 (24 h)
[31]	**16** 2.5	r.t.	Toluene	Cyclooctene	TBHP (1.5:1)	-	-	-	25 (22 h)
[31]	**16** 2.5	r.t.	Toluene	Limonene	TBHP (1.5:1)	-	-	10 0	13 (22 h)
[31]	**17** 2.5	r.t.	Toluene	Cyclooctene	TBHP (1.5:1)	-	-		17 (22 h)
[31]	**17** 2.5	r.t.	Toluene	Limonene	TBHP (1.5:1)	-	-	50	24 (22 h)
[32]	**18** 1	55	-	Cyclooctene	TBHP (1.5:1)	1916	-	-	96 (5 min)
[33]	**18** 1	55	$bmimNTf_2$	Cyclooctene	TBHP (2:1)	113	-	-	41 (24 h)
[32]	**19** 1	55	-	Cyclooctene	TBHP (1.5:1)	1871	-	-	95 (5 min)
[34]	**20** 0.1	r.t.	CH_2Cl_2	Cyclooctene	TBHP (2:1)	3650	-	-	100 (24 h)
[36]	**20** 1	r.t.	$bmimNTf_2$	Cyclooctene	TBHP (2:1)	4130			100 (4 h)
[38]	**22** 1	55	-	Cyclooctene	TBHP (1.6:1)	1003	-	-	100 (24 h)
[39]	**23** 0.1	80	$C_2H_4Cl_2$	Styrene	TBHP	-	189	-	79 (12 h)
[40]	**24** 1	55	$CHCl_3$	Cyclooctene	TBHP (3:1)				91 (20 h)

[41]	**25** 1	55	$bmPyBF_4$	Cyclooctene	TBHP (1.5:1)	62	-	-	79 (24 h)
[42]	**26** 0.025	r.t.	CH_3CN/ Acetone	Cyclooctene	H_2O_2 (3-6:1)	3291	3840	-	96 (1 h)
[42]	**26** 0.05	r.t.	CH_3CN/ Acetone	Styrene	H_2O_2 (3-6:1)	360	1800	-	90 (5 h)
[43]	**27** 0.02	80	$C_2H_4Cl_2$	Cyclooctene	TBHP (1:1)	4800	-	-	96 (1 h)
[43]	**27** 0.02	80	$C_2H_4Cl_2$	Styrene	TBHP (1:1)	1495	-	-	30 (1 h)
[44]	**28** 1	70	CH_3CN	Cyclooctene	H_2O_2 (3:1)	-	-	-	100 (8 h)
[45]	**29** 1	55	-	Cyclooctene	TBHP (2:1)	-	-	-	100 (24 h)
[46]	**30** 1	55	$C_2H_4Cl_2$	Cyclooctene	TBHP (1.5:1)	201	-	-	96 (24 h)
[47]	**31** 2.5	65	Toluene	Styrene	TBHP (2.5:1)	-	-	-	56 (26 h)
[48]	**32** 1	80	$C_2H_4Cl_2$	Cyclooctene	TBHP (2:1)	-	-	-	100 (0.75 h)
[49]	**33** 0.1	r.t.	$bmimNTf_2$	Cyclooctene	TBHP (1.5:1)	8090	-	-	100 (25 h)
[50]	**34** 1	75	$C_2H_4Cl_2$	Cyclooctene	TBHP (1.5:1)	518	-	-	100 (1 h)
[51]	**35** 1	55	CH_2Cl_2	Cyclooctene	TBHP (2:1)	244	-	-	81 (24 h)
[51]	**35** 1	55	CH_2Cl_2	Styrene	TBHP (2:1)	220	-	-	20 (24 h)
[52]	**36** 1	110	Toluene	Soybean oil	TBHP (1:1)	7.5	15	-	42 (2 h)
[53]	**37** 1	55	-	Cyclooctene	TBHP (1.5:1)	-	-	-	90 (24 h)
[54]	**38** 1	55	-	Cyclooctene	TBHP (1.7:1)	-	-	-	100 (6 h)
[55]	**39** 1	55	$CHCl_3$	Cyclooctene	TBHP (2:1)	-	-	-	98 (0.5 h)
[55]	**39** 1	r.t.	$CHCl_3$	*trans*-β- Methyl- styrene	TBHP (2:1)	-	-	-	14 (16 h)
[55]	**39** 1	70	CH_3CN	Cyclooctene	H_2O_2 (2:1)	-	-	-	92 (11 h)

Tungsten. In 2008, peroxotungstate $[W_2O_3(O_2)_4]^{2-}$ (**40**) was synthesized and deployed as catalyst for epoxidation for the first time [56]. The catalysis with H_2O_2 gave very good results for tungsten, which is known to be normally less active than molybdenum (Table 3). Many molybdenum complexes have similar corresponding tungsten compounds due to similar reactivities of the two metals. The ansa-catalyst **20** was also synthesized and tested as a tungsten complex (**41**) but compared to its molybdenum form, it was much less active (Table 2, 3) [34]. The tungsten derivative **42** of the bis-peroxo-complex **26** yielded similar results for tungsten and molybdenum as central atom (Table 2, 3) [42]. Other metal changes from molybdenum to tungsten were performed with **31** [47]. The resulting tungsten form (**43**) was less active under identical reaction conditions (Table 3). **44**, the tungsten complex of **28** showed similar reactivity compared to **28** with hydrogen peroxide as oxidant, only the reaction time lasted longer (Table 3) [44].

Peroxotungstates were again part of a study in 2010. As new feature, selenium was inserted to yield a complex of the form $[SeO_4\{WO(O_2)_2\}_2]^{2-}$ (**45**) with tetrabutylammonium as counter ion [57]. The epoxidation of cyclohexene is displayed in Table 3. Simple phosophotungstic acid (**46**) was chosen as catalyst for the epoxidation of terpenes, among them limonene (Table 3) [58]. The catalysis was carried out in an isopropanol-water mixture together with UHP as oxidant and worked quite well. Later, phosophotungstates with bigger tungsten clusters were investigated to find out the best cation for the reaction [59]. The ethyl-methyl-imidazolium cation together with $[PW_{11}O_{39}]^{7-}$ (**47**) showed the best activity in butadiene epoxidation (Table 3).

Dinoi et al. studied the kinetics of di-Cp*-complexes of tungsten namely $[Cp^*_2W_2O_5]$ (**48**) [60]. They found clear first order kinetics for the substrate. The experimental results are depicted in Table 3.

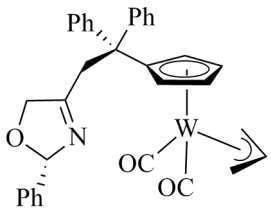


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Figure 10. Cp-W-complex by Reis et al.

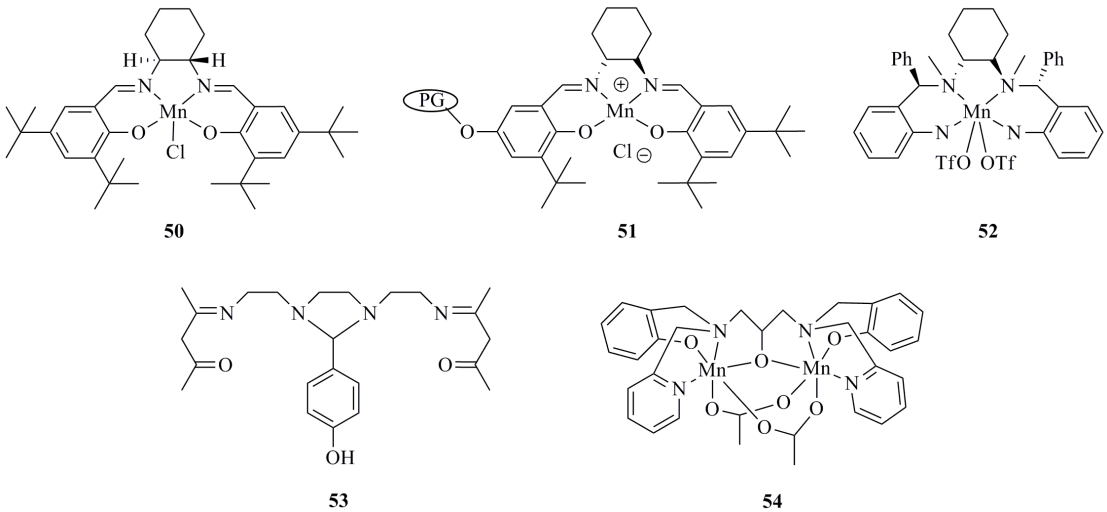
Cp-complexes of tungsten that are applied in epoxidation catalysis are rare. One of them is compound **49** [55]. It was used to epoxidize cyclooctene in good yields with H_2O_2 as oxidant (Table 3).

Table 3. Epoxidation with W-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TOF [h^{-1}]	TON	Yield [%]
[56]	**40** 0.17	80	CH_3CN	Cyclooctene	H_2O_2 (1:1)	-	600	100 (4 h)
[56]	**40** 0.3	r.t.	CH_3CN	Geraniol	H_2O_2 (4.5:1)	-	293	83 (5 h)
[34]	**41** 0.1	r.t.	CH_2Cl_2	Cyclooctene	TBHP (2:1)	160	-	67 (24 h)
[42]	**42** 0.025	r.t.	CH_3CN/ Acetone	Cyclooctene	H_2O_2 (3-6:1)	3257	3800	95 (1 h)
[42]	**42** 0.05	r.t.	CH_3CN/ Acetone	Styrene	H_2O_2 (3-6:1)	450	1800	90 (4 h)
[47]	**43** 2.5	65	Toluene	Styrene	TBHP (2.5:1)	-	-	19 (26 h)
[44]	**44** 1	70	CH_3CN	Cyclooctene	H_2O_2 (3:1)	-	-	100 (10 h)
[57]	**45** 0.4	55	CH_3CN	Cyclohexene	H_2O_2 (-:-)	-	-	84 (40 min)
[58]	**46** 3	r.t.	Isopropanol/ H_2O	Limonene	UHP (2.3:1)	-	-	78 (2 h)
[59]	**47** -	60	CH_3CN	Butadiene	H_2O_2 (-:-)	-	64	76 (5 h)
[60]	**48** 1	55	CH_3CN/ Toluene	Cyclooctene	H_2O_2 (-:-)	-	-	80 (2 h)
[55]	**49** 1	70	CH_3CN	Cyclooctene	H_2O_2 (2:1)	-	-	88 (2 h)

Manganese, Rhenium

Manganese. After the introduction of Jacobsen's catalyst in the 1990s a lot of work has been done to find optimum conditions for asymmetric epoxidation [2]. This investigation still goes on [61, 62]. Jacobsen's catalyst (**50**) was investigated for the epoxidation of styrene together with co-catalyst NH_4OAc (Figure 11) [61]. Good ee and yields were achieved after 2 h (Table 4). A polyglycol (PG) derivative (**51**) was examined in more general epoxidations (Figure 11, Table 4) [62]. A modification of the original salen ligands are the *N,N,N,N*-chiral ligands as used for complex **52** [63]. The asymmetric epoxidation of styrene did not work as well as with chiral salen complexes but this could also be due to the milder reaction conditions that were applied (Table 4). Another approach of manganese catalyzed epoxidation was done with a complex consisting of $MnCl_2$ and **53** [64]. The catalytic experiments were supported by co-catalyst NH_4OAc and performed in an acetone-methanol mixture. A bi-nuclear complex consisting of a Mn(II) and a Mn(III) core was synthesized by Castaman et al. in 2009 (Figure 11 (**54**)) [65]. The experiments were done with a large excess of substrate compared to the oxidant, iodosylbenzene. The oxidation of cyclooctene yielded only medium amounts of the epoxide (Table 4).



50 51 52

53 54

Figure 11. Mn-complexes and ligand from 2008 and 2009.

Jacobsen's catalyst in the *R,R*-conformation (**55**) turned out to be the most active and enantioselective catalyst in a study comparing homogeneous and heterogeneous Jacobsen-type catalysts [66]. An anionic directed approach with a similar catalyst (**56**)

was also performed in 2010 [67]. The results for the most common substrates are selected in Table 4. Ligand **57** was added to $Mn(ClO_4)_2$ for epoxidation of cyclooctene. Hydrogen peroxide was used as oxidant at 0 °C and moderate yields were obtained, taking the reaction conditions into account (Table 4) [68]. The bi-metallic bipyridine complex **58** was examined with peracetic acid as oxidant. Under these harsh conditions very good results were recorded for the epoxidation of cyclooctene and styrene already after 3 min reaction time (Table 4) [69]. Similar conditions were used for epoxidation runs with **59** but the results did not match those of complex **58** [70]. Porphyrin derived manganese complexes (**60**, **61**) were used as catalysts for the epoxidation of cyclooctene [71, 72]. Compared to salen-manganese catalysts the porphyrines were not competitive regarding yield and activity of the catalyst (Table 4). Catalyst **61** worked much better with imidazole as additive. The yield rose from 5 % to 43 % after 5 h reaction time.

In 2011, Chico et al. and Song et al. applied the complexes **62** and **63** as epoxidation catalysts [73, 74]. With compound **62** as catalyst, styrene oxide was obtained only as racemate. Even the bulky *tert*-butyl-groups could not increase the enantiomeric excess very much (Table 4). Kwong et al. deployed $(PPh_4)_2[Mn(N)(CN)_4]$ (**64**) together with H_2O_2 as oxidant and obtained good results [75]. Since acetic acid was added to the reaction solution it is very likely that peracetic acid was formed up to certain content and could have acted as oxidant as well.

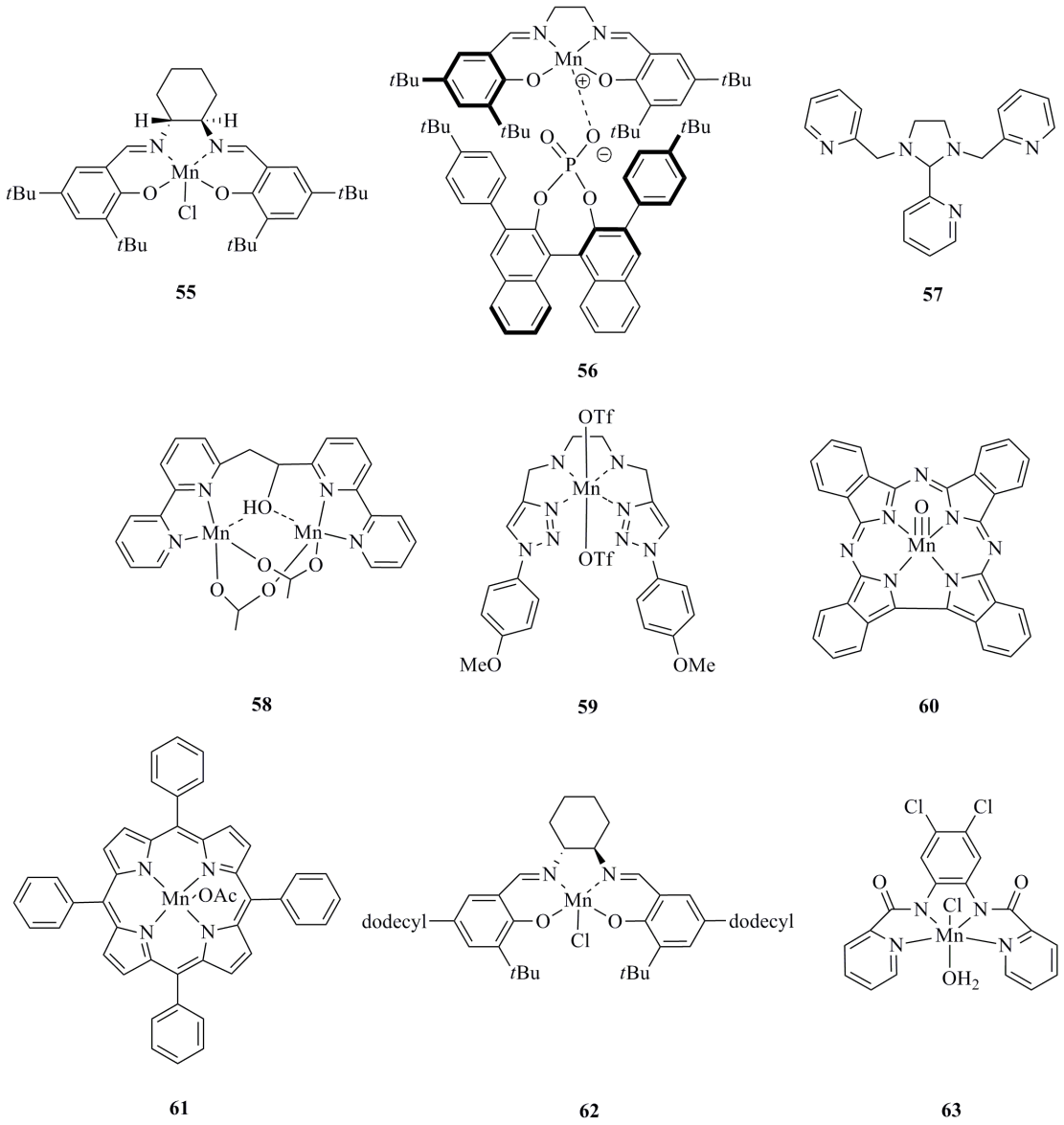


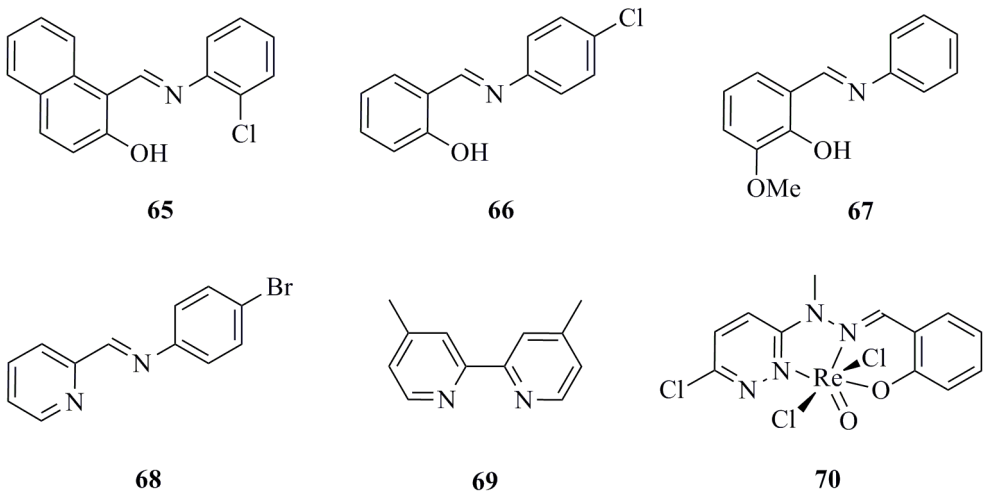
Figure 12. Manganese catalysts from 2010 and 2011.

