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Rhenium(V)-complexes as catalysts in oxygen atom transfer reactions

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Abstract

A series of tetradentate phenolate-based Schiff base ligands with various substituents and variable flexibility (alkyl-bridged **1 a-c**, cycloalkyl-bridged **2 a-c** and phenylene-bridged **3 a-c**, respectively) was used to prepare oxorhenium(V)-complexes. Three asymmetric coordinated complexes of the type [ReOCl(L)] (**I a-c**) employing alkyl-bridged ligands have been synthesized via reacting $[ReOCl_3(OPPh_3)(SMe_2)]$ with the respective ligand in acetonitrile. The compound [ReOCl(1 b)] (**I b**) has not been reported previously. Within the syntheses in acetonitrile solvent, the formation of hitherto unknown symmetric stereoisomers (**I a'-c'**) was observed in varying quantities, dependent on the ligands substituents. The stereoisomers **I a'** and **I b'** have been characterized with ^{1}H-NMR spectroscopy and show in contrast to the asymmetric isomers only one set of resonances. Whereas isolation of isomeric pure **I a** and **I b** was successful by recrystallization from acetonitrile, bulk **I a'**, **I b'**, **I c** and **I c'** could not be obtained. Upon using another, previously published synthetic procedure in ethanol, the formation of a μ-oxo bridged dimeric species $[\{ReO(1\ a)\}_2(\mu\text{-}O)]$ (**IV**) was observed in small quantities. The dimer was characterized with ^{1}H-NMR spectroscopy, in the spectrum one set of resonances, clearly distinguishable from **I a'**, was observed. A synthesis employing the cyclohexyl-bridged ligand **2 c** led to the formation of a symmetric (**II c**) and an asymmetric monomeric compound (**II c'**) of the type [ReOCl(2 c)], characterized with ^{1}H-NMR spectroscopy. Whereas in the spectrum of **II c'** two sets of resonances were observed, **II c** exhibits an unusual spectrum where one set of resonances for the aromatic protons can be observed whereas the remaining protons show two sets of resonances. Furthermore, ^{1}H-NMR spectroscopy shows two additional sets of resonances of different intensity, indicating the formation of two putative dimeric species of the type $[\{ReO(2\ c)\}_2(\mu\text{-}O)]$ (**V**, **VI**).

This is possible due to the use of a racemic chiral ligand. In a synthesis of ligands **3 a** and **3 c** with $[ReOCl_3(OPPh_3)(SMe_2)]$ two rare examples of symmetric coordinated complexes of the type [ReOCl(L)] (**III a**, **III c**) exhibiting a *trans*-$[OReCl]^{2+}$ moiety were obtained. The new compounds **1 b**, **I b** and **III c** have been characterized by ^{1}H-NMR spectroscopy, ^{13}C-NMR spectroscopy and EI-MS, the ligand **1 b** and the complex **III c** have additionally been characterized by elemental analysis. The solid state molecular structures of compounds **I a**, **II c**, **III a** and **IV** have been substantiated by single crystal X-ray diffraction analyses. Isolation of compounds **I c**, **I c'**, **I a'**, **I b'**, **II c**, **II c'** and **IV** in bulk was not possible. However, ^{1}H-NMR spectroscopy provides evidence for their existence in solution. The initial isomeric ratios of **I a**/**I a'** (4:1) and **I b**/**I b'** (3:1) have been determined via ^{1}H-NMR spectroscopy. Compounds **I a**, **I b** and **III a-c** have been tested as catalysts for the epoxidation of cyclooctene and led, with the exception of **III a**, to moderate yields of epoxide (41 - 65 %). Furthermore compounds **I a**, **I b** as well as **III a-c** have been tested in the catalytic reduction of perchlorate, where only **I b** and **III c** showed activity (22 and 24 % reduction of ClO_4^- after 48 h). The surprising catalytic activity of the symmetric compound **III c** in the reduction of perchlorate indicates a mechanism fundamentally different to the mechanism proposed for non-symmetric oxazoline-based oxorhenium(V)-catalysts.