Table 4. Epoxidation with Mn-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TOF [h^{-1}]	TON	ee	Yield [%]
[61]	**50** 10	0	bmimPF_6 /H_2O	Styrene	NaClO (2.9:1)	-	-	88	99 (2 h)
[62]	**51** 4	0	CH_2Cl_2	Styrene	*m*CPBA/ NMO (2:1)	-	-	50	100 (10 min)
[63]	**52** 1	r.t.	CH_3CN	Styrene	H_2O_2/ AcOH (6:1)	-	-	46	89 (1.5 h)
[64]	$MnCl_2$/	r.t.	Acetone/	Cyclooctene	H_2O_2	239	718	-	72

	53 0.1		MeOH		(2:1)				(3 h)
[64]	$MnCl_2$/ **53** 0.1	r.t.	Acetone/ MeOH	Styrene	H_2O_2 (2:1)	200	600	-	59 (3 h)
[65]	**54** 0.1	r.t.	CH_3CN/ CH_2Cl_2	Cyclooctene	PhIO (0.01:1)	-	-	-	74 (6 h)
[66]	**55** 1	r.t.	Acetone	Limonene	$KHSO_4$/ $NaHCO_3$ (1:1)	-	46	56	55 (35 min)
[67]	**56** 5	r.t.	Benzene	Styrene	PhIO (1.2:1)	-	-	85	80 (-)
[68]	**57** 10	0	Acetone	Cyclooctene	H_2O_2 (9.6:1)	-	-	-	79 (16 h)
[69]	**58** 3	r.t.	CH_3CN	Cyclooctene	CH_3CO_3H (2:1)	-	-	-	100 (3 min)
[69]	**58** 3	r.t.	CH_3CN	Styrene	CH_3CO_3H (2:1)	-	-	-	52 (3 min)
[70]	**59** 0.5	0	CH_3CN	Cyclooctene	CH_3CO_3H (2:1)	-	-	-	92 (3 min)
[71]	**60** 0.4	r.t.	CH_2Cl_2	Cyclooctene	PFIB (1:10)	-	-	-	34 (3 h)
[72]	**61** 0.14	r.t.	CH_3CN	Cyclooctene	H_2O_2 (5:1)	-	-	-	43 (5 h)
[73]	**62** 3.4	r.t.	CH_3CN/ hexane	Styrene	PhIO (2:1)			11	89 (24 h)
[74]	**63** 2.9	r.t.	CH_3CN/ CH_2Cl_2	Cyclooctene	*m*CPBA (2:1)	-	-	-	86
[74]	**63** 2.9	r.t.	CH_3CN/ CH_2Cl_2	Styrene	*m*CPBA (2:1)	-	-	-	53
[75]	**64** 1	r.t.	CH_3CN	Cyclooctene	H_2O_2 (1:1)	-	-	-	96 (5 min)
[75]	**64** 1	r.t.	CH_3CN	Styrene	H_2O_2 (1:1)	-	-	-	87 (0.5 h)

Rhenium. Homogeneous epoxidation with rhenium is in virtually all cases performed with methytrioxorhenium(VII) (MTO) and its respective Lewis base adducts. By adding Lewis base additives to MTO, the reaction can be increased and the formation of undesired side products is suppressed [76-90]. One class of additives consists of Schiff bases (Figure 13, **65**-**68**) [33, 78, 91, 92], which are quite good additives, but exhibited a somewhat limited spectrum of substrates giving satisfying results (Table 5). Unconventional solvents such as ionic liquids did not enhance the reaction in terms of activity or selectivity [33]. Schiff bases like **65**-**67** tether MTO via the oxygen atom. In order to have nitrogen as donor atom Schiff base, **68** was introduced for the oxidation of cyclohexene and styrene (Table 5) [92]. Other widely applied additives were pyridine derivatives like bipyridine **69**. They act as bidentate ligands, at least in solid phase [89]. For most substrates pyridine ligands worked better under identical conditions than Schiff base ligands (Table 5). Pure MTO worked also without any additive very well and was applied for epoxidation of terpenes [93]. A rare example of Re(V) epoxidation catalysts is complex **70** [94]. It was used to oxidize cyclooctene with TBHP but only with medium success (Table 5).



65 **66** **67**

68 **69** **70**

Figure 13. Additives to MTO (**65**-**69**) and Re(V)-catalyst (**70**).

Table 5. Epoxidation with Re-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TOF [h^{-1}]	Yield [%]
[78]	MTO/**65** 1	r.t.	CH_2Cl_2	Cyclooctene	H_2O_2 (2:1)	-	100 (24 h)
[33]	MTO/**66** 1	r.t.	$bmimPF_6$	Cyclooctene	H_2O_2 (2.2:1)	479	95 (24 h)
[91]	MTO/**67** 1.5	r.t.	CH_2Cl_2	Cyclooctene	H_2O_2 (6.8:1)	-	70 (24 h)
[92]	MTO/**68** 1	r.t.	CH_3OH	Cyclohexene	H_2O_2 (2:1)	-	71 (1.5 h)
[92]	MTO/**68** 1	r.t.	CH_3OH	Styrene	H_2O_2 (2:1)	-	12 (2 h)
[89]	MTO/**69** 1	r.t.	CH_2Cl_2	Cyclooctene	H_2O_2 (2:1)	870	100 (2 h)
[93]	MTO 2.7	r.t.	$bmimBF_4$	Limonene	UHP (2:1)	-	88 (2 h)
[94]	**70** 1	50	$CHCl_3$	Cyclooctene	TBHP (2:1)	-	65 (4 h)

Iron, Ruthenium

Iron. Iron catalyzed reactions are especially favorable since iron is a cheap and readily available metal. It is possible to synthesize iron-complexes before application as catalyst or just add an iron salt and the ligand to the reaction mixture. This method was chosen by Bitterlich et al. in 2008 [95]. Ligand **71** was added to a $FeCl_3$ and pyridine-2,6,-dicarboxylic acid containing solution and epoxidation of 1-octene and styrene was performed (Table 6). The dimeric complex **72** was used for the epoxidation of cyclooctene only with limited success [96]. The imidazole derived complex **73** performed not much better in catalysis [97]. The oxidation with TBHP instead of hydrogen peroxide was examined with complex **74** with remarkable yields [98]. Iodosylbenzene was the oxidant of choice for compound **75** [99]. The catalytic results did not match those of TBHP. Slightly modified versions of **75** showed better results [100]. Ligand **76** could form a Fe(III) complex that was catalytically active for cyclooctene and styrene oxidation [101]. An Fe(II)-complex could be synthesized from three bik-ligands (**77**) namely $[Fe(bik)_3](OTf)_2$ (bik = bis(1-methylimidazol-2-yl)ketone) [102]. Its application in catalysis was done with H_2O_2 as oxidant with moderate success (Table 6).

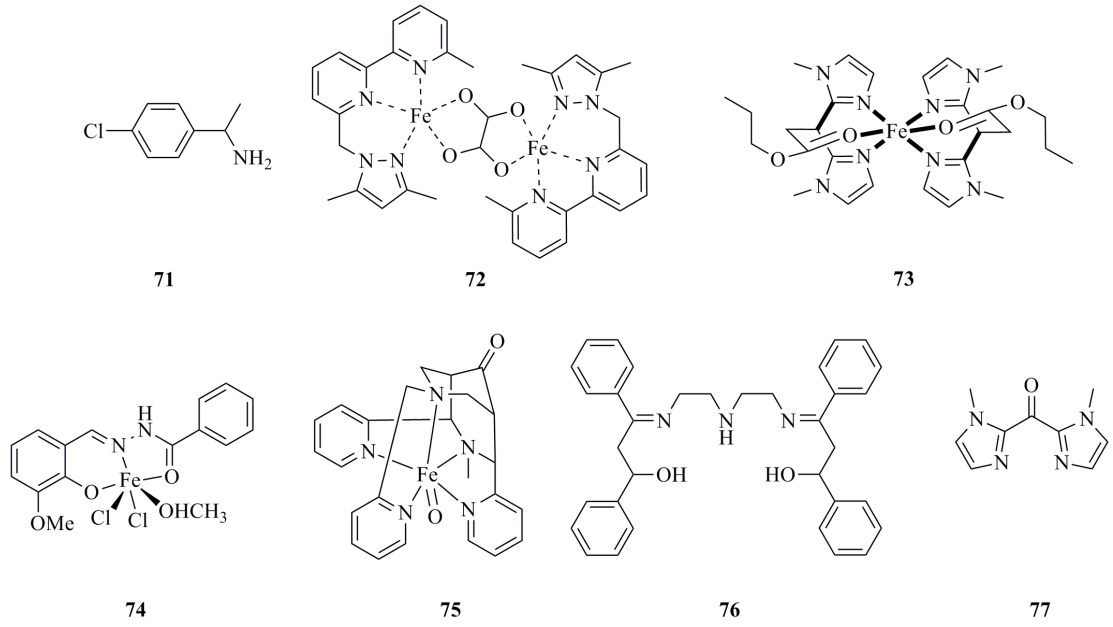


Figure 14. Ligands for Fe(III) (**71**, **76**, **77**) and iron-based catalysts.

Table 6. Epoxidation with Fe-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TON	Yield [%]
[95]	$FeCl_3$/**7** **1** 5	r.t.	*t*-amyl alcohol	1-Octene	H_2O_2 (2:1)	-	32 (1 h)
[95]	$FeCl_3$/**7** **1** 5	r.t.	*t*-amyl alcohol	Styrene	H_2O_2 (2:1)	-	91 (1 h)
[96]	**72** 0.2	r.t.	CH_3CN	Cyclooctene	H_2O_2 (0.14:1)	4	0.8 (1 h)
[97]	**73** 0.1	r.t.	CH_3CN	Cyclooctene	H_2O_2 (0.02:1)	4	0.4 (1 h)
[97]	**73** 0.1	r.t.	CH_3CN	Styrene	H_2O_2 (0.02:1)	5	1.4 (1 h)
[98]	**74** 0.22	60	CH_3CN	Cyclooctene	TBHP (2:1)	-	70 (24 h)
[98]	**74** 0.22	60	CH_3CN	*trans*-β-Methyl-styrene	TBHP (2:1)	-	60 (24 h)
[99]	**75** 0.1	r.t.	CH_3CN	Cyclooctene	PhIO (0.1:1)	7	0.7 (24 h)
[99]	**75** 0.1	r.t.	CH_3CN	Styrene	PhIO (0.1:1)	37	3.7 (24 h)
[101]	Fe/**76** 0.1	r.t.		Cyclooctene	H_2O_2 (0.02:1)	-	37 (4 h)
[101]	Fe/**76**	r.t.		Styrene	H_2O_2	-	7.5

	0.1				(0.05:1)		(4 h)
[102]	Fe/**77**	r.t.	CH_3CN	Cyclooctene	H_2O_2	15	1.5
	0.1				(0.1:1)		(7 h)
[102]	Fe/**77**	r.t.	CH_3CN	Styrene	H_2O_2	15	1.5
	0.1				(0.1:1)		(7 h)

Ruthenium. Ruthenium catalysts are not very common in homogeneous epoxidation catalysis. Nevertheless, there are some examples that use complexes with ruthenium as central atom (Figure 15). The Ru-analogue (**78**) of the iron catalyst **75** was used under the same conditions as **75** with limited success (Table 7) [99]. An important step towards sustainability was made by Tanaka et al. who used molecular oxygen as oxidant and **79** as catalyst. The results for *trans*-β-methylstyrene were quite remarkable (Table 7) [103]. The two ionic complexes **80** and **81** were both examined with $PhI(OAc)_2$ as oxidant. The yields, especially for the styrenes, were good (Table 7) [104, 105].

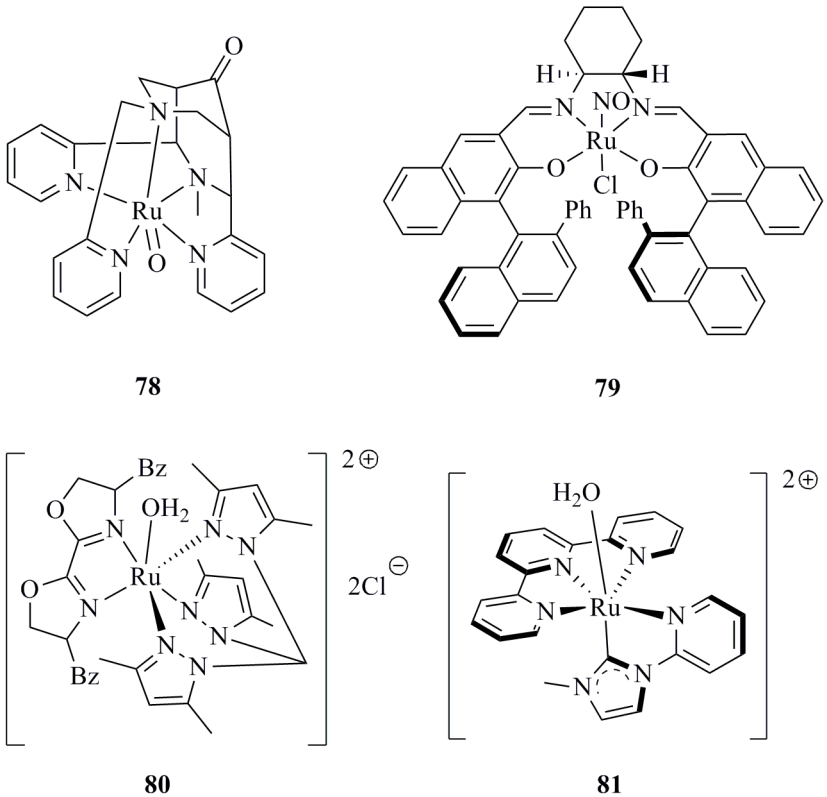


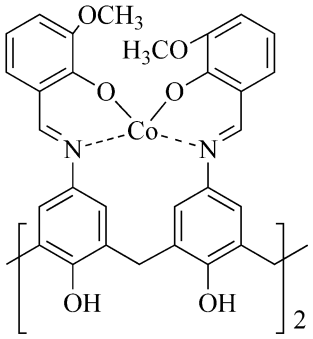
Figure 15. Ru-catalysts.

Table 7. Epoxidation with Ru-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TON	ee	Yield [%]
[99]	**78** 0.1	r.t.	CH_3CN	Cyclooctene	PhIO (0.1:1)	11	-	1.1 (24 h)
[99]	**78** 0.1	r.t.	CH_3CN	Styrene	PhIO (0.1:1)	14	-	1.4 (24 h)
[103]	**79** 5	r.t.	ClC_6H_5	*trans*-β-Methyl-styrene	O_2/hν	-	86	58 (36 h)
[104]	**80** 1	r.t.	CH_2Cl_2	*cis*-β-Methyl-styrene	$PhI(OAc)_2$ (2:1)	-	100	65 (24 h)
[105]	**81** 1	r.t.	CH_2Cl_2	Cyclooctene	$PhI(OAc)_2$ (2:1)	-	-	95 (24 h)
[105]	**81** 1	r.t.	CH_2Cl_2	Styrene	$PhI(OAc)_2$ (2:1)	-	-	61 (24 h)

Cobalt

The two cobalt catalysts (**82**, **83**) shown in Figure 16 had a good activity in epoxidation if the oxidant/substrate ratio is taken into account and when strong oxidants like PhIO or *m*CPBA were used (Table 8) [106, 107]. Nevertheless, the yield did not exceed the ones of commonly used epoxidation catalysts based on molybdenum or rhenium.



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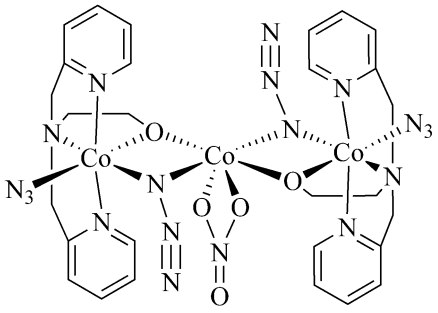


83

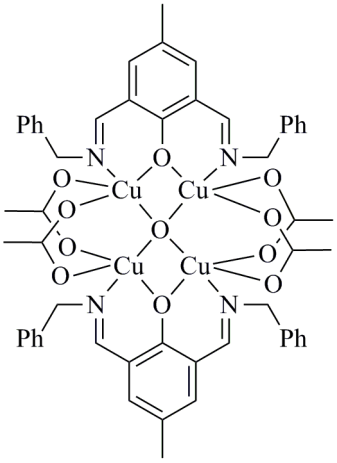
Figure 16. Co-catalysts.

Table 8. Epoxidation with Co-catalysts.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TOF [h^{-1}]	TON	Yield [%]
[106]	**82** 0.4	r.t.	CH_3CN/ H_2O	Cyclohexene	PhIO (0.04:1)	0.9	-	3 (4 h)
[106]	**82** 0.4	r.t.	CH_3CN/ H_2O	Styrene	PhIO (0.04:1)	0.8	-	3 (4 h)
[107]	**83** 1	r.t.	CH_3CN	Cyclooctene	*m*CPBA (0.35:1)	-	27	27 (- h)
[107]	**83** 1	r.t.	CH_3CN	Styrene	*m*CPBA (0.35:1)	-	22	22 (- h)

Copper

Copper is an exception regarding homogeneous epoxidation catalysis. Only one example can be found in recent literature (Figure 17, Table 9) [108]. Originally, complex **84** was a precursor for heterogenization on solid materials but was also used as homogeneous catalyst with a yield of 75 % for styrene oxide.



84

Figure 17. Cu-catalyst.

Table 9. Epoxidation with Cu-catalyst **84**.

Ref.	**Cat.** [mol%]	Temp. [°C]	Solvent	Substrate	Oxidant	TOF [h^{-1}]	Yield [%]
[108]	**84** 0.16	r.t.	CH_3CN	Cyclohexene	H_2O_2 (1:1)	24	80 (24 h)
[108]	**84** 0.21	r.t.	CH_3CN	Styrene	H_2O_2 (1:1)	16	75 (24 h)

Summary. The most prominent metals as central atoms in epoxidation catalysts are doubtlessly molybdenum, manganese and rhenium. Molybdenum-based catalysts have been synthesized with a large variety of different ligands: Ansa-briged Cps, carbenes or nitrogen-donors. Catalysts precursors could be carbonyl-, halide- and/or oxide-complexes. Molybdenum catalysts have been successfully applied as neutral or ionic complexes. All these different possibilities make molybdenum catalysis a vivid field with lots of opportunities for new approaches. Only enantiomeric catalysis, although tried, was so far not very competitive to established systems.

Enatiomeric catalysis is still made with derivatives of Jacobsen's catalyst. Recent ionic complexes showed very good ee. Besides enantiomeric catalysis, the advantage of manganese catalysts over molybdenum ones lies in the partially application of H_2O_2 as oxidant. Some manganese complexes work with this environmental friendly oxidant.

Methyltrioxorhenium, the most prominent rhenium catalyst, uses only H_2O_2 as oxidant. Another great advantage of MTO is the easy way of tuning the catalysis via Lewis base additives. Therefore, the application for different substrates is very simple.

Catalytic epoxidation with iron-derived catalysts is probably the most sustainable approach, although the activities do not match the ones of molybdenum- or rhenium-catalysts. In contrast to molybdenum or rhenium, iron is cheap and non-toxic. The catalysis works also at room temperature. Therefore, iron displays the most interesting metal for industrial usage.

Other metals often have the disadvantage of substrate-limitations or harsh reaction conditions like *m*CPBA as oxidant or high reaction temperatures. Their application as homogeneous epoxidation catalysis is therefore not as focused on as molybdenum, manganese, rhenium or iron as catalyst metals. Iron catalysts have to become more active to compete with molybdenum and rhenium. Molybdenum and rhenium on the other hand have to overcome their high prices by lowering the catalyst amount while keeping the high activity of the whole catalytic system.

1.2 Objectives of this work

The search for the highest possible catalytic activity is part of this study. A very high catalytic activity makes it possible to use very low catalyst loadings. The high prices of transition metal complexes as well as the separation of product and catalyst would not play a major role during the catalytic process any longer. Low catalyst concentrations mean low metal weight and therefore low material costs. Additionally, the catalyst could remain in the product solution if the concentration of catalyst is very low.

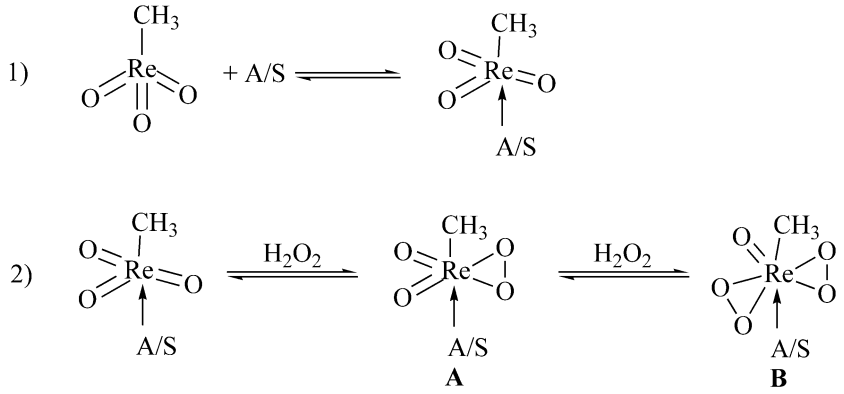
Methyltrioxorhenium is still one or probably the most active epoxidation catalyst in homogeneous phase. It works perfectly with environmental friendly oxidant hydrogen peroxide at room temperature under air. The different reaction conditions in homogeneous catalytic epoxidation of olefins like temperature, solvent, catalyst concentration and additive are examined and optimized in this work. Especially the direct comparison of different types of additives under identical reaction conditions and Schiff bases as additives are investigated. Uncommon solvents like fluorinated alcohols are examined and compared to their common opponents.

Beside the epoxidation of olefins, MTO is also able to oxidize unreactive substrates like pseudocumene under mild conditions. The resulting product trimethyl-benzoquinone is one of the two important starting-materials for synthetic vitamin E synthesis. As for all MTO catalyzed oxidations the search for the right reaction conditions is the main problem and was investigated in the work.

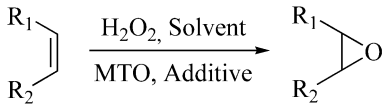
2. Results and Discussion

2.1 Methyltrioxorhenuim catalyzed oxidations

Since the discovery of the catalytic activity of methyltrioxorhenium by Herrmann et al. in the late 1980ies [109] this compound received a great deal of attention as a homogeneous catalyst for a variety of reactions, including olefin metathesis [110], aldehyde olefination [111], and above all, olefin epoxidation [8, 78, 85, 88-90, 112-120]. 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 (Scheme 1) [121, 122]. 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 et al. [76, 80, 86] and other groups [79, 83, 84]. In the past, a plethora of different ligands for MTO has been investigated [117, 123-125] and pyridine and its derivatives were found to belong to the most efficient catalysts, increasing the catalytic performance in terms of activity and selectivity [78, 86, 89, 90, 120-122, 126]. In 2007, Kühn et al. introduced Schiff bases as a new group of additives with very good results in cyclooctene epoxidation [78, 90, 120, 127]. Most *N*-donors readily form complexes with MTO and are catalytically active in the presence of H_2O_2 (Scheme 1) [78, 90, 120-122, 127]. Previous articles already described the coordination of N-donors to MTO [76, 78, 79, 90, 120-122, 127-130]. The common epoxidation of olfins proceeds as shown in Scheme 2. Beside the catalyst concentration, the additive and the solvent play very important roles.



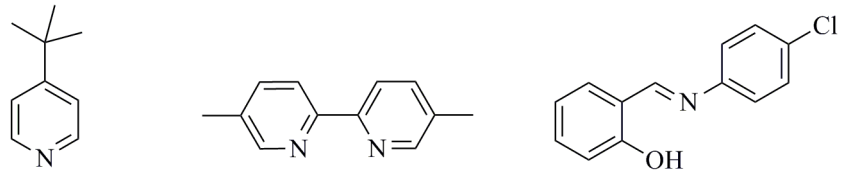
Scheme 1. 1) Reaction of MTO with additive (A) or solvent molecule (S). 2) Reaction of MTO-complex with H_2O_2, forming the mono- and the bis(peroxo)complex.



Scheme 2. Oxidation of olefins to epoxides.

2.2 Methyltrioxorhenium catalyzed epoxidations: A comparative study of different *N*-donor ligands

This chapter presents a direct comparison between three different types of *N*-donor ligands that were reported to display good results in previous papers [78, 90, 120-122, 127]. As *N*-donor ligands, a pyridine derivative, 4-*tert*-butylpyridine (**85**), a chelate ligand, 4,4'-dimethyl-2,2'-bipyridine (**86**) and a Schiff base (**66**) were selected (Figure 18). In this chapter, a direct comparison between a monodentate, a bidentate and a Schiff base ligand under identical conditions is reported for the first time. 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*-β-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.



85 **86** **66**

Figure 18: Used additives to MTO: 4-*tert*-butylpyridine (**85**), 4,4'-dimethyl-2,2'-bipyridine (**86**) and the Schiff base (**66**).

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.

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-nitrogen bond is rather

weak; hence, the MTO-base adduct is in equilibrium with the dissociated molecules [78, 90, 120-122, 127]. Accordingly, an excess of base shifts the equilibrium to the adduct complex [89, 131-135]. Already with 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 [121, 122]. 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 Scheme 1 is sufficiently shifted to the MTO-Lewis base complex. Figure 19 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 turn-over frequencies , summarized in Table 10, show the increase in activity from 1:5 to 1:10 for systems **85** and **86**. 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.

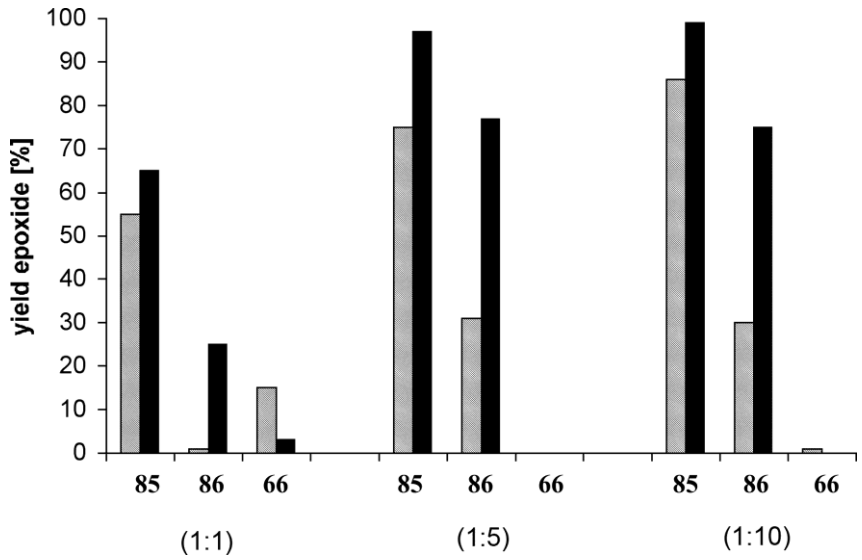


Figure 19. Epoxide yield with different MTO/ligand ratios (1:1, 1:5, 1:10), 25 °C, catalyst/substrate/oxidant 1/100/300, *trans*-β-methylstyrene, after 30 minutes (grey bars) and after 180 minutes (black bars).

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 center significantly and therefore do not lead to a good epoxide selectivity, at least for sensitive epoxides such as those obtained from *trans*-β-methylstyrene. As the ratio of 1:5 turned out to be sufficient in the catalysis it was applied for all following experiments. System MTO/**66** was no longer investigated because the epoxide yields were too low to be competitive with the more selective Lewis base adduct systems.

Table 10. TOFs (mol(epoxide)*mol(cat)$^{-1}$*h^{-1}) measured after 5 minutes, solvent: *tert*-butanol, substrate: *trans*-β-methylstyrene.

Experiment	**85**	**86**	**66**
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	a
45 °C	740	410	a
55 °C	270	170	a
75 °C	200	230	a
1 mol% cat	590	380	0
0.5 mol% cat	690	190	a
0.1 mol% cat	3160	2500	a

[a] not determined.

Temperature effects. For the MTO/**85** system, the highest yields are reached between 25 °C and 45 °C. The yields obtained with MTO/**86** are generally lower compared to those obtained with the system MTO/**85**. Again, best yields are reached somewhat above room temperature. From 55 °C onwards decomposition of the catalyst is observed leading to decreasing yields and TOFs (Table 10 and Figure 20). This is in accordance with the reported decomposition of MTO adducts to methanol, pyridinium cations and perrhenate at elevated temperatures [126, 136] and the comparatively weak interaction of MTO with the ligand [137]. Furthermore, ring opening reactions can be observed at 45 °C and higher temperatures, pointing at decreasing ligand influence due to the increased ligand fluctionality at high temperatures [137]. 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 (Figure 20). Whereas epoxidation catalyzed 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.

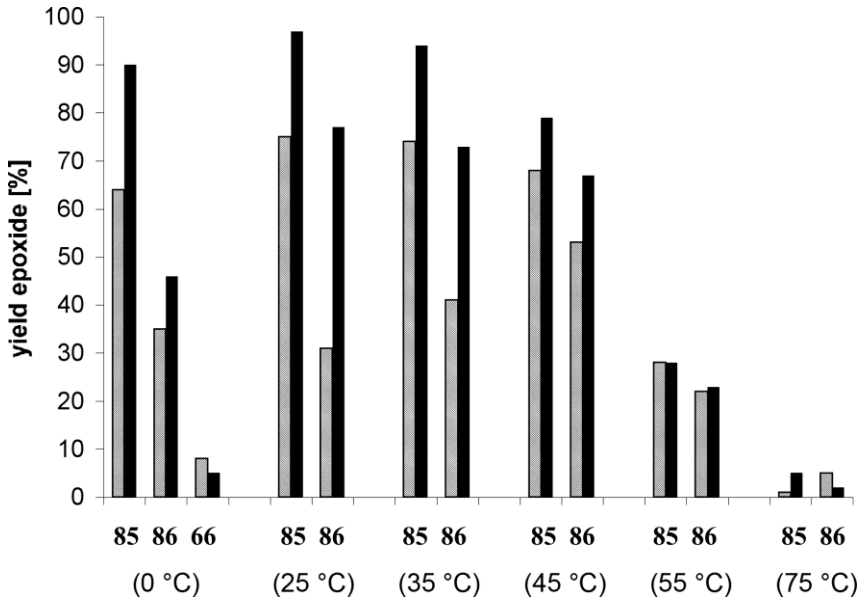


Figure 20. Epoxide yields at different temperatures, MTO/ligand 1:5, catalyst/substrate/oxidant 1/100/300, *trans*-β-methylstyrene, after 30 minutes (grey bars) and after 180 minutes (black bars).

Catalyst concentration. In an additional set of experiments, the catalyst concentration was reduced from 1 mol % to 0.5 mol % and 0.1 mol % (Figure 21). The turn-over frequencies (Table 10) 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 utilized at high catalyst concentrations as these epoxidation reactions follow a first order kinetics with respect to catalyst and substrate concentration [126]. 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/**85** drops to the value reached by catalyst MTO/**86**. The 30 min value of MTO/**86** 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 (Scheme 1). Furthermore, 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 (see below).

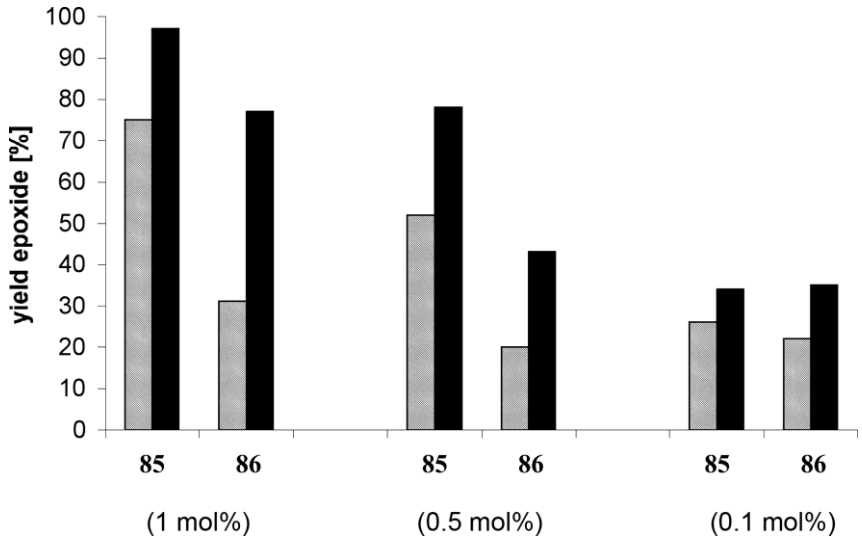


Figure 21. Epoxide yield with different catalyst concentrations, MTO/ligand 1:5, 25 °C, *trans*-β-methylstyrene, after 30 minutes (greyars) and after 180 minutes (black bars).

Table 11. Yields and TOFs (after 5 min) of **66** in different solvents, catalyst/substrate/oxidant 1/100/300, substrate: cyclooctene, 25 °C.

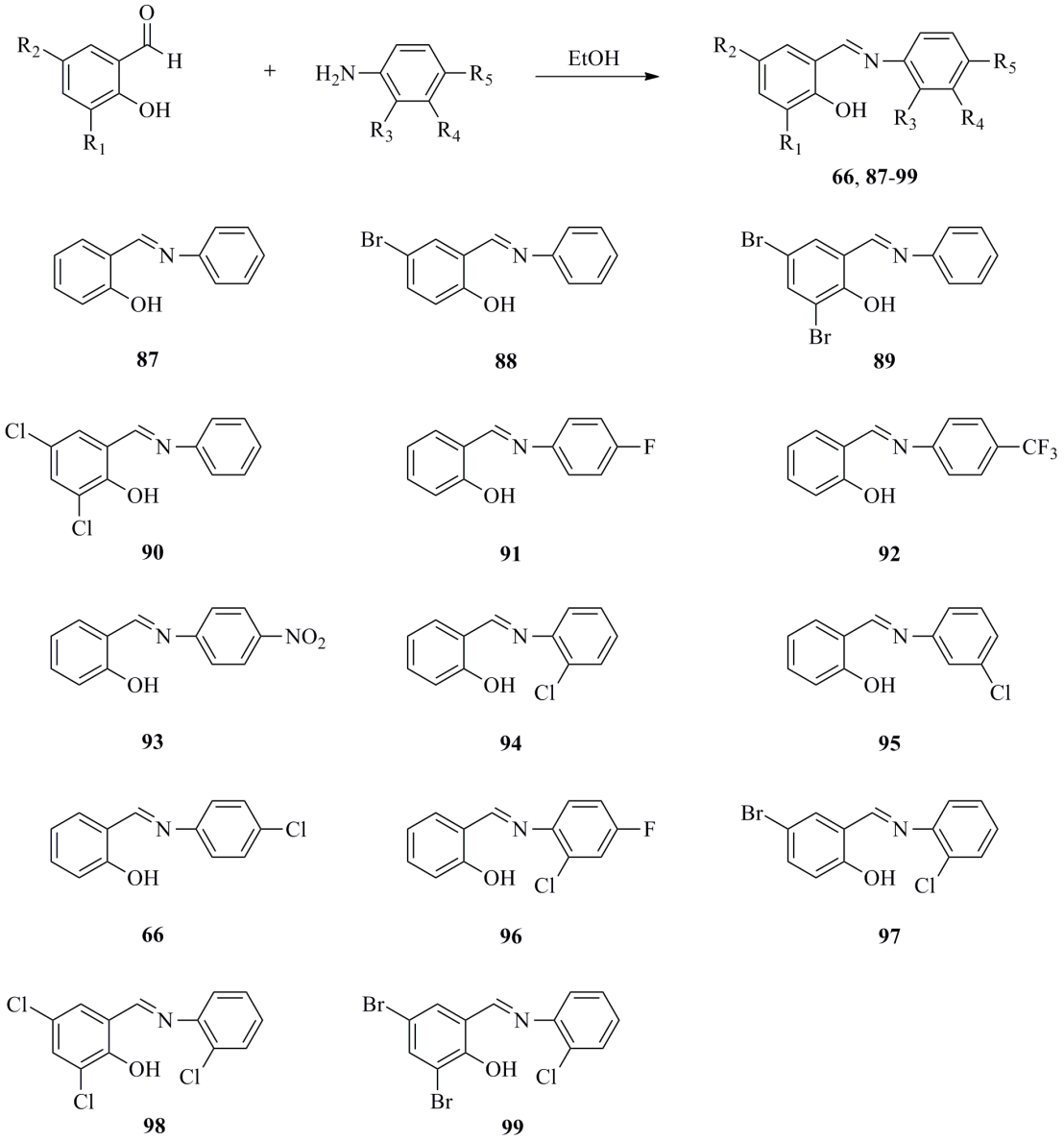
Experiment	yield 30 min [%]	yield 180 min [%]	TOF
tert-butanol	78	99	430
CH_2Cl_2	25	85	180
CH_2Cl_2 Doubled stirring frequency	55	98	350

Solvent effects. The effect of solvents has already been reported [121, 131, 138, 139]. 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*-β-methylstyrene was used, but also cyclooctene, which is known to give very good results in the case of epoxidation reactions [78, 90, 120-122, 127]. 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

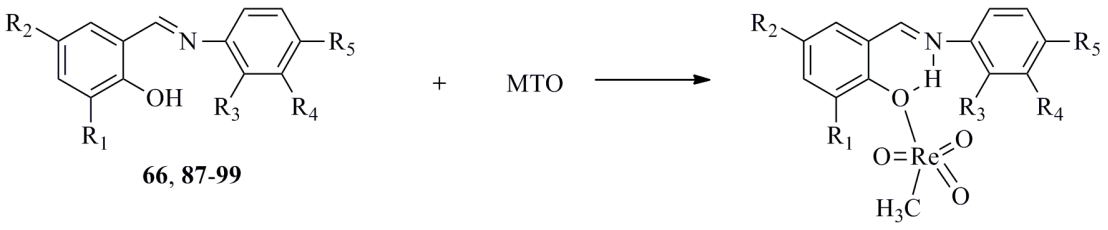
very strong dependency of the TOFs on the stirring frequency could be observed as described already before [79]. Doubling the stirring speed from 400 to 800 rotations per minute leads to almost doubled TOFs (Table 11). Hence, it is obvious that an exact comparison between different examinations published 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 [140]. Generally, the bidentate base system is superior to the monodentate in two-phase systems in CH_2Cl_2 solution.

2.3 Halide substituted Schiff bases: Different activities in methyltrioxorhenium catalyzed epoxidation via different substitution patterns

In this part the influence of different electron withdrawing groups, especially halides at different positions is examined. Two different substrates, cyclooctene and 1-octene have been chosen. Cyclooctene was selected because of its widespread use in former studies. Many scientific reports are available based on this substrate to compare the obtained results with respect to the general activity of the catalytic system. 1-octene is chosen since its oxidation is much slower than that of cyclooctene and comparison of the two substrates should reveal the influence of the different substituents quite well. A set of substituted Schiff bases was synthesized (Scheme 3). All Schiff bases were obtained by reacting different hydroxy-benzaldehydes with aniline derivatives in ethanol according to published procedures [78, 85, 88, 90, 120, 141]. Based on former research results, indicating that electron-donating groups decrease the catalyst activity and reduce the lifetime of the catalyst, electron withdrawing groups, especially halides were chosen for this study.



Scheme 3. Reaction of hydroxy-benzaldehydes and aniline derivatives to Schiff bases.



Scheme 4. Formation of MTO-Schiff base complex.

All obtained Schiff bases react with MTO to form stable complexes (Scheme 4). In accordance with earlier examinations the ^{1}H-NMR data show a high field shift of the

methyl group of MTO adducts of **66**, **87**-**99** compared to free MTO (Table 12). This observations proof the tethering of the Schiff base to MTO [90, 120]. Among the Schiff base-adducts no significant difference between halide or nitro (**93**) substitution can be observed.

Table 12. Selected ^{1}H-NMR spectroscopic data for MTO-Schiff base complexes in $CDCl_3$.

Compound	$\delta(^{1}H)$ MTO-CH_3	Compound	$\delta(^{1}H)$ MTO-CH_3
MTO	2.68	+**93**	2.62
+**88**	2.60	+**96**	2.62
+**90**	2.62	+**97**	2.62
+**91**	2.62	+**98**	2.62
+**92**	2.62		

To rule out solvent molecules as ligands to MTO instead of Schiff bases we chose nitromethane (CH_3NO_2) as a very weak coordinating solvent for the catalysis tests [141]. Furthermore, blank experiments without catalyst show no formation of epoxide neither with cyclooctene nor with 1-octene.

For the first part of the catalysis examination cyclooctene was applied as substrate, as it is a very active starting material, leading to a comparatively stable epoxide. Based on earlier experiments, MTO and the Schiff base-ligands have been used in a ratio of 1:1 for this study [78, 90, 120]. The catalyst:substrate:oxidant ratio was chosen to be 1:100:200 and the substrate concentration in the reaction solution was 1 M. Hydrogen peroxide (aqueous solution 27 %) was used as oxidant. All of the ligands examined with MTO show similar results (Table 13). The turn-over-frequencies are ranging between 700 h^{-1} and 800 h^{-1} and the yield is quantitative after 30 minutes reaction time in almost every case. Only the non-substituted Schiff base **87** as well as the nitro-substituted Schiff base **93** are worse, reaching TOFs of around 650 h^{-1} and yields of 78 % and 88 %, respectively (Table 13, entries 2 and 8). As indicated in earlier examinations, a reason for that might be the relatively good donor ability of **87** compared to the halide substituted Schiff bases [120]. The nitro-group, as very strong electron acceptor, seems to withdraw too much electron density from the Schiff base to operate the catalysis satisfactorily. The catalytic performance of MTO-Schiff base adducts relies most likely on an equilibrium of electron donating and electron

accepting effects. If the equilibrium is shifted too much towards one side, the activity of the catalyst decreases.

Chlorine and bromine substituents lead to similar results (Table 13, entries 3-5, 9-11). The performance of the fluorine-substituted compounds **91** and **92** is slightly lower (Table 13, entries 6 and 7). The position of the halide has no visible influence on the fast cyclooctene-epoxidation (Table 13, entries 9-11). It does also not matter if the halide is located at the hydroxy-benzaldehyde moiety or at the aniline moiety (Table 13, entries 3-5, 9-11). Substituting both aromatics does also not increase the catalyst's activity (Table 13, entries 12-14).

Lower catalyst concentrations of 0.1 mol% give 40 % yield after 30 minutes with a TOF of 2600 h^{-1} for **94** as ligand of MTO. When comparing to an earlier study of Sharpless et al. who also worked with nitromethane as solvent, activities are quite similar. Using MTO and pyridine in a ratio of 1:1 leads to 40 % yield after 5 minutes in the experiments performed by Sharpless et al. 70 % yield are obtained after 5 minutes with pure MTO and doubled catalyst concentration as applied in ref. [86]. Experiments with 4-*tert*-butylpyridine (1:5) yielded 95 % product after 5 minutes whereas 90 % yield are reported for the MTO-pyridine ratio of 1:12 [86].

Compared to other experiments with Schiff bases, carried out earlier in our group, the results in nitromethane are much better than those in dichloromethane or without solvent (Table 15) [78, 90, 120]. 78 % yield is obtained with Schiff base **87** after 30 minutes compared to 4 h in earlier studies without solvent, which equals to an acceleration by factor eight [120]. When the Schiff base is replaced by a 4-*tert*-butylpyridine ligand, the expected increase in activity can be observed. 95 % yield after 5 minutes and a TOF of 1100 h^{-1} are reached (Table 13, entry 15). Changing the solvent from nitromethane to dichloromethane results in a slightly lower activity (Table 13, entries 19, 20). Generally, former experiments confirm the observation that nitromethane seems to be a better or at least an equal solvent if the different experimental setups are taken into account (Table 15).

Table 13. Cyclooctene epoxidation yields and TOFs[a] catalyzed by MTO.

Entry	Ligand	MTO [mol%]	Solvent	Yield 30 min [%]	TOF [h^{-1}]
1	-	1	CH_3NO_2	100	840
2	**87**	1	CH_3NO_2	78	650
3	**88**	1	CH_3NO_2	99	790
4	**89**	1	CH_3NO_2	100	840
5	**90**	1	CH_3NO_2	99	750
6	**91**	1	CH_3NO_2	99	720
7	**92**	1	CH_3NO_2	99	760
8	**93**	1	CH_3NO_2	88	660
9	**94**	1	CH_3NO_2	100	700
10	**95**	1	CH_3NO_2	91	670
11	**66**	1	CH_3NO_2	99	740
12	**97**	1	CH_3NO_2	100	770
13	**98**	1	CH_3NO_2	96	770
14	**99**	1	CH_3NO_2	92	710
15	[t]butylpyridine (1:5)[b]	1	CH_3NO_2	100	1100
16	**94**	0.1	CH_3NO_2	39	2600
17	**95**	0.1	CH_3NO_2	33	2100
18	**66**	0.1	CH_3NO_2	33	2100
19	**88**	1	CH_2Cl_2	90	670
20	**89**	1	CH_2Cl_2	83	490

[a]TOF calculated: [(mol epoxide)/(mol catalyst * h)], [b]ratio MTO:ligand.

Using a terminal alkene like 1-octene as substrate leads to similar results as obtained with cyclooctene with respect to the differences between pure MTO and MTO plus Schiff base. The yield after 3 h ranges between 61 % and 74 % and the TOFs vary from 70 h^{-1} to 80 h^{-1} (Table 14). All examined systems are almost equal except nitro-substituted compound **7** (56 % yield, 50 h^{-1}) (Table 14, entry 8). The reasons are most likely the same as described for cyclooctene. Again, using nitromethane as solvent shows very good results compared to other systems working with 1-octene (Table 15). Slight differences occur between chlorine-substituted ligands leading to an activity order *o* > *p* > *m* (Table 14, entries 9-11). The highest activity can be achieved with the trichloro-substituted compound **98** (74 % yield). Interestingly, with 4-*tert*-butylpyridine as additive the catalyst system decomposes rapidly. In the beginning it is more active indicated by the higher TOF of 100 h^{-1} but after 3 h the yield remains at 31 %, whereas the stability of the Schiff base supported catalyst lasts longer and

higher conversions are reached. For an equal stabilization a higher amount of pyridine is needed for the MTO/pyridine catalyst system.

Table 14. 1-Octene epoxidation yields and TOFs[a] catalyzed by MTO.

Entry	Ligand	MTO [mol%]	Solvent	Yield 3h [%]	TOF [h^{-1}]
1	-	1	CH_3NO_2	69	70
2	**87**	1	CH_3NO_2	61	70
3	**88**	1	CH_3NO_2	72	70
4	**89**	1	CH_3NO_2	72	70
5	**90**	1	CH_3NO_2	69	70
6	**91**	1	CH_3NO_2	62	80
7	**92**	1	CH_3NO_2	69	70
8	**93**	1	CH_3NO_2	56	50
9	**94**	1	CH_3NO_2	72	70
10	**95**	1	CH_3NO_2	67	70
11	**66**	1	CH_3NO_2	69	70
12	**96**	1	CH_3NO_2	66	80
13	**97**	1	CH_3NO_2	73	80
14	**98**	1	CH_3NO_2	74	80
15	**99**	1	CH_3NO_2	67	70
16	^{t}butylpyridine (1:5)[b]	1	CH_3NO_2	31	100

[a]TOF calculated: [(mol epoxide)/(mol catalyst * h)], [b]ratio MTO:ligand.

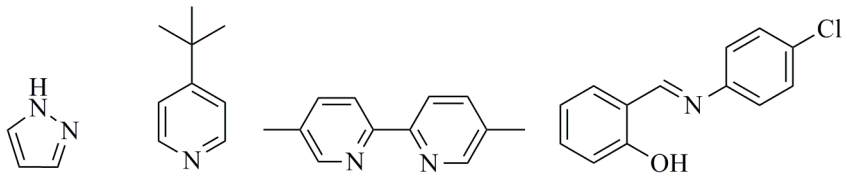
Table 15. Collected data concerning MTO catalyzed epoxidation of cyclooctene and 1-octene.

Ref	Ligand	Substrate c [mol/l][a]	MTO [mol%]	Solvent	Reaction Time [h]	Yield [%]
[86]	Pyridine	Cyclooctene 0.8	0.5	CH_3NO_2	0.5	95
[86]	Pyridine	Cyclooctene 2.0	0.5	CH_2Cl_2	2	99
[122]	3-Cyanopyridine	Cyclooctene 2.3	1	-	4	75
[120]	**87**	Cyclooctene 2.0	1	-	4	70
[120]	**66**	Cyclootene 2.0	1	-	4	79
[121]	4,4'-Dimethyl-2,2'-bipyridine	Cyclooctene 0.9	1	CH_2Cl_2	4	78
[83]	Pyridine	Cyclootene 1.3	0.5	$CHCl_3$	0.5	79
[128]	3-Methylpyrazole	Cyclootene 1.1	0.1	CH_2Cl_2	2	> 99
[142]	3-Methylpyrazole	Cyclootene 3.5	0.1	-	3	> 99
[143]	Pyrazole	Cyclooctene 1.2	0.1	TFE	1	100
[78]	Schiff base	Cyclooctene 0.2	1	CH_2Cl_2	4	70
[144]	4-*tert*-Butylpyridine	Cyclooctene 0.7	1	*tert*-butanol	0.5	78
[128]	3-Methylpyrazole	1-Octene 1.1	0.5	CH_2Cl_2	8	91
[142]	3-Methylpyrazole	1-Octene 3.5	0.5	-	8	62
[78]	Schiff base	1-Octene 0.2	1	CH_2Cl_2	24	100
[143]	Pyrazole	1-Octene 1.2	0.1	TFE	21	100

[a]If not given directly, calculated from experimental sections.

2.4 Applying fluorinated solvents for methyltrioxorhenium catalyzed olefin epoxidations

Fluorinated solvents are successfully applied in many homogeneous catalyzed reactions [145, 146]. Among these reactions, the application of fluorinated solvents in epoxidation reactions is a topic of continuing interest [143, 147-155]. The epoxidation of olefins in fluorinated solvents such as hexafluoroisopropanol is possible even without any further catalyst, as the solvent alone is able to activate the oxidant [147, 148, 151-156]. In combination with methyltrioxorhenium(VII), which is one of the most efficient olefin oxidation catalysts [76-90, 109, 113, 115, 120, 122, 126, 142, 157-162], highly active catalytic media are formed [143, 150]. Although, the system MTO/fluorinated solvent attracted already some attention [143, 150], optimized reaction protocols and detailed comparisons are lacking. Various reaction parameters are therefore examined in this work under identical reaction conditions using cyclooctene as benchmark substrate and trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP) as fluorinated standard solvents. Again, a set of the most common additives is used in this study (Figure 22)



100 **85** **86** **66**

Figure 22. Used additives in the oxidation of cyclooctene in fluorinated solvents.

NMR-Spectroscopy

The ^{1}H-, ^{13}C- and ^{17}O-NMR shifts of MTO are summarized in Table 16. Comparison between fluorinated and non-fluorinated solvents shows the pronounced influence of TFE and HFIP on the electronic characteristics of MTO. The ^{1}H-NMR values are shifted 0.2 – 0.5 ppm to low field compared to $CDCl_3$, indicating a more pronounced electron deficiency at the methyl protons. It is noteworthy that the ^{1}H-NMR-shift of the H_3C-Re moiety in the pyrazole adduct is comparable to the shift of the H_3C-Re moiety in free MTO in $CDCl_3$. The ^{17}O-NMR data for TFE and HFIP are 824 ppm

and 813 ppm respectively for the oxygen atoms of free MTO. While the shift in TFE is in the range of that observed in toluene and benzene (823 ppm) [118], the shift of 813 ppm in HFIP is the most high field shifted MTO signal observed so far in any solvent. Additionally, the ^{17}O-NMR signal of the MTO base adducts in fluorinated solvents is more high field shifted than that of free MTO itself, opposite to the effect observed in conventional solvents. Additionally, the ^{17}O-NMR shift difference between free and coordinated MTO is somewhat more pronounced in fluorinated solvents than in $CDCl_3$, indicating that the ligand effect of pyrazole on the oxygen atoms is more pronounced in fluorinated solvents than in $CDCl_3$. The opposite is the case for the carbons and hydrogen atoms. In this case, the shift difference between free and coordinated MTO in $CDCl_3$ is more pronounced than in fluorinated solvents. Additionally, both in ^{13}C- and ^{1}H-NMR the chemical shifts of MTO and its pyrazole adduct are not reversed in fluorinated solvents with respect to field strength. Nevertheless, the shift values of the pyrazole adduct in fluorinated solvents are almost identical to that of free MTO in $CDCl_3$.

Table 16. NMR data of MTO with and without pyrazole in different solvents.

	$CDCl_3$ (ref. [122])			TFE			HFIP		
	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^{17}O)$	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^{17}O)$	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^{17}O)$
MTO	2.67	19.03	829	2.88	17.87	824	2.84	18.49	813
MTO + pyrazole	2.18	24.62	832	2.70	19.63	817	2.64	19.18	807

Effect of Additives

The Lewis bases shown in Figure 22 have proven to be very efficient as additives in olefin epoxidation with MTO [76, 79, 80, 83, 84, 86, 141, 143, 144, 150]. Blank experiments without MTO lead only to yields of 3 % in TFE and 7 % yield in HFIP at room temperature (r.t.). At 0 °C no yield is detectable in both solvents. Without any additive to MTO in the catalytic system the reaction starts in HFIP with a TOF of 1640 h^{-1} and a yield of 48 % after 3 h. The reaction is slower in TFE without additive (TOF: 660 h^{-1}) than in HFIP but the system is active over a longer period of time with a 3 h-yield of 67 %. This is even superior to 4-*tert*-butylpyridine or Schiff base **66** as additives in HFIP (Figure 23). Comparing MTO (0.1 mol%) together with different additives (100-fold excess with respect to MTO), pyrazole and 4-*tert*-butylpyridine

show the best activities with quantitative yields after 1 h. Pyrazole leads to a slightly higher activity just after starting the reaction resulting in a higher TOF of 7800 h^{-1} compared with 7000 h^{-1} for **85**. Appling the Schiff base **66** and 4,4´-dimethyl-2,2´-bipyridine resulted in more or less equal yields of ca. 50 % (Figure 23). Interestingly, Schiff base **66** shows a much better performance than deduced from previously published results [144].

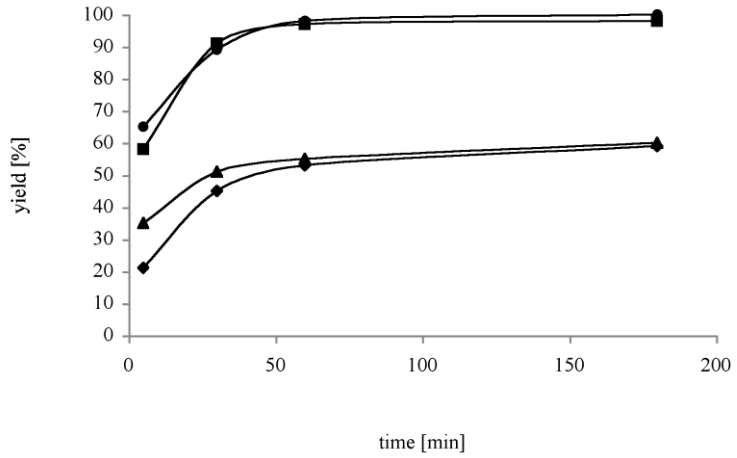


Figure 23. Oxidation of cyclooctene with different additives. Cyclooctene (12 mmol), MTO (0.1 mol%), H_2O_2 (27 %, 24 mmol), HFIP, 0 °C, Additive (10 mol%) (◆ = **86**, ■ = **85**, ● = **100**, ▲ = **66**).

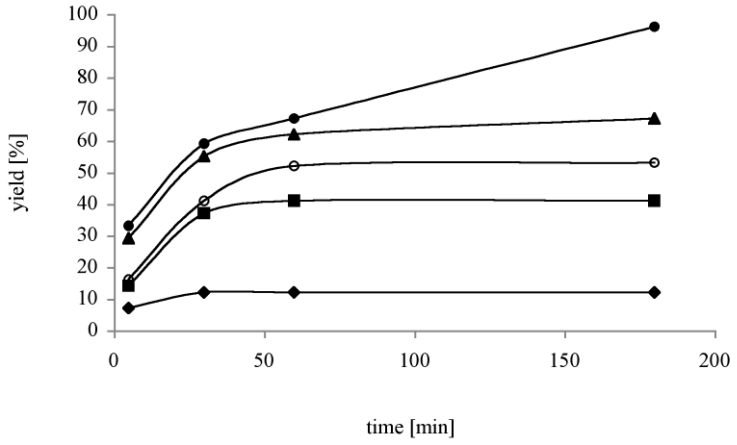


Figure 24. Effect of concentration of pyrazole on the oxidation of cyclooctene with MTO. Cyclooctene (12 mmol), MTO (0.01 mol%), H_2O_2 (27 %, 24 mmol), HFIP, 0°C, **100** (● = 50 mol%.,○ = 25 mol%/0.005 mol% MTO ▲ = 30 mol%, ■ = 10 mol%, ◆ = 1 mol%).

For all following experiments pyrazole was the additive of choice, since it performs as good as 4-*tert*-butylpyridine and the results obtained here are more convenient to compare to published work [143, 150].

The concentration of the additive plays an important role in the MTO-catalyzed epoxidation of olefins. Figure 24 clearly shows the correlation between pyrazole concentration and yield. Pyrazole stabilizes the catalytically active species of MTO better when more pyrazole is present (equation 2 in Scheme 1). The low catalyst concentration of 0.01 mol% reveals the beneficial effect of the additive even more than the normally used concentrations between 1 mol% and 0.1 mol% [80, 83, 89, 90, 121, 122, 126, 142, 143, 150, 163]. With 100 equiv. (1 mol%) pyrazole per molecule MTO the reaction stops after 30 min due to catalyst decomposition. The TOF is also the lowest, 8200 h^{-1}. Employing 1000 equiv. (10 mol%), 3000 equiv. (30 mol%), and 5000 equiv. (50 mol%) lead to a constant increase of yield and TOF peaking in quantitative conversion of cyclooctene after 3 h and a TOF of 39000 h^{-1} for 5000 equiv. of pyrazole. This is to the best of our knowledge the first quantitative conversion of cyclooctene to cyclooctene oxide with such a small concentration of MTO and it is also the highest TOF ever reported for a MTO-catalyzed epoxidation of an olefin. So far, the best conversion with 0.01 mol% MTO was 72 %, achieved by Yamazaki in a 35 %-H_2O_2/3-methylpyrazole/CH_2Cl_2-system [128]. Blank experiments with 50 mol% pyrazole and without MTO show no activity in both solvents. Reducing the catalyst concentration to 0.005 mol% with 5000 equiv. of pyrazole leads to a yield of about 50 %. It remains constant after 1 h. Most likely, MTO and pyrazole are too diluted in this solution to maintain a highly stabilized catalytic system.

When TFE is used as solvent instead of HFIP the effect of the pyrazole concentration is similar but the overall results (with respect to yield and TOF) are lower (see Table 17).

Table 17. Oxidation of cyclooctene in TFE.[a]

Entry	equiv. Pyrazole	Yield 1 h [%]	TOF [h^{-1}]
1	10	26	5500
2	100	25	7000
3	1000	46	16600

[a]Cyclooctene (12 mmol), MTO (0.01 mol%), TFE, 0 °C, H_2O_2 (27 %, 24 mmol).

Solvent

The experimental results match those of Iskra et al. for TFE, HFIP, and CH_2Cl_2 (Table 18) [150]. It is very interesting that nitromethane (CH_3NO_2) is as good as TFE after 3 h. In contrast to TFE as solvent the reaction in nitromethane is slower in the beginning of the reaction. However, in nitromethane the catalysis proceeds over a longer period of time with good activity in contrast to TFE so that the yields after 3 h are nearly identical, namely 90 - 93 %. Reasons for this behavior are most likely the reduced stability of the catalytically active species in TFE [150], and the positive effect nitromethane has on the oxidation of olefins with MTO as catalyst [141].

Table 18. Oxidation of cyclooctene in various solvents.[a]

Entry	Solvent	Yield 30 min [%]	Yield 3 h [%]	TOF [h^{-1}]
1	CH_2Cl_2	28	71	1100
2	CH_3NO_2	48	93	2300
3	TFE	66	90	5600
4	HFIP	89	100	7800

[a]Cyclooctene (12 mmol), MTO (0.1 mol%), H_2O_2 (27 %, 24 mmol), 0 °C, pyrazole (10 mol%).

H_2O_2-Concentration and Temperature Effects

The catalytic reactions carried out at various temperatures are depicted in Table 19. It is obvious that the catalysis is either quantitative (Table 19, Entry 1), almost inactive (Entry 2) or completely inactive (Entry 3) after 30 min at the selected temperatures. As mentioned before, the reason is the decomposition of the catalyst at elevated temperature. In fluorinated solvents this temperature induced decomposition seems to be significantly faster than in other solvents [144]. The difference in yield between -10 °C and 0 °C is much smaller compared to the gap from 0 °C to r.t. The TOF at -10 °C is the highest and stands for the most active system. Nevertheless, after 1 h the yields at both -10 °C and 0 °C are identical and quantitative. It has to be considered if

the additional effort to cool the system to -10 °C is worth the benefit of the faster starting period.

Table 19. Oxidation of cyclooctene at different temperatures.[a]

Entry	Temp. [°C]	Yield 30 min [%]	Yield 1 h [%]	TOF [h^{-1}]
1	-10	99	99	9000
2	0	89	98	7800
3	r.t.	56	57	6600

[a]Cyclooctene (12 mmol), MTO (0.1 mol%), HFIP, H_2O_2 (27 %, 24 mmol), pyrazole (10 mol%).

The concentration of the aqueous hydrogen peroxide solution i.e. the water concentration also has an influence on the catalytic reaction in fluorinated solvents. Carried out in TFE, the yield with 27 % H_2O_2-solution is 57 %, with 50 % H_2O_2-solution it is 64 % at r.t. after 3 h. The TOFs also show this effect with 6100 h^{-1} and 4700 h^{-1}, respectively. Generally, the lower the water concentration, the higher is the activity with only small differences after 3 h. At higher water concentrations, the equilibrium of the stabilized MTO-additive-complex is stronger shifted to an MTO-water-complex (Scheme 1). This MTO-water-complex can lead to direct decomposition of MTO [126].

Epoxidation of Other Olefins

Cyclooctene is easy to oxidize, forming a quite stable epoxide. It is, however, well known that open-chained, terminal olefins such as 1-octene are more difficult to epoxidize and they have a stronger tendency to form diols [76, 79, 80, 83, 84, 109, 161]. Therefore, we investigated the effect of fluorinated solvents on the MTO-catalyzed epoxidation of 1-octene in TFE and HFIP at different temperatures and different H_2O_2-concentrations (Table 20). Blank experiments without MTO lead to no detectable product yields. No significant diol formation was observed in any of the following experiments. Again, HFIP appeared to be the solvent of choice. Under identical conditions, the TOFs and yields derived in HFIP are superior to those from TFE. Application of higher concentrated hydrogen peroxide solution leads, similar to cyclooctene, to higher yields. This difference is more pronounced for 1-octene than for cyclooctene. Hence, the water concentration plays a more significant role in the

oxidation of 1-octene than in the oxidation of cyclooctene. The oxidation of 1-octene is much slower than the oxidation of cyclooctene (see TOFs in Table 20) and competing reactions including water have a greater impact. The most interesting point is the influence of the temperature. It has an opposite effect as in the epoxidation of cyclooctene. At r.t., the yields and TOFs are higher, especially in HFIP (Table 20, entries 3-6). A reason for this is most likely the lower reactivity of 1-octene. The faster decomposition of the catalyst at higher temperatures has a smaller effect than the increase of the general activity of 1-octene achieved by higher temperatures.

Table 20. Oxidation of 1-octene.[a]

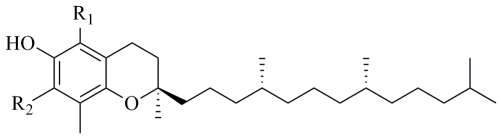
Entry	Solvent	Temp. [°C]	Conc. H_2O_2 [%]	Yield 30 min [%]	Yield 3 h [%]	TOF [h^{-1}]
1	TFE	0	27	4	26	200
2	HFIP	0	27	20	33	330
3	TFE	0	50	16	41	400
4	HFIP	0	50	40	52	1700
5	TFE	r.t.	50	27	65	400
6	HFIP	r.t.	50	71	89	4900

[a]1-octene (12 mmol), MTO (0.1 mol%), H_2O_2 (27 %, 24 mmol), pyrazole (10 mol%).

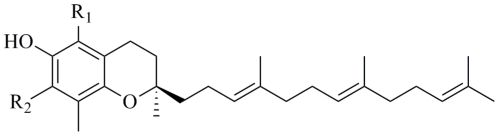
The use of limonene as substrate leads to 37 % yield in TFE and 46 % yield in HFIP. Both yields remain constant after 5 min. This indicates a very fast decomposition of the catalyst in the presence of this substrate. Only 8-10 % of α-pinene is oxidized with accompanying diol-formation. The fluorinated solvents used here seem to create a media too active for such labile epoxides.

2.5 Methyltrioxorhenium catalyzed oxidation of pseudocumene for vitamin E synthesis: A study of solvent and ligand effects

Vitamins are essential food components for both animals and humans, only produced in small amounts in the body. Among them, vitamin E is of particular economical relevance and industrial interest due to its anti-oxidizing properties and its biological activity. The term "vitamin E" comprises a group of four tocopherols and four tocotrienols with a characteristic chromene core (Figure 25). Tocopherols have received more attention than tocotrienols on account of their superior antioxidant activity [164-167].



tocopherol-	α	β	γ	δ
R_1	Me	Me	H	H
R_2	Me	H	Me	H



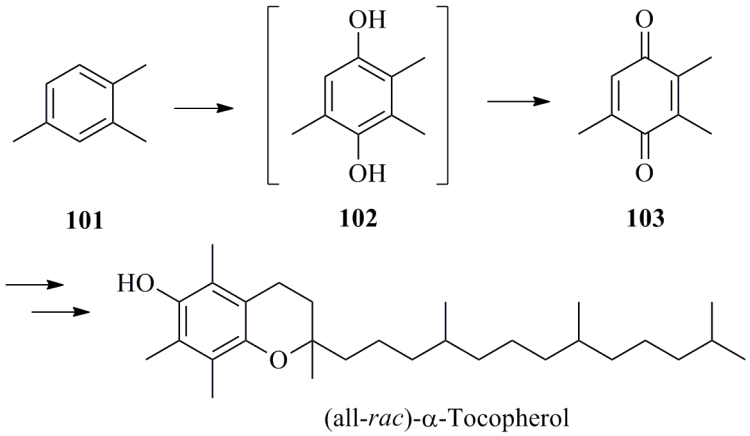
tocotrienol-	α	β	γ	δ
R_1	Me	Me	H	H
R_2	Me	H	Me	H

Figure 25. Compounds with vitamin E activity.

Adequately substituted hydroquinone or benzoquinone derivatives, in particular 2,3,5-trimethyl substituted ones, are important intermediates in the early stages of the industrial synthesis of α-tocopherol, which is the most active component of vitamin E. Therefore, the design of selective catalytic methods for α-tocopherol large scale production are particularly appealing from an industrial point of view [168-171].

A number of diverse methods for the synthesis of 2,3,5-trimethylhydroquinone (**102**) or its corresponding benzoquinone derivative **103** are documented in the literature (Scheme 5). Such methods usually start from a conveniently substituted phenol derivative and often involve costly transition metal catalysts (e.g. cobalt, titanium or vanadium) in high loadings or heteropolyacids. Despite the remarkable performance of some of them, the latter substances are still economically disadvantageous and yield substantial amounts of waste by-products [163, 172-201].

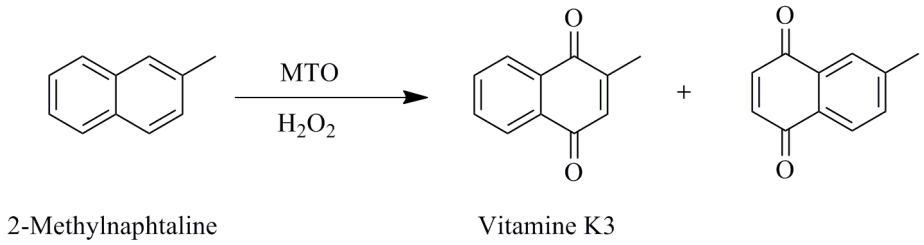
On an industrial scale the production of 2,3,5-trimethylquinone is performed under air or oxygen atmosphere, 332 K-380 K and copper chloride based catalysts. With optimized conditions the oxidation reaches yields between 86% and 95% [169].



Scheme 5. Synthesis of tocopherol from pseudocumene.

The most interesting but at the same time most challenging approaches are those starting from inexpensive pseudocumene (**101**), which is submitted to selective oxidation in the presence of a catalyst [202-206]. Although certainly appealing, the difficulty of selective arene oxidations when starting from non-hydroxylated substrates, such as pseudocumene, must be taken into account. Furthermore, the intrinsic reactivity of the so-obtained hydroquinone **102**, which is not isolated and usually easily further oxidized under the reaction conditions to the corresponding benzoquinone derivative **103** (Scheme 5), renders this process particularly challenging. Herrmann et al. were the first to report an efficient and novel pathway to synthesize vitamin K_3 based on the MTO-catalyzed selective oxidation of methyl-substituted naphthalene derivatives to deliver the corresponding quinones (Scheme 6) [157]. Further extensions of this methodology involved the MTO-catalyzed oxidation of phenol, anisol and phenyl derivatives, including pseudocumene and 2,3,5-trimethylphenol [172-174, 190, 203]. However, although promising, the so far reported MTO-based protocols require a large excess of often highly concentrated hydrogen peroxide, highly activated starting materials such as naphthalene or phenoxy derivatives for achieving good selectivities and they are frequently carried out in acetic acid and/or anhydride, with concomitant formation of potentially

hazardous peracetic acid. Accordingly, to date, none of the published routes meets industrial requirements.



2-Methylnaphtaline Vitamine K3

Scheme 6. Vitamin K synthesis by Herrmann et al.

Hence, the search for milder reaction conditions for the oxidation of pseudocumene (**101**) involving catalytic amounts of MTO in combination with inexpensive hydrogen peroxide remains a challenge of substantial interest. Due to its importance, we set out to revisit the MTO-catalyzed oxidation of arenes, especially pseudocumene, for the synthesis of **102**, which is one of the two major building blocks for the synthesis of α-tocopherol.

Solvent effects.

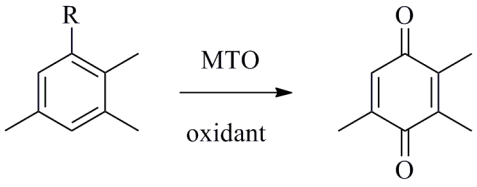
As mentioned above, MTO-catalyzed oxidations of arenes are often carried out in highly diluted solutions of acetic acid or in combination with acetic anhydride in the presence of usually high catalyst loadings (8 mol%) and large excesses of oxidant (up to 20 equiv.), especially when non-hydroxylated starting materials are utilized [203]. Though efficient and certainly of some academic interest, these reaction conditions are considered too harsh and economically disadvantageous for industrial applications. Accordingly, the main goal of the present research was to improve the conditions for the oxidation of pseudocumene (**101**) in the presence of MTO to pave the way for economically appealing applications. Firstly, the effect of solvents others than those already reported, as well as the use of lower amounts of inexpensive and commercially available hydrogen peroxide (30 % and 50 %) were studied for the target reaction. In all cases, formation of the corresponding benzoquinone **103** is observed due to the known over-oxidation of hydroquinone **102**, often accompanied by oxidation of the methyl groups, or partially oxidized forms (phenols) of **101**, which

act as intermediates towards the formation of benzoquinone **103**. When the target oxidation is carried out in different solvents but in the absence of MTO, no reaction takes place and the starting material is recovered unreacted. For the sake of comparison, several experiments using 2,3,5-trimethylphenol (**104**) as substrate were also performed (Table 21).

When the reaction is carried out in a diluted aqueous solution of hydrogen peroxide in the absence of organic solvent or in the presence of methanol, the highest selectivities for benzoquinone **103** are obtained, although the yields are low (Table 21, entries 1 and 7). Interestingly, when methanol is replaced by other alcohols, such as EtOH, ^{t}BuOH or ^{i}PrOH, the reaction barely takes place and nearly no conversion of **101** is observed. Likewise, the use of neither apolar hexane nor relatively polar CH_3CN or DMF affords the target compound **3** (Table 21, entries 15-17). However, in the presence of other types of solvents such as nitromethane and chloroform, yields are higher, and selectivities are relatively good (Table 21, entries 18-20). Taking the higher amount of catalyst into account, the catalytic performance with DMC or MeOH as solvents is nearly equal (Table 21, entries 7 and 9).

When the reported conditions for the oxidation of **104** in DMC [163] are applied to both pseudocumene (**101**) and 2,3,5-trimethylphenol (**104**), different results are obtained. The selectivity data obtained for the oxidation of **104** are excellent regardless of the concentration of hydrogen peroxide, although conversions are lower than those reported by Bernini et al. (Table 21, entries 12 and 13) [163]. However, when **101** is submitted to similar conditions, both selectivities and yields drop significantly relative to those observed for the oxidation of **104** (Table 21, entries 9 and 10). This result is in accordance with the oxidation of pseudocumene to intermediate hydroquinone **102** being a more challenging transformation than the benzoquinone formation from an already hydroxylated starting material, such as **104**.

Table 21. Solvent influences in the MTO-catalyzed oxidation of **101**.[a)]



101 R = H
104 R = OH

103

Entry	MTO (mol %)	Oxidant	Equiv. oxidant	Solvent	Temp. (°C)	Conv. (%)[b)]	Yield **103** (%)	Sel. **103** (%)
1	2	H_2O_2 (30 %)	4	-	50	13	13	100
2	2	H_2O_2 (30 %)	5	Ac_2O	60	63	37	59
3	2	SPC	4	CH_3COOH	r.t.	Tr.	Tr.	-
4	2	H_2O_2 (30 %)	4	CH_3COOH	r.t.	n.c.	36	-
5	2	H_2O_2 (27 %)	4	$MeSO_3H$/ CH_3COOH	0-r.t.	n.c.	26	-
6	2	H_2O_2 (27 %)	4	H_2SO_4/ CH_3COOH	r.t.	n.c.	13	-
7	2	H_2O_2 (30 %)	4	MeOH	50	10	9	90
8	2	UHP	4	MeOH	40	24	10	42
9	5	H_2O_2 (30 %)	10	DMC	60	35	15	43
10	5	H_2O_2 (50 %)	10	DMC	60	62	26	42
11	5	UHP	4	DMC	60	70	Tr.	-
12[b)]	2	H_2O_2 (30 %)	4	DMC	60	67	66	98.5
13[b)]	2	H_2O_2 (50 %)	4	DMC	60	73	69	94.5
14[b)]	2	UHP	4	DMC	60	47	24	51
15	2	H_2O_2 (50 %)	4	DMF	60	5	Tr.	-
16	2	H_2O_2 (50 %)	4	CH_3CN	60	13	Tr.	-
17	2	H_2O_2 (30 %)	4	Hexane	60	0	0	0
18	2	H_2O_2 (50 %)	4	$CHCl_3$	55	38	23	60.5
19	2	H_2O_2 (30 %)	4	CH_3NO_2	60	25	15	60
20	2	H_2O_2	4	CH_3NO_2	60	46	25	54

21[b)]	2	(50 %) H_2O_2 (50 %)	4	CH_3NO_2	60	92	61	66

[a)] Reaction conditions: **101** (1 equiv), solvent (1 mL $mmol^{-1}$), 6-24 h. [b)] **104** was used as starting material instead of **101**. Tr. = trace amount. n.c. = not calculated. UHP = urea hydrogen peroxide, DMC = dimethyl carbonate, DMF = dimethylformamide, SPC = sodium percarbonate.

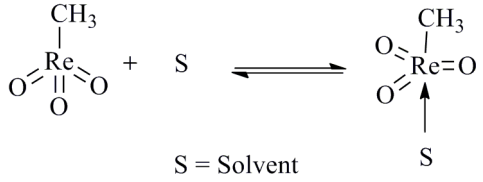
Additionally, when more diluted hydrogen peroxide (30 % vs. 50 %) is employed in the oxidation of **101**, the yield decreases (Table 21, entry 9 vs. 10). This is certainly the main reason why literature procedures usually use over 80 % hydrogen peroxide [157, 172, 207]. Furthermore, several decomposition pathways for MTO in diluted aqueous solutions are known [8, 78, 85, 88-90, 116-120, 136, 144, 162]. Batchwise MTO-addition also leads only to low yields. Compared to nitromethane, DMC as solvent leads to lower activities. The yields and selectivities being almost equal, however, with the catalyst and oxidant equivalents are at least twice as high for the DMC system (Table 21, entry 10 vs. 20).

Nevertheless, the use of water-free hydrogen peroxide sources such as urea hydrogen peroxide (UHP) or sodium percarbonate (SPC) does not afford better results (Table 21, entries 3, 8, 11 and 14). However, the reactions starting from **104** do not seem to be affected by the amount of water present in the system in contrast to the oxidation of pseudocumene. The negative effect of water must therefore be limited to the first oxidation step to form a hydroxylated intermediate from pseudocumene (**101**).

As a benchmark, the reaction is carried out in acetic anhydride and acetic acid as solvent, as well as in acetic acid solutions containing H_2SO_4 and $MeSO_3H$ (Table 21, entries 2-6), to elucidate how high the yield under mild reaction conditions is in comparison to previously published procedures [172-174, 190, 203]. When the desired reaction is carried out in acetic anhydride without MTO, benzoquinone **103** is obtained in 31 % yield, being a very similar value to that obtained when the same reaction is carried out in the presence of MTO (Table 21, entry 2). This observation suggests that peracetic acid is the real oxidant under these conditions and MTO does not play a major role. When the reaction is performed in acetic acid, the oxidation takes place not only because of in situ formed peracid, but also due to a MTO contribution [172]. Indeed, when the reaction is performed in acetic acid but in the

absence of MTO, **103** only 15 % yield is obtained. However, attempts to improve the product yield by increasing the amount of peracid formed by addition of acid catalysts such as methanesulfonic [208] or sulphuric acid [209], only lead to very exothermic reactions and decomposition of both starting material and catalyst (Table 21, entries 5, 6).

In an attempt to rationalize the solvent effect with respect to the solvent coordinating properties to MTO forming MTO·S, ^{17}O-NMR investigations of ^{17}O-labelled MTO in different solvents were performed and compared to the catalytic performance of MTO in these solvents in the oxidation of pseudocumene (**101**) (Table 22). The coordination ability of the solvent to MTO can be evaluated by the chemical shift of the terminal oxygen atoms of MTO. According to the equilibrium shown in Scheme 7, the more the signals are shifted to low field, the higher is the degree of solvent coordination [118, 210-213].



Scheme 7. Adduct formation of MTO with solvent molecules.

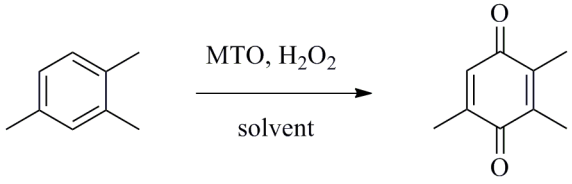
In the range of solvents analyzed, methanol would rank as the best coordinating solvent and acetonitrile would be that of lowest coordination ability [118, 210-213]. Based on the obtained results, MeOH coordination provides the best selectivity but very low conversion (Table 22, entry 1). Less coordinating solvents such as $CHCl_3$ and CH_3NO_2 afford improved conversions and still good selectivities for the benzoquinone formation (Table 22, entries 3-5). Interestingly, solvents such as CH_3CN and n-hexane, with similar coordinating ability towards MTO as chloroform and nitromethane, only furnish target benzoquinone **103** in traces and no significant yield (Table 22, entries 2 and 4).

When the coordination ability of the solvent is expressed in a more general way with donor numbers (DN) and not exclusively towards MTO they rank as followed: MeOH (DN = 30) > DMF (DN = 26.6) > DMC (DN = 17.2) > CH_3CN (DN = 14.1) > CH_3Cl

(DN = 4) > CH_3NO_2 (DN = 2.7) > *n*-hexane (DN = 0) [214]. But with this general approach no correlation with reaction performance is detectable.

The solvent effect was also examined in relation to the polarity of the media employed. According to their normalized empirical parameter of solvent polarity, the solvents examined for this reaction rank from more polar to less polar in the order: water > MeOH > EtOH > ^{i}PrOH > CH_3NO_2 > CH_3CN > ^{t}BuOH > DMF > $CHCl_3$ > *n*-hexane [215]. Acetic acid and acetic anhydride have not been taken into account for this comparison due to their particular role in this reaction through in situ formation of peracetic acid. Unfortunately, no trend is obvious and neither the coordination ability nor the polarity seems to account for the significantly different catalytic performance of MTO in different solvents. This might indicate that there are other influences, which are more difficult to evaluate, e.g. the solubility of intermediate species.

Table 22. Relationship between the coordinating ability of solvent and MTO catalytic performance in the oxidation of **101**.

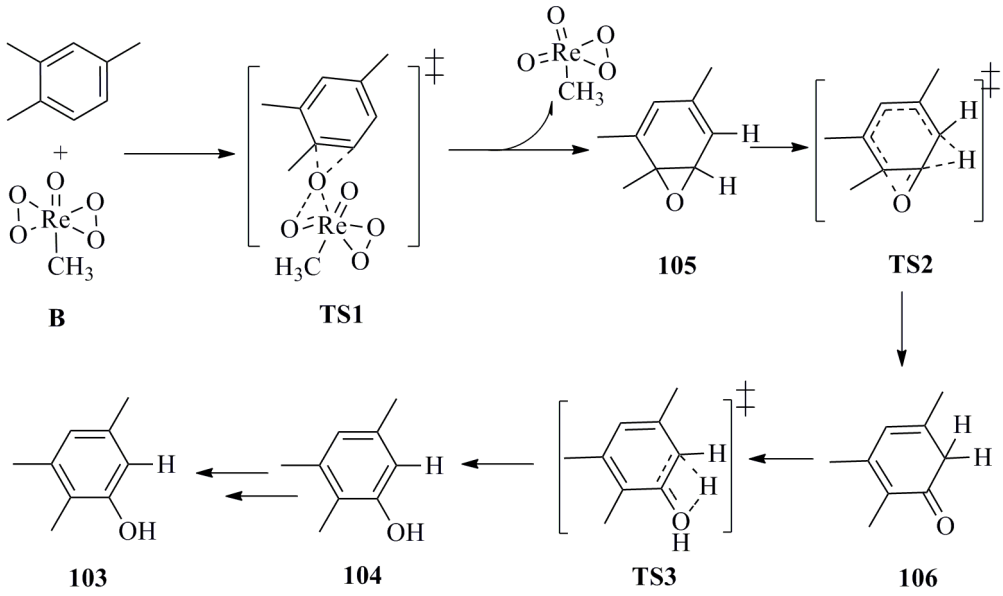


101 **103**

Entry	Solvent	δ (^{17}O) ppm	Oxidation conditions (from Table 1)	Conv. (%)	**103** (%)	Sel. **103** (%)
1	MeOH	861 [118]	**101** (1 equiv.), MTO (2 mol%), H_2O_2 (30 %, 4 equiv.), MeOH, 50 °C (Table 1, entry 7).	10	9	90
2	*n*-Hexane	835 [118]	**101** (1 equiv.), MTO (2 mol%), H_2O_2 (30 %, 4 equiv.), *n*-Hexane, 50 °C (Table 1, entry 17).	0	0	0
3	CH_3NO_2	833	**101** (1 equiv.), MTO (2 mol%), H_2O_2 (30 %, 4 equiv.), CH_3NO_2, 60 °C (Table 1, entry 19).	25	15	60
4	CH_3NO_2	833	**101** (1 equiv.), MTO (2 mol%), H_2O_2 (50 %, 4 equiv.), CH_3NO_2, 60 °C (Table 1, entry 20).	46	25	54
5	$CHCl_3$	829 [211, 212]	**101** (1 equiv.), MTO (2 mol%), H_2O_2 (50 %, 4 equiv.), $CHCl_3$, 60 °C (Table 1, entry 18).	38	23	60.5
6	CH_3CN	824 [118]	**101** (1 equiv.), MTO (2 mol%), H_2O_2 (50 %, 4 equiv.), CH_3CN, 60 °C (Table 1, entry 16).	13	Trace	-

The mechanism of the reaction is thought to proceed through the formation of an arene oxide **5** [172]. As previously stated, MTO forms the catalytically active species **B** upon addition of excess of hydrogen peroxide. Peroxorhenium(VII) **B** is electrophilic and would be attacked by electron rich nucleophilic arenes, to form an intermediate epoxide as shown in Scheme 6. Such an epoxide would open under the reaction conditions producing a very nucleophilic phenolic intermediate, which would further oxidize to the corresponding ketonic derivative, following the same reaction

pathway. As part of this study we look at the first half of the mechanism from the first epoxidation of the aromatic ring to the phenolic intermediate. There is no experimental observation of the formation of such an arene oxide thus far, but its presence is confirmed to some extent through the analysis of by-products (e.g. phenols) and DFT calculations on this mechanism (Scheme 8). The mechanism was adjusted from the benzene oxidation mechanism of Kudrik and Sorokin [216] and shows clearly that the arene oxide route is reasonable under certain conditions. The calculated Gibbs free energies obtained for gas-phase and different solvents are summarized in Table 23, especially the calculations for the solvents support the experimental results. Therein nitromethane is the only solvent able to lower ΔG of transition state **TS1** significantly in comparison to methanol, dichloromethane or dimethyl carbonate. This would be a reason why the catalytic reaction shows higher activities in nitromethane than in other solvents. Similar to the experimental data, the energies of **TS1** for the different solvents do not show a correlation with solvent parameters like coordination ability or polarity.



Scheme 8. Proposed mechanism of pseudocumene oxidation.

Table 23. Gibbs free energies of the calculated mechanism.

	Gas-phase	Nitromethane	Methanol	DCM	DMC
Pseudocumene					
+ **B**	0.0	0.0	0.0	0.0	0.0
TS1	35.3	14.8	32.7	32.7	33.4
105	-21.6	-24.9	-30.3	-24.5	-26.0
TS2	14.5	2.4	-7.5	3.6	2.4
106	-53.0	-57.6	-61.6	-57.0	-58.0
TS3 (H_2O)	-26.1	-26.4	-27.1	-26.4	-26.3
104	-66.6	-66.5	-73.3	-69.1	-69.9

B3LYP/6-31+G**; Re-ECP (Hay-Wadt); PCM (UAKS radius); ΔG (Gibbs free energy, kcal/mol).

The mechanism starts with the attack of the bisperoxo MTO derivative. The oxidation might occur on different position of the pseudocumene. The barrier for **TS1** shown in Table 23 is corresponding to the epoxidation of the phenyl ring at the 1,6 position. We also calculated the barriers for the epoxidations on other positions at the pseudocumene, the free energies of these barriers for gas-phase and nitromethane can be found in Table 24.

Table 24. Comparison of the different epoxidation barriers.

Position	Gas-phase	Nitromethane
1,6 (TS1)	35.3	14.8
5,6	36.7	33.4
2,3	35.1	16.9
3,4	37.5	33.6

B3LYP/6-31+G**,Re-ECP; ΔG (Gibbs free energy, kcal/mol).

Based on these values we conclude that the mechanism in nitromethane yielding product **103** proceeds as shown in Scheme 8. It starts with **TS1** at position 1,6 leading us to the interim product **104** via **105**, **TS2**, **106** and **TS3**. **TS2** features the concerted formation of a carbonyl group and H transfer to a neighboring ring atom to form a sp^3 carbon in intermediate **106**. **TS3** is water assisted and restores the aromatic system, while transforming the ketone to a phenol through H transfer. Starting from intermediate **104**, another epoxidation is likely to occur at the 2,3 position according to Table 24. Via two similar H transfers, a hydroquinonic system is generated, being able to undergo a conversion to the desired quinone **103**.

However, it cannot be ruled out that the 2,3 position is also available also from the beginning of the reaction as the barrier in the gas-phase is equal, but for nitromethane it is 2 kcal/mol apart. Anyway this reaction cycle has to be repeated on the opposite

side of the aromatic ring in order to come from **104** (or the non-numbered corresponding alternative from the other side) to the desired quinone **103**. As the other two possibilities show higher epoxidation barriers, our conclusion is that both the 1,6 and 2,3 epoxidation occurs at the phenyl ring during the reaction and proceeds via a set of two H transfers on each attacked sides to product **103**.

Ligand influence.

In order to reach improved reaction conditions and selectivities for the MTO-catalyzed oxidation of pseudocumene (**101**) to its corresponding quinone derivative **103**, the next step was to explore the ligand influence on the catalytic performance [77, 78, 80-82, 84-90, 120]. Among the most easily accessible ligands, pyridine derivatives [80-82, 86, 87] and Schiff bases [78, 85, 88-90, 120] have afforded the most promising results by displaying increased selectivities and reaction rates. Several ligands have not been applied as additives for the MTO-catalyzed oxidation of **101** before (Table 25).

As shown above, when the oxidation is carried out in the presence of MTO, but without the addition of a ligand, the results are very dependent on the solvent. In order to obtain selectivities higher than 90 %, the reaction has to be run either without solvent or in methanol, although the yields obtained under those reaction conditions are low. By using other solvents such as nitromethane, however, yields increase but unfortunately, the selectivity values observed are often between only 50 % and 60 % (Table 21 and 22). Nevertheless, by addition of some ligands it has been possible to increase the yields to more than 20 % and to obtain selectivities of around 70 % (Table 25).

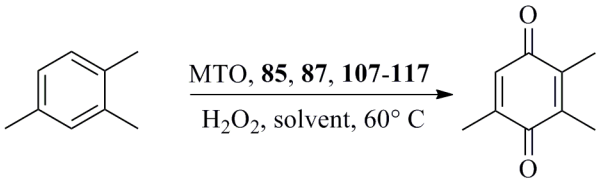
It is known that excess of aromatic Lewis bases such as pyridine lead to significantly higher activities and selectivities than MTO alone. While literature reports on the optimal pyridine excess differ from 5- to 24-fold [193], we found that a ligand:MTO ratio of 2:1 or 1:1 leads to the best results for the reaction under examination (Table 25, entries 1-4).

When the oxidation of **101** is carried out in the presence of oxime derivatives **109** and **110** and particularly in nitromethane, selectivity values ranging from 55 % to 71 % are obtained (Table 25, entries 5-10). When using **109** as ligand, the use of

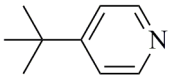
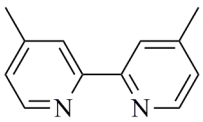
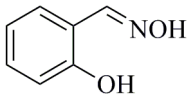
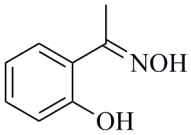
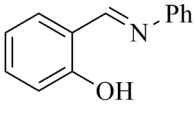
either H_2O_2 (30 % or 50 %) with a MTO:ligand ratio of 1:1 affords very similar results in terms of both yield and selectivity, (Table 25, entry 5 vs. 7). Interestingly, when the reaction is allowed to run for 72 h instead of 6 h, the conversion barely changes but the selectivity increases slightly from 66 % to 71 % (Table 25, entries 5 and 6). Additionally, when a 1:2 ratio of MTO:ligand is employed the yield improves without selectivity loss (Table 25, entry 9).

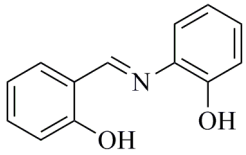
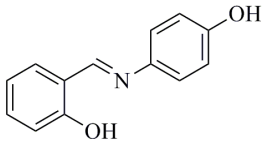
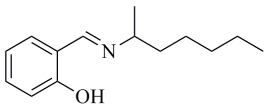
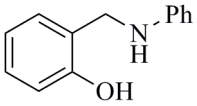
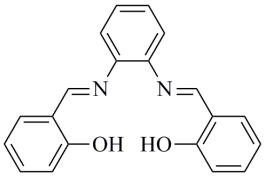
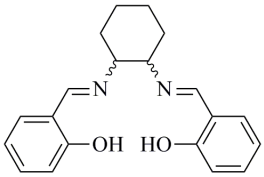
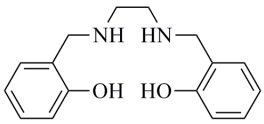
Furthermore, we examined the target oxidation with some (*N*-salicylidene)aniline derived Schiff bases such as **87**, **111**, **112** [78, 85, 89, 90].

Table 25. Ligand assisted MTO-catalyzed oxidation of **101**.[a)]



101 **103**

Entry	Ligand		Methanol Yield **103** (%)	Methanol Sel. **103** (%)	Nitromethane Yield **103** (%)	Nitromethane Sel. **103** (%)	Chloroform Yield **103** (%)	Chloroform Sel. **103** (%)
1[d)]		**107**	13	54	3	43	1.5	30
2[e)]		**107**	23	57.5	-	-	-	-
3[d)]		**85**	7	47	-	-	-	-
4		**108**	10	33	6	25	8	50
5		**109**	22	44	21	66	14	32
6[f)]		**109**	-	-	24	71	-	-
7[f),g)]		**109**	-	-	22	59.5	-	-
8[f),g),h)]		**109**	-	-	33	55	-	-
9[e),f)]		**109**	-	-	32	67	-	-
10		**110**	28	53	28	68	15.5	48
11		**87**	25	50	16	43	12	35

12[i)]		**87**	-	-	54	61	-	-
13		**111**	23.5	51	20	51	15	45.5
14		**112**	28	64	24	63	-	-
15		**113**	10	43.5	10	41	8	31
16		**114**	19	63	18	50	9	64
17		**115**	4	21	8	46	-	-
18[j)]		**115**	15	67	-	-	-	-
19		**116**	-	-	11	85	-	-
20		**117**	-	-	12	75	-	-

Reaction conditions: **101** (1 equiv.), MTO (2 mol %), **85**, **87**, **107**-**117** (2 mol %), H_2O_2 (50 %, 4 equiv.), solvent (methanol, nitromethane or chloroform) (1mL $mmol^{-1}$), 60 °C, 6-24 h. [d)] MTO:ligand = 1:24. [e)] MTO:ligand = 1:2. [f)] Reaction time 72 h. [g)] H_2O_2 (30%) was employed. [h)] MTO (10 mol %) was employed. [i)] 2,3,5-trimethylphenol (**104**) was used as starting material instead of pseudocumene (**101**). [j)] MTO:ligand = 2:1. Sel. = Selectivity.

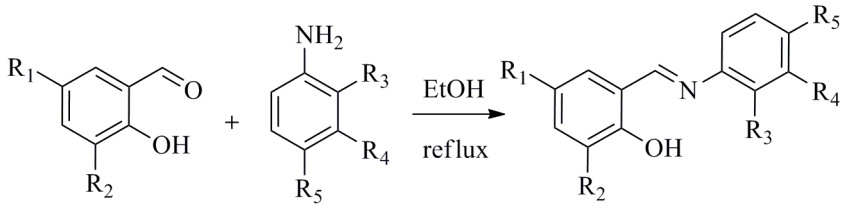
When the reaction is run in the presence of ligands **87** and **111**, the obtained selectivity values are moderate and very similar regardless of the solvent (Table 25, entries 11 and 13). However, the results obtained in the presence of ligand **112**, which is known to be very active in epoxidation reactions [90], are slightly better yielding selectivities over 60 % (Table 25, entry 14). While the oxidation of **101** is generally

improved by the addition of ligands, the oxidation starting from 2,3,5-trimethylphenol (**104**), delivers both lower yields and selectivities with a Lewis base present (Table 21, entry 21; Table 25, entry 12). In some cases the imine bond of the ligands hydrolyses during the course of the reaction. Despite the higher basicity of ligand **114**, which is known to be detrimental to MTO lifetime [8, 117, 118, 162], the results afforded with **114** are similar to those obtained by its oxidized analogue **87**. When performing the reaction in chloroform, **114** delivers much higher selectivity than **87**, 64 % *vs.* 35 % respectively (Table 25, entry 16 *vs*. 11).

Recently it was shown that MTO can coordinate to salen-type ligands [88]. Dependent on the ligand:MTO ratio salen compounds can ligate one or two MTO molecules, with both types of complexes active in epoxidation reactions. Hence, some related salen-type ligands were tested in the oxidation of pseudocumene (**101**) in both 1:1 and 1:2 ratios with respect to MTO (Table 25, entries 17-20). The selectivities obtained in the presence of **116** and **117** are 85 % and 75 % respectively, but the yields are just above 10 % (Table 25, entries 19-20). Additionally, a combination of MTO, imidazol as ligand, Oxone® as oxidant in ethylacetate as solvent at room temperature, based on similar conditions reported by Wei and Liu [217], was tested but starting material **101** was recovered unreacted.

Schiff base ligands.

Schiff bases bearing chlorine substituents in certain aromatic positions generally afford better results in the oxidation of pseudocumene (**101**) in comparison with those ligands bearing electron donating groups or hydrogen. Similar effects in the presence of electron withdrawing substituents have been observed previously, especially with Lewis bases [79, 84, 123, 218], but never studied in detail for Schiff bases [88, 90, 120]. A number of salicyladehyde and aniline derivatives, **118** and **119** respectively, bearing fluorine, chlorine, bromine, nitro and trifluoromethyl groups were selected and subsequently condensed in a solution of refluxing ethanol, to obtain the corresponding Schiff bases **66**, **88**, **90**-**98**, **120** in yields ranging from 40 % to 97 % (Scheme 9).

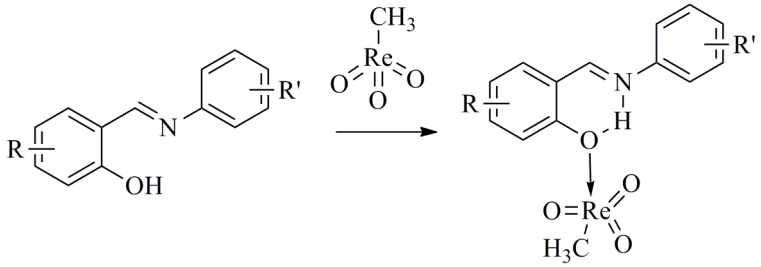


107 **108** **66**, **88**, **90-98**, **120**

66 R_1, R_2, R_3, R_4 = H; R_5 = Cl
88 R_1 = Br; R_2, R_3, R_4, R_5 = H
90 R_1,R_2 = Cl; R_3, R_4, R_5 = H
91 R_1, R_2, R_3, R_4 = H; R_5 = F
92 R_1, R_2, R_3, R_4 = H; R_5 = CF_3
93 R_1, R_2, R_3, R_4 = H; R_5 = NO_2
94 R_1, R_2, R_4, R_5 = H; R_3 = Cl
95 R_1, R_2, R_3, R_5 = H; R_4 = Cl
96 R_1, R_2, R_4 = H; R_3 = Cl; R_5 = F
97 R_1 = Br; R_2, R_4, R_5 = H; R_3 = Cl
98 R_1, R_2, R_3 = Cl; R_4, R_5 = H
120 R_1 = NO_2; R_2, R_3, R_4, R_5 = H

Scheme 9. Synthesized Schiff bases.

The ligands, **94** and **66** have already proven to be beneficial additives in MTO-catalyzed epoxidation reactions [90, 120]. As it has been shown, (*N*-salicylidene)aniline Schiff bases coordinate to MTO through the oxygen atom (Scheme 10) [78, 90, 120]. The interaction of MTO with such ligands results in a small shift of the methyl protons in MTO to higher field in the ^{1}H-NMR spectra in $CDCl_3$. Among other options, such a shift can be a simple and easy way to determine the degree of MTO ligand coordination. Donor ligands lead to greater high field shifts of around 0.15 ppm of the methyl protons. Weaker coordinating ligands cause smaller high field shifts of approximately 0.05 ppm and deliver more active catalysts. In the ^{17}O-NMR spectra of MTO with Schiff bases, a comparatively small shift change of 2-3 ppm can be observed for the MTO oxygen atoms compared to those of free MTO recorded in the same solvent [78, 90, 120]. For the oxidation of **101**, a weakly coordinating ligand being able to deliver a very active MTO derivative would be needed. Likewise, the chosen ligand should also be able to reduce the Lewis acidity of the metal center and enable increased chemoselectivity towards benzoquinone **103**. Hence, the employment of electron withdrawing ligands **66**, **88**, **90-98**, **120** should decrease the donating ability of the Schiff bases creating optimized ligands.



Scheme 10. MTO-Schiff base complex.

In order to check whether such weakly coordinating ligands **66**, **88**, **90**-**98**, **120** could actually link to MTO some NMR experiments were performed. Spectroscopic data obtained from ^{1}H-NMR spectra of equimolecular mixtures of MTO and **66**, **88**, **90**-**98**, **120** confirm the existence of coordination between MTO and the ligands. For the methyl protons of MTO in its adducts with ligands **66**, **88**, **90**-**98**, **120** a chemical shift of 2.61 or 2.62 ppm has been observed in $CDCl_3$, which is within the expected range for relatively weakly coordinating ligands (see Experimental Section). Likewise, the ^{17}O-NMR of MTO and **98** in nitromethane was recorded affording a 2.5 ppm shift change in comparison to free MTO ($\delta(^{17}O)$ = 833 ppm), which is also consistent with reported data for similar compounds (see Experimental Section) [78, 88, 120].

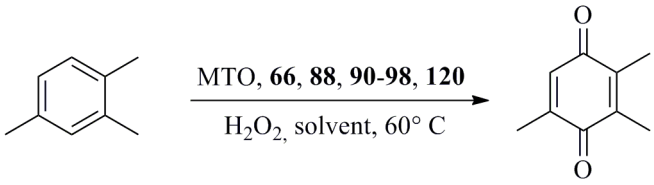
According to previous results from solvent studies on the oxidation of pseudocumene, the best results are obtained when using 2 mol % of MTO and 4 equiv. H_2O_2 (50 %) in the presence of methanol, nitromethane or chloroform as solvents at 60 °C. The newly prepared ligands **66**, **88**, **90**-**98**, **120** were applied in the oxidation of pseudocumene (**101**) under those reaction conditions and compared to previous results with non-substituted Schiff base **87**. The most relevant results are included in Table 26. Oxidation attempts starting from 2,3,5-trimethylphenol (**104**) have also been performed.

As it can be seen from Table 26, ligands **66**, **88**, **90**-**98**, **120** in combination with MTO afford the best selectivity values (compared to results depicted in Tables 24). The selectivities obtained by using such ligands are higher than 60 %, in some cases >80 %, with yields of around 30 %. When comparing with non-substituted Schiff base **87**, the most pronounced differences in selectivity values are observed when the reaction takes places in non-coordinating nitromethane and chloroform, although in general the best results in terms of both yield and selectivity are obtained in

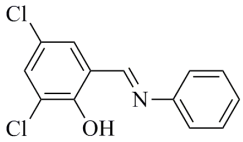
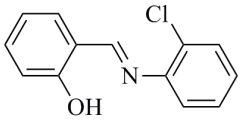
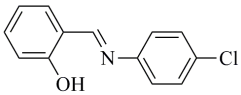
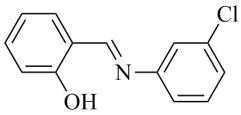
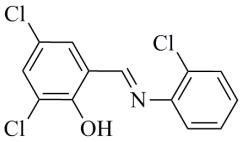
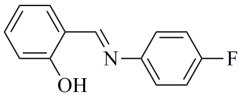
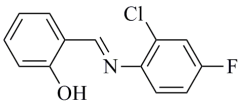
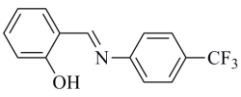
nitromethane as solvent. Nevertheless, the use of ligands in the oxidation of **104** does only have a small benefical effect and the reaction proceeds almost as in the absence of ligand (Table 25, entry 12; Table 26, entries 2 and 3). In the case of the ligands bearing exclusively chlorine atoms as substituents (Table 26, entries 1-7), the best selectivities are observed when the chlorine atom is in the aromatic ring derived from the aniline counterpart, particularly in the *ortho*- or *meta*-position (Table 26, entry 4). According to the coordination mode of these types of ligands (shown in Scheme 7), the substituents present on that part of the molecule should not directly affect the coordination ability of the salicylic oxygen. However, they can also have an electronic effect on the iminic nitrogen and therefore on the strength of the intramolecular hydrogen bond. Indeed, previous research on the MTO-Schiff base complexes shows very different values for the N-H bond lengths for two MTO adducts, one with a chlorine atom (**66**) and another with a donating methoxy substituent, both in the *para*-position to the iminic nitrogen. The chlorine substituted adduct displays a shorter N-H bond than the methoxy one [120]. How such an intramolecular hydrogen bond affects the adduct formation or the resulting catalyst performance is not clear yet.

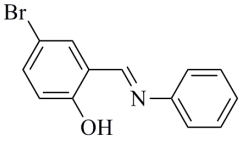
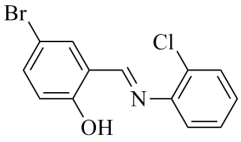
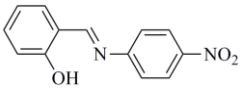
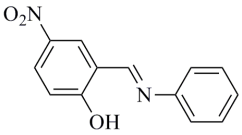
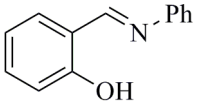
Additionally, the presence of a fluorine atom *para* to the iminic nitrogen (**91**) results in improved selectivity and yield with respect to **87** in non-coordinating nitromethane or chloroform as solvents. However, it makes virtually no difference when using the coordinating solvent methanol (Table 26, entry 8 *vs*. 15). Interestingly, the presence of an *ortho*-chlorine in addition to a *para*-fluorine (**96**) does affect the selectivity to a significant extent for MeOH and it increases the yield to 35 % (Table 26, entries 8 *vs*. 9). Likewise, bromine atoms *para* to the hydroxyl moiety (**88**) have a moderate effect on the yield, but deliver selectivities of ca. 60 % (Table 26, entry 11 *vs*. 15). Once again, when there is an additional *ortho*-chlorine, a selectivity of 70 % is obtained (Table 26, entry 12).

Table 26. Ligand assisted MTO-catalyzed oxidation of **101**.[a)]



101 **103**

Entry	Ligand		Methanol Yield **103** (%)	Methanol Sel. **103** (%)	Nitromethane Yield **103** (%)	Nitromethane Sel. **103** (%)	Chloroform Yield **103** (%)	Chloroform Sel. **103** (%)
1		**90**	32.5	53	35	56.5	28	60
2[d)]		**90**	-	-	66.5	87.5	-	-
3[d),e)]		**90**	-	-	57	95	-	-
4		**94**	30	79	28	68	20	56
5		**66**	32	65	30	59	22.5	59
6		**95**	24	61.5	30	73	16	70
7		**98**	33	63	32	62	25	66
8		**91**	27	48	20	67	21	67
9		**96**	35	64	29	62	22	58
10		**92**	31	69	29	66	23	64

11		**88**	20	57	21	64	18	64
12		**97**	32	62	28	70	17	59
13		**93**	27	69	20	67	17	59
14		**120**	31	60	27	84	24	80
15		**87**	25	50	16	43	12	35

Reaction conditions: **101** (1 equiv.), MTO (2 mol %), **66**, **88**, **87**, **90**-**98**, **120** (2 mol %), H_2O_2 (50 %, 4 equiv.), solvent (methanol, nitromethane or chloroform) (1mL $mmol^{-1}$), 60 °C, 6-22 h. [d] 2,3,5-trimethylphenol (**104**) was used as starting material instead of pseudocumene (**101**) and 3 equiv. of oxidant were employed. [e] H_2O_2 (27 %) was employed as oxidant.

Very strongly electron withdrawing groups in *para*-position to the iminic nitrogen, such as trifluoromethyl (**92**) or nitro substituents (**93**) have both a similar effect, affording high selectivities of nearly 70 % depending on the solvent and yields close to 30 % (Table 26, entries 10 and 13). Nonetheless, the best results are obtained when using **120** bearing a nitro group in the *para*-position to the hydroxyl group on the salicylic counterpart. Yields of around 30 % and selectivity values of 80 % and 84 % are obtained in the presence of **120** when using chloroform and nitromethane as solvents, respectively (Table 26, entry 14). It must be emphasized that given the great economical and industrial relevance of the target oxidation, these results can indeed be considered as an important step forward, despite the seemingly moderate yields (Table 26, entry 14). The high selectivity values would allow an easier purification of the product during large-scale production, as well as recovery of the unreacted starting material, if desired. Compared to other catalytic systems (Table 27) using pseudocumene as starting material, the selectivity is again the most striking point.

Although the catalyst loading is the smallest the highest selectivity values are reached. It is also obvious that no harsh conditions like acetic acid as solvent or *m*-chloroperbenzoic acid as oxidant are used in our experiments. Nevertheless, the presented data in Table 27 is only a qualitative comparison as the experimental setup is not identical.

Table 27. Comparison of different pseudocumene oxidations.

Entry	Reaction conditions	Time [h]	Temp. [°C]	Conv. [%]	Yield [%]
1 [206]	Catalyst: Pd(II)–SP resin (0.24 wt %); solvent: AcOH; H_2O_2 (60 %) 3 equiv.	10	70	77.6	3.3
2 [202]	Catalyst: -; solvent: $CHCl_3$; *m*CPBA 2.2 equiv.	0.5	60-70	-	16.5
3 [203]	Catalyst: MTO (8 mol %); solvent: AcOH; H_2O_2 (30 %) 20 equiv.	4	57	75	67
4 [185]	Catalyst: $FeCl_3$ + additives (7.5 mol %); solvent: *t*-amyl alcohol; H_2O_2 (30 %) 4 equiv.	1.5	0	69	Sel.: 38
5	Catalyst: MTO + **95** (2 mol %); solvent: nitromethane; H_2O_2 (50 %) 4 equiv.	20	60	41	30

2.6 Methyltrioxorhenium catalyzed oxidation of pseudocumene in the presence of amphiphiles for the synthesis of vitamin E

A possible approach to improve the activity of the catalytic system - likely hampered by the presence of two liquid phases - could be the use of amphiphiles with their known beneficial effects in catalysis [219-222]. Furthermore, the use of an imidazole-functionalised amphiphilic copolymer linked to MTO has been recently reported as a recyclable catalyst for epoxidation, setting a precedent in its field [217].

Hence, given the high importance of benzoquinone **103** as intermediate in the synthesis of vitamin E, we report herein the MTO-catalyzed selective oxidation of pseudocumene in the presence of different amphiphiles as an appealing alternative to the existing methods and to improve product selectivity of **103**.

First, a number of commercially available neutral, anionic and cationic amphiphiles, shown in Figure 26, were probed in the target oxidation of pseudocumene, at 50 °C, using MTO as catalyst and hydrogen peroxide (30 % aqueous solution) as oxidant. The results are summarized in Table 28. Side-products of the reaction are generally trimethylphenol, which acts as intermediate towards **103** [141], or forms of **101** with oxidized methyl groups. These by-products were observed qualitatively by GC/MS. As it can be seen from Table 1, the use of certain amphiphiles can have a positive effect on the conversion of the reaction while maintaining a high selectivity. Indeed, the best results are obtained when using the inexpensive, neutral amphiphile Brij 30. When this additive is used in the presence of aqueous H_2O_2 solution as only solvent, the product selectivity is 67 % (Table 28, entry 3). A reduction of the amount of amphiphile leads to a slightly increased conversion, but is accompanied by a significantly lower selectivity (Table 28, entry 3 vs. 4). Interestingly, the use of an additional solvent, such as nitromethane, affords a selectivity of 80 %, which is the highest from all experiments with amphiphiles shown in this work (Table 28, entry 5). A water-miscible solvent such as methanol has no particular effect (Table 28, entry 3 vs. 6).

We have shown that the use of salicylaldoxime as ligand in combination with MTO

improved the yield and selectivity of the oxidation of pseudocumene in comparison with the ligand-free analogue oxidation [141]. Hence, salicylaldoxime was tested as a ligand for the target oxidation in the presence of Brij 30, yielding benzoquinone **103** with a selectivity of 72 % (Table 28, entry 7). Interestingly, the amount of nitromethane added to the system seems to have two contrary effects reflected by different selectivities (Table 28, entries 7, 10, 11).

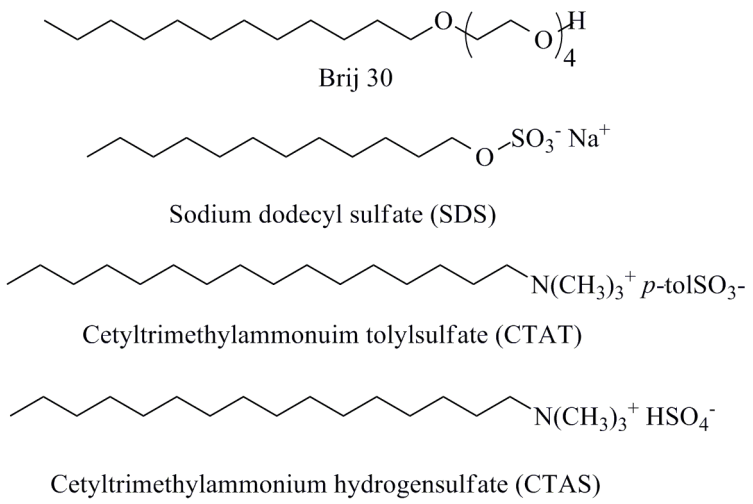
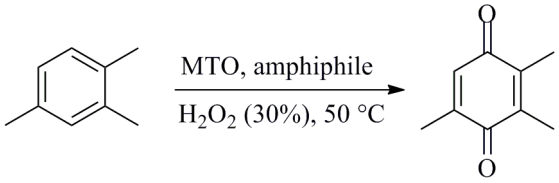


Figure 26. Amphiphilic additives used in this work.

Higher diluted systems (Table 28, entry 11) probably lack amphiphile/salox coordination to MTO, while too concentrated systems (Table 28, entry 10) lose the beneficial effect nitromethane seems to induce during the first oxidation step [141]. In both cases, the selectivity is lower than in the medium diluted case (Table 28, entry 7). The addition of ammonium salts as phase transfer catalysts (PTC) to the Brij 30-containing reaction mixture does not improve the conversion or product yield. Nevertheless, the anion of a PTC seems to have an effect on the reaction. For instance, $(Bu_4N)Br$ inhibits the reaction, whereas $(Bu_4N)PF_6$, and $(Bu_4N)HSO_4$ afford selectivities of around 50 % (Table 28, entries 12-14). Common cetyltrimethyl derived cationic amphiphiles lead to low selectivities (Table 28, entry 16-18), while anionic sodium dodecyl sulfate (SDS) affords moderate selectivity values (Table 28, entry 19). Generally, the use of ionic additives to the reaction lowers the selectivity significantly. Non-ionic amphiphile Brij 30 alone provides much better selectivities and the probing of similar amphiphiles appears reasonable.

Table 28. MTO-catalyzed oxidations of **101** in the presence of various amphiphiles.



101 **103**

Entry	Reaction conditions[a]	Time [h]	Temp. [°C]	Conv. **101** [%]	Sel. **103** [%]
1		20	50	13	100
2	Brij 30/ without MTO	20	50	0	0
3	Brij 30	20	50	27	67
4[b]	Brij 30	20	50	38	47
5[c]	Brij 30, CH_3NO_2	20	50	28	80
6[c]	Brij 30, MeOH	20	50	31	52
7[c]	4 mol% salox, Brij 30, CH_3NO_2	22	50	29	72
8[c]	2 mol% salox, Brij 30, CH_3NO_2	72	50	39	62
9[c]	2 mol% salox, Brij 30, H_2O_2 (50 %), CH_3NO_2	72	50	50	60
10[d]	4 mol% salox, Brij 30, CH_3NO_2	72	50	37	57
11[e]	4 mol% salox, Brij 30, CH_3NO_2	72	50	35	63
12	4 mol% $(Bu_4N)Br$, Brij 30	22	50	21	0
13	4 mol% $(Bu_4N)PF_6$, Brij 30	19	50	28	46
14	4 mol% $(Bu_4N)HSO_4$, Brij 30	22	50	24	54
15[e]	4 mol% salox, 10 mol% $(Bu_4N)HSO_4$, Brij 30, CH_3NO_2	72	50	21	24
16	1 mol% CTAS	72	50	36	44
17	50 mol% CTAT	72	50	55	11
18[c]	4 mol% $N(Dodec)_3$, 2 mol% CTAT, $CHCl_3$	72	40	30	27
19	2 mol% SDS	72	40	31	55

[a] Reaction conditions: **101** (1.44 mmol; 1 equiv.), MTO (2 mol%), H_2O_2 (30 % 4 equiv.), H_2O_2 (aq. solution):Brij 30 = 12 (v/v, when indicated in the Table), conversion of starting material and formation of **103** were quantified by GC-MS using an internal standard, selectivity of **103** refers to the amount of converted starting material that turned into target product **103**, salox = salicylaldoxime. [b] H_2O_2 (30 %):Brij 30 = 30 (v/v). [c] 0.35 mL of solvent per mmol of **101**. [d] 0.14 mL of solvent per mmol of **101**. [e] 0.7 mL of solvent per mmol of **101**.

Such amphiphiles could be improved by additional functionalities like Lewis basic moieties. Such a combination of the positive effects of Lewis bases in MTO catalyzed oxidation (higher catalyst stability and improved selectivity) and the positive effect of amphiphiles shown in this work. Amphiphile and Lewis base combined to one molecule could lead to a superior behavior compared to adding the two separate substances to the reaction mixture (Table 28, entries 7-11, 15).

3. Conclusion

In a comparative study, the differences between three different types of donor ligands in the MTO catalyzed olefin epoxidation were examined. 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 11). Using *trans*-β-methylstyrene leads to poor results in all examined cases (Table 10). This indicates the low ability of the Schiff base to decrease the Lewis-acidity at the rhenium center. In one-phase reactions in *tert*-butanol, 4-*tert*-butylpyridine as additive is superior to 4,4'-dimethyl-2,2'-bipyridine (Figure 19-21). 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^{-1} for MTO/**85** and 2500 h^{-1} for MTO/**86** are achieved (Table 10). 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 CH_2Cl_2, the bipyridine system shows the best performance. However, particularly two-phase experiments highlight the difficulties in comparing systems with different rotational speeds of the stirrer (Table 11).

Several halide substituted Schiff bases have been examined in epoxidation for cyclooctene- and 1-octene-epoxidation in the presence of MTO and with H_2O_2 as oxidizing agent. The addition of Schiff bases does not have a pronounced influence on the catalytic activity and selectivity. In some cases a small increase of yield and TOF is observed if Schiff bases are added to the reaction solution (Tables 12, 14). Fluorine substitution (**91**, **96**) leads to slightly lower yields than substitution with other halides. No significant differences occur when chlorine and bromine moieties are applied. The yields of such systems range between 67 % and 74 % after 5 minutes reaction time. It also has no significant influence whether the hydroxy-benzaldehyde or the aniline moiety or both of them are substituted. The *ortho*-, *meta*-, *para*-substitution at the aniline moiety shows a reaction order of $o > p > m$. The exchange of Schiff bases as

ligands by 4-*tert*-butylpyridine leads to a higher conversion and turn-over frequency if cyclooctene is used as substrate. The epoxidation of 1-octene displays a higher activity only in the initial phase of the reaction. The overall yield after 3 h is lower than that of MTO plus Schiff bases. The catalytic optimum of MTO-Schiff base systems is based on fine-tuning the electron donating and the electron accepting character of the Schiff base. The utilization of nitromethane as solvent for the catalysis turned out to be much more rewarding than catalysis with other or without solvents.

A comprehensive comparison between the two most widely applied fluorinated solvents trifluoroethanol and hexafluoroisopropanol has also been made. The main substrate was cyclooctene, acting as a benchmark in most articles dealing with olefin epoxidation. From the "common" organic solvents, only nitromethane is competitive with at least one fluorinated solvent (TFE). 4-*tert*-butylpyridine and pyrazole are more or less equal additives in the oxidation under applied conditions. Pyrazole affords a slightly higher TOF. The amount of pyrazole plays a decisive role with respect to catalyst stability. With 5000 equiv. of additive it is possible to apply catalyst concentrations of only 0.01 mol% and still reach quantitative yields. A TOF of 39000 h^{-1} is the highest ever observed for epoxidations with MTO. The amount of water in the system, controlled by the hydrogen peroxide concentration, leads to small increases in yield and TOF for lower water concentrations. In contrast to cyclooctene as substrate, 1-octene requires higher temperatures to form epoxides in sufficient amounts. The overall activation of the catalytic system seems to play a more important role than the increased decomposition of the catalytically active species at elevated temperatures.

From all examined catalytic systems, MTO is the most efficient one for the oxidation of pseudocumene in terms of both yield and selectivity. The performance of MTO in the oxidation of pseudocumene is strongly affected by the solvent. The solvent effect appears to be related to the solubility of the reaction intermediates. Calculations on the possible mechanism reveal a significant barrier drop of **TS1** with nitromethane as solvent. By shifting from the previously reported solvents for the oxidation of non-hydroxylated arenes (mainly AcOH and Ac_2O) to nitromethane, chloroform or dimethyl carbonate, it is possible not only to considerably reduce the number of

equivalents of oxidant per catalyst (from up to 20 to 4) in the presence of 2 mol % of MTO, but also the concentration of H_2O_2 itself (from 85 % to 50 % or 30 %), leading to comparable results as those already reported under far less favorable conditions. The use of ligands in the MTO-catalyzed oxidation of pseudocumene (**101**) to the corresponding benzoquinone derivative **103** has a beneficial effect on both yield and selectivity. The use of salicylaldoxime **109** and its derivative **110** is particularly efficient when nitromethane is applied as the solvent, delivering selectivities of around 70 % and yields of around 30 % within 72 h. Additionally, selected salen-type ligands also lead to a highly selective oxidation of pseudocumene (up to 85 % selectivity), although the obtained yields are low. These results are nevertheless remarkable considering the difficulty of selective oxidations of simple un-activated arenes, where several ring carbon atoms are equally prone to oxidation. The use of (*N*-salicylidene)aniline derived Schiff bases bearing electron withdrawing substituents as ligands in the MTO-catalyzed oxidation of pseudocumene increases the selectivity of the reaction towards the formation of benzoquinone **103**. In particular, the presence of a nitro group in the *trans*-position to the hydroxyl moiety in the salicylaldehyde derived part of the ligand leads to selectivities as high as 84 %. The Schiff base ligands coordinate weakly to the rhenium center of MTO. This results in active catalysts with reduced Lewis acidity, leading to increased chemoselectivity. The presence of electron withdrawing groups in the ligands might not only affect the strength of the coordination but also the intramolecular hydrogen bond formation.

A mild procedure for the MTO-catalyzed oxidation of pseudocumene based on the use of amphiphiles to improve the selectivity of the product distribution is presented. The applied strategy leads to good selectivity values of up to 80 % and generally improve the values with respect to the same reaction conditions in the absence of amphiphile.[141] The use of sustainable hydrogen peroxide and the economical relevance of benzoquinone **103** in the production of vitamin E render the presented procedure very appealing from an industrial point of view. Further, the design of amphiphilic ligands that could also coordinate to MTO and decrease its Lewis acid character is an object of future studies.

4. Experimental Section

Experimental for 2.2

Trans-β-methylstyrene, cyclohexene and cyclooctene were purchased from Aldrich and Acros. The solvents *tert*-butanol and CH_2Cl_2 were used without further drying or purification. H_2O_2 was used as the oxidizing agent in a 35 % aqueous solution for the epoxidation 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 29. The catalysis experiments were carried out in double walled glass vessels that could be tempered. 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 CH_2Cl_2.

Table 29. Amounts of MTO and ligand.

Experiment	MTO	**85**	**86**	**66**
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

Solvent, oxidizing 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 CH_2Cl_2, the samples were analyzed with a calibrated VarianWS gas chromatograph.

Experimental for 2.3

Catalysis: Method A: 441 mg cyclooctene (4 mmol, 0.52 mL), 0.5 mL mesitylene (internal standard), 1 mol% catalyst (0.04 mmol MTO + 0.04 mmol Schiff base), 2 mL nitromethane.

Method B: 449 mg 1-octene (4 mmol, 0.63 mL), 0.2 ml mesitylene (internal standard), 0.2 ml toluene (internal standard), 1 mol% catalyst (0.04 mmol MTO + 0.04 mmol Schiff base), 2 mL nitromethane.

The compounds from methods A and B were combined in tempered glas vessles. The reaction was started by addition of 0.91 mL aqueous H_2O_2 solution (27 %, 8 mmol). Samples were treated with MnO_2 and $MgSO_4$ to destroy hydrogen peroxide and to remove water. They were subsequently filtered and afterwards diluted with dichloromethane. Analysis was carried out by calibrated GC methods in all cases.

General procedure for the synthesis of ligands: A solution of salicylaldehyde derivative (1.0 equiv.) in ethanol (5.0 mL $mmol^{-1}$) was added into a solution of aniline derivative (1.0 equiv.) in ethanol (5.0 mL $mmol^{-1}$). After stirring at room temperature for 1 h, the mixture was refluxed until complete consumption of the starting materials. Subsequently, ethanol was removed under reduced pressure and the obtained imines were purified by crystallization. All analytical data is in accordance with literature [78, 85, 88, 90, 120, 141].

Experimental for 2.4

All solvents, as well as compounds **100**, **85**, and **86** were purchased from commercial sources and used without further purification. **66** was synthesized according to literature procedure [141].

MTO-catalyzed epoxidation

To a solution of MTO, ligand, solvent (8 mL) and substrate (12 mmol, 1 equiv.), H_2O_2 (27 %, 24 mmol, 2 equiv.) was added. The reaction was stirred at a selected temperature and samples were taken at different reaction times. The samples were

treated with MnO_2 to destroy hydrogen peroxide and subsequently dried over $MgSO_4$, filtered and analyzed by gas chromatography (standards: indene/*p*-xylene).

Experimental for 2.5

All oxidants, solvents, ligands **85**, **107-109**, aniline and salicylaldehyde derivatives are commercially available and were used as received, except for MTO, which was prepared following a standard literature procedure [223, 224]. Ligand **110** was prepared by reaction of the corresponding ketone with hydroxylamine following a common procedure [42] and **87**, **111-117** were prepared through standard condensation reactions between an aldehyde and an amine derivative in ethanol and are well-known in the literature [78, 85, 88-90, 120, 144]. Ligands **94** and **66** are known in the literature and have been previously prepared in our group [88, 90, 120].

Reactions were monitored by GC-MS in a Hewlett-Packard HP-6890 instrument with a mass selective detector and a DB-225 column, and yields were measured using 4-methylbiphenyl and decane as internal standards. Those standards were added to the samples after the reactions were quenched to prevent their oxidation under the reaction conditions and possible interference with the study of the solvent effect. No inert atmosphere was employed for the oxidation reactions.

^{1}H-, ^{13}C- and ^{17}O-NMR spectra were measured in a Bruker Avance DPX-400 spectrometer.

Chemical shifts (ppm) for the methyl protons of MTO in ^{1}H NMR ($CDCl_3$) spectra: for free MTO $\delta(CH_3)$ = 2.67 ppm; for MTO + **66**, **87** and **94** $\delta(CH_3)$ = 2.63-2.62 ppm; for MTO + **90**, **93**, **95** and **98** $\delta(CH_3)$ = 2.62 ppm; for MTO + **88**, **91**, **92**, **96**, **97** and **120** $\delta(CH_3)$ = 2.61 ppm.

Chemical shifts (ppm) for the oxygens of MTO in ^{17}O NMR (CH_3NO_2) spectra: for free MTO $\delta(O)$ = 833 ppm; for MTO + **98** $\delta(O)$ = 835.5 ppm.

Ligand-assisted MTO-catalyzed oxidation of pseudocumene (101).

To a solution of MTO (2 mol %), Ligand **66**, **85**, **87**, **88**, **90-98**, **107-117** and **120** (2 mol %, see Table 25), **101** (1 equiv.) and the solvent of choice (1 mL mmol^{-1}), was added H_2O_2 30 % or 50 % (4 equiv.). The reaction was stirred at the selected temperature for at least 6 hours. For the characterization of **103**, after the reaction was stopped, the crude mixture was extracted three times with diethyl ether. Subsequently,

a catalytic amount of MnO_2 was added to destroy traces of peroxide if necessary, and the resulting solution was dried over anhydrous sodium sulfate, filtered and the solvent carefully removed under vacuum. 2,3,5-Trimethyl-1,4-benzoquinone **103** was purified through flash chromatography (dichloromethane/pentane 4:6) and obtained as a pale orange solid. Spectroscopic data are in accordance with literature data [163].

General procedure for the synthesis of ligands 90 and 88, 91-93, 95-98, 120.

A solution of salicylaldehyde derivative **106** (1.0 equiv.) in ethanol (5.0 mL $mmol^{-1}$) was added into a solution of aniline derivative **107** (1.0 equiv.) in ethanol (5.0 mL $mmol^{-1}$). After stirring at room temperature for 1 h, the mixture was refluxed until complete consumption of the starting materials. Subsequently, ethanol was removed under reduced pressure and the so-obtained imines were purified by crystallization.

***N*-(3,5-Dichlorosalicylidene)aniline (90)** [225]. The general procedure was followed using 3,5-dichlorosalicylaldehyde (634.6 mg, 3.29 mmol) and aniline (0.3 mL, 3.29 mmol) to afford 724.4 mg (83 % yield) of the product as an orange solid after crystallization in ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.27 (s, 1H), 8.58 (s, 1H), 7.47-7.44 (m, 3H), 7.36-7.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 156.1, 146.8, 132.7, 129.7, 129.6, 127.9, 123.3, 122.9, 121.2, 120.2; anal. calcd. for $C_{13}H_9Cl_2NO$: C 58.67, H 3.41, N 5.26, Cl 26.64; found: C 58.31, H 3.34, N 5.21, Cl 26.77.

***N*-Salicylidene-3-chloroaniline (95)** [226]. The general procedure was followed using salicylaldehyde (0.35 mL, 3.22 mmol) and 3-chloroaniline (0.34 mL, 3.22 mmol) to afford 524.8 mg (70 % yield) of the product as a yellow solid after crystallization in hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.91 (s, 1H), 8.62 (s, 1H), 7.45-7.40 (m, 2H), 7.37 (d, *J* = 8.07 Hz, 1H), 7.31-7.27 (m, 2H), 7.20-7.17 (m, 1H), 7.06 (d, *J* = 8.19 Hz, 1H), 6.98 (dt, *J* = 7.51, 1.03 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 161.2, 149.9, 135.1, 133.6, 132.5, 130.4, 126.8, 121.2, 119.7, 119.2, 118.9, 117.3; anal. calcd. for $C_{13}H_{10}ClNO$: C 67.39, H 4.35, N 6.05, Cl 15.30; found: C 67.11, H 4.08, N 5.90, Cl 15.38.

***N*-(3,5-Dichlorosalicylidene)-2-chloroaniline (98)** [227]. The general procedure was followed using 3,5-dichlorosalicylaldehyde (634.6 mg, 3.29 mmol) and 2-chloroaniline (0.35 mL, 3.29 mmol) to afford 628.4 mg (64 % yield) of the product as an orange solid after crystallization in ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ =

13.88 (s, 1H), 8.48 (s, 1H), 7.42-7.38 (m, 2H), 7.28-7.15 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 160.9, 155.97, 143.9, 133.1, 130.4, 129.9, 128.7, 127.8, 123.5, 123.1, 120.2, 118.9; anal. calcd. for $C_{13}H_8Cl_3N$: C 51.95, H 2.68, N 4.66, Cl 35.39; found: C 51.55, H 2.69, N 4.55, Cl 35.39.

***N*-Salicylidene-4-fluoroaniline (91)** [228]. The general procedure was followed using salicylaldehyde (0.35 mL, 3.22 mmol) and 4-fluoroaniline (0.31 mL, 3.22 mmol) to afford 553.9 mg (80 % yield) of the product as a yellow solid after crystallization in hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.07 (s, 1H), 8.59 (s, 1H), 7.40-7.36 (m, 2H), 7.27-7.24 (m, 2H), 7.11 (t, *J* = 8.54 Hz, 2H), 7.02 (d, *J* = 8.67 Hz, 1H), 6.95 (t, *J* = 7.45 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 162.4, 161.7 (d, *J* = 246.49 Hz), 161.1, 144.7 (d, *J* = 2.94 Hz), 133.2, 132.3, 122.6 (d, *J* = 8.28 Hz), 119.1, 117.3, 116.2 (d, *J* = 22.74 Hz); anal. calcd. for $C_{13}H_{10}FNO$: C 72.55, H 4.68, N 6.51, F 8.83; found: C 72.11, H 4.66, N 6.44, F 9.00.

***N*-Salicylidene-2-chloro-4-fluoroaniline (96)**. The general procedure was followed using salicylaldehyde (0.35 mL, 3.22 mmol) and 2-chloro-4-fluoroaniline (0.43 mL, 3.22 mmol) to afford 782.5 mg (97 % yield) of the product as a yellow solid after crystallization in hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.20 (s, 1H), 8.78 (s, 1H), 7.61-7.57 (m, 2H), 7.44-7.40 (m, 2H), 7.25-7.21 (m, 2H), 7.14 (t, *J* = 7.48 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 161.3, 160.9 (d, *J* = 249.89 Hz), 141.9 (d, *J* = 3.46 Hz), 133.8, 132.5, 130.4 (d, *J* = 10.46 Hz), 119.8 (d, *J* = 8.87 Hz), 119.2, 118.9, 117.6 (d, *J* = 12.72 Hz), 114.8 (d, *J* = 22.49 Hz); anal. calcd. for $C_{13}H_9ClFNO$: C 62.54, H 3.63, N 5.61, F 7.61; found: C 62.93, H 3.64, N 5.66, F 7.80.

***N*-Salicylidene-4-trifluoromethylaniline (92)** [229]. The general procedure was followed using salicylaldehyde (0.35 mL, 3.22 mmol) and 4-trifluoromethylaniline (0.41 mL, 3.22 mmol) to afford 791.4 mg (93 % yield) of the product as a yellow solid after crystallization in hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.79 (s, 1H), 8.62 (s, 1H), 7.74-7.63 (m, 1H), 7.44-7.41 (m, 2H), 7.35 (d, *J* = 8.41 Hz, 2H), 7.05 (d, *J* = 8.78 Hz, 1H), 6.97 (t, *J* = 7.49 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 161.2, 151.7, 133.9, 132.7, 128.7 (q, *J* = 32.79 Hz), 126.6 (q, *J* = 7.15 Hz), 124.1 (q, *J* = 271.71 Hz), 121.4, 119.3, 117.4; anal. calcd. for $C_{14}H_{10}F_3NO$: C 63.40, H 3.80, N 5.28, F 21.49; found: C 63.49, H 3.60, N 5.27, F 21.20.

***N*-(5-Bromosalicylidene)aniline (88)** [230]. The general procedure was followed using 5-bromosalicylaldehyde (667.8 mg, 3.29 mmol) and aniline (0.3 mL, 3.29 mmol) to afford 844 mg (93 % yield) of the product as an orange solid after crystallization in ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.26 (s, 1H), 8.54 (s, 1H), 7.50 (d, *J* = 1.90 Hz, 1H), 7.45-7.41 (m, 3H), 7.32-7.26 (m, 3H), 6.93 (d, *J* = 8.92 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 160.2, 147.9, 135.7, 134.2, 129.5, 127.3, 121.2, 120.6, 119.3, 110.5; anal. calcd. for $C_{13}H_{10}BrNO$: C 56.55, H 3.65, N 5.07, Br 28.94; found: C 56.30, H 3.59, N 5.02, Br 29.33.

***N*-(5-Bromosalicylidene)-2-chloroaniline (97)** [231]. The general procedure was followed using 5-bromosalicylaldehyde (667.8 mg, 3.29 mmol) and 2-chloroaniline (0.35 mL, 3.29 mmol) to afford 667.9 mg (65 % yield) of the product as a dark yellow solid after crystallization in a mixture of diethyl ether and hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.16 (s, 1H), 8.56 (s, 1H), 7.53-7.46 (m, 3H), 7.35-7.31 (m, 1H), 7.25-7.21 (m, 2H), 6.95 (d, *J* = 8.83 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 160.4, 144.9, 136.2, 134.4, 130.4, 129.7, 128.2, 127.8, 120.5, 119.5, 119.1, 110.5; anal. calcd. for $C_{13}H_9BrClNO$: C 50.27, H 2.92, N 4.51, Br 25.73, Cl 11.42; found: C 50.04, H 2.85, N 4.51, Br 25.93, Cl 11.82.

***N*-Salicylidene-4-nitroaniline (93)** [232]. The general procedure was followed using salicylaldehyde (0.35 mg, 3.22 mmol) and 4-nitroaniline (453.7 mL, 3.22 mmol) to afford 313.3 mg (40 % yield) of the product as a brown solid after crystallization in hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.56 (s, 1H), 8.63 (s, 1H), 8.28 (d, *J* = 8.68 Hz, 2H), 7.46-7.42 (m, 2H), 7.35 (d, *J* = 8.72 Hz, 2H), 7.04 (d, *J* = 8.65 Hz, 1H), 6.98 (t, *J* = 7.37 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 161.32, 154.2, 146.1, 134.5, 132.9, 125.2, 121.8, 119.5, 118.7, 117.5; anal. calcd. for $C_{13}H_{10}N_2O_3$: C 64.46, H 4.16, N 11.56; found: C 64.08, H 3.99, N 11.25.

***N*-(5-Nitrosalicylidene)aniline (120)** [233]. The general procedure was followed using 5-nitrosalicylaldehyde (560.8 mg, 3.29 mmol) and aniline (0.3 mL, 3.29 mmol) to afford 568.6 mg (72% yield) of the product as a pale orange solid after crystallization in ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.43 (s, 1H), 8.71 (s, 1H), 8.38 (d, *J* = 2.74 Hz, 1H), 8.25 (dd, *J* = 9.18, 2.76 Hz, 1H), 7.49-7.44 (m, 2H), 7.38-7.32 (m, 3H), 7.08 (d, *J* = 9.17 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

166.8, 160,6, 160.6, 146.7, 139.9, 129.7, 128.3, 128.1, 121.2, 118.3, 118.1; anal. calcd. for $C_{13}H_{10}N_2O_3$: C 64.46, H 4.16, N 11.56; found: C 64.35, H 4.05, N 11.41.

Computational Details

All calculations were performed with GAUSSIAN-03 [234] using the density functional/Hartree-Fock hybrid model Becke3LYP [235-238] and the split valence double-z (DZ) basis set 6-31+G** [239]. Re atoms have to be treated with an effective core potential, we chose the Hay-Wadt LANL2DZ [240] basis set for this metal. No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis. Transition-state structures (indicated by TS) were located using the Berny algorithm [241] until the Hessian matrix had only one imaginary eigenvalue. The identities of all transition states were confirmed by IRC calculations, and by animating the negative eigenvector coordinate with MOLDEN [242] and GaussView [243].

Approximate free energies (ΔG) and enthalpies (ΔH) were obtained through thermochemical analysis of frequency calculations, using the thermal correction to Gibbs free energy as reported by GAUSSIAN-03. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper, unless otherwise noted, are free energies or enthalpies at 298 K, using unscaled frequencies. All transition states are maxima on the electronic potential energy surface (PES), which may not correspond to maxima on the free energy surface. Solvation effects are added with the application of the PCM method [244, 245] as implemented in GAUSSIAN-03. The solvents used are methanol (dielectric constant ε = 32.63), dichloromethane (ε = 8.93), dimethyl carbonate (ε = 3.09) and nitromethane (ε = 38.20), according to the experimental study. All calculated data are available as supporting information upon request from the authors.

Experimetal for 2.6

To a solution of MTO (2 mol%), **101** (1.4 mmol, 1 equiv.), the amphiphile of choice (Table 28) and solvent (when indicated, Table 1) H_2O_2 30 % (4 equiv.) was added to start the reaction. The reaction was stirred at 40-50 °C temperature for 20-72 h. After

the reaction was stopped, the crude mixture was extracted with diethyl ether. Subsequently, a catalytic amount of MnO_2 was added to destroy traces of peroxide if necessary, and the resulting solution was dried over anhydrous sodium sulfate, filtered and analysed by GC-MS using 4-methylbiphenyl and n-decane as internal standard. For characterisation, 2,3,5-trimethyl-1,4-benzoquinone (**103**), was purified through flash chromatography (dichloromethane/pentane 4:6) after work-up and obtained as a pale orange solid. Spectroscopic data are in accordance with literature data.[163]

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Publication List

“Methyltrioxorhenium catalysed epoxidations: A comparative study of different N-donor ligands“
Philipp Altmann, F. E. Kühn, J. Organomet. Chem. 694 (2009) 4032-4035.

„η^5,η^1-Coordinated cyclopentadienyl transition metal complexes featuring σ-metal-carbon *ansa* bridges”
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„Recent advances in oxidation catalysis using ionic liquids as solvents“
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“Methyltrioxorhenium-catalyzed oxidation of pseudocumene for vitamin E synthesis: A study of solvent and ligand effects“
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“Methyltrioxorhenium-catalysed oxidation of pseudocumene in the presence of amphiphiles for the synthesis of vitamin E”
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Philipp Altmann, Mirza Cokoja, Fritz E. Kühn, J. Organomet. Chem. 701 (2012) 51-55.

“Applying Fluorinated Solvents for Methyltrioxorhenium-Catalyzed Olefin Epoxidations”
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