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Chapter 1: Introduction

1.1. Rhenium - a brief introduction

Rhenium is element number 75, located in the seventh group of the periodic table of elements together with manganese and the unstable technetium. It was the last stable element to be discovered by Noddack, Tacke and Berg in 1925. With an average molar abundance in the range of part per billion (ppb) on earth and in the range of part per trillion (ppt) in the solar system respectively, rhenium is considered to be one of the rarest elements known.[1,2] The electron configuration of rhenium is $[Xe]4f^{14}5d^{5}6s^{2}$. Therefore, due to the partially-filled d-orbitals, Rhenium is classified as a transition metal. Rhenium occurs naturally only in two isotopes, ^{185}Re with an abundance of 37.4 % and ^{187}Re with an abundance of 62.6 %. Interestingly, only the minor isotope is stable, whereas ^{187}Re is a β-emitter with a half life period of $4.12 \cdot 10^{10}$ years which gives it quasi-stable characteristics.[3,4]

With an atomic weight of 186.207 $\frac{g}{mol}$ and with a density of 21 $\frac{g}{cm^3}$ it has the fourth highest density among the known elements.[5] Manganese, also a group seven transition metal has high biological relevance. It is employed in various enzymes such as for example manganese superoxide dismutase, manganese(II) dioxygenase, manganese peroxidase and manganese catalase as well as in metalloproteins in the human brain.[6,7] Manganese is also part of the oxygen-evolving cluster in photosystem II.[8]

In contrast to manganese, rhenium has no known biological role although its toxicity is believed to be very low.[5] Generally, the chemical properties of rhenium are much more similar to those of technetium than manganese. This group-internal property differences can be accounted for by the effects of the lanthanide contraction which causes almost similar ionic radii of rhenium and technetium.[9] Due to the similarity and the existence of the accessible radioisotope ^{188}Re, rhenium compounds gained some importance as model systems for radiopharmaceuticals.[10,11]

Table 1.1.: Comparison of group seven elements.

	Mn	Tc	Re
Atomic number	25	43	75
Electron configuration	[Ar]3 d^5 $4s^2$	[Kr]4 d^5 $5s^2$	[Xe]4 f^{14} $5d^5$ $6s^2$
Oxidation states	+I to + VII	-III to + VII	-III to + VII
Atomic radius exp.	140 pm	135 pm	135 pm
Atomic radius calc.	160 pm	185 pm	188 pm
Electronegativity	1.55 (Pauling)	1.90 (Pauling)	1.90 (Pauling)
Molecular weight	54.94 g·mol^{-1}	98.91 g·mol^{-1}	186.21 g·mol^{-1}
Density	7.4 g·cm^{-3}	11.5 g·cm^{-3}	21.0 g·cm^{-3}

Rhenium can practically occur in every oxidation state from -III to +VII, making eleven oxidation states in total. Especially carbonyl derivatives, halides and oxides can occupy most oxidation states.[4,12] Despite that, the more common oxidation states are +I, +II, +IV, +VI, +VII and in coordination chemistry also especially +III and +V.[1,4]

1.2. Oxygen atom transfer involving metal centers

Oxygen atom transfers involving metal centers are part of a variety of chemical reactions both in biological systems as well as in industrial application. Examples for biological oxygen atom transfers are aerobic oxidation reactions by monooxygenase enzymes, e.g. cytochrome P450 and isoenzymes.[13]

An example for industrial use on the other hand would be the heterogeneous catalyzed production of propylene oxide.[14]

In the most generalized view, oxygen atom transfer reactions involving metal centers are simply the transfer of one or more oxygen atoms from a donor species to an oxygen acceptor via an oxo-metal intermediate. In such reactions a donor is reduced and an acceptor oxidized which is presented in Figure 1.1:

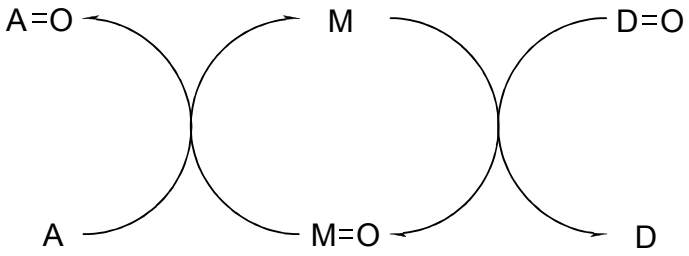

Figure 1.1.: Generalized reaction pathway for oxygen atom transfer.

Oxygen atoms which are directly bound to the metal center as oxide ligands, O^{2-}, are called "oxo".[15] Another possibility is the coordination of dioxygenic species such as O_2 or HOO^- as ligand. These "peroxo" type ligands can coordinate either end-on (η^1) or side-on (η^2). Furthermore also polynuclear complexes with bridging oxygen atoms can be observed.[16,17] A compilation of various coordination motifs is given in Figure 1.2.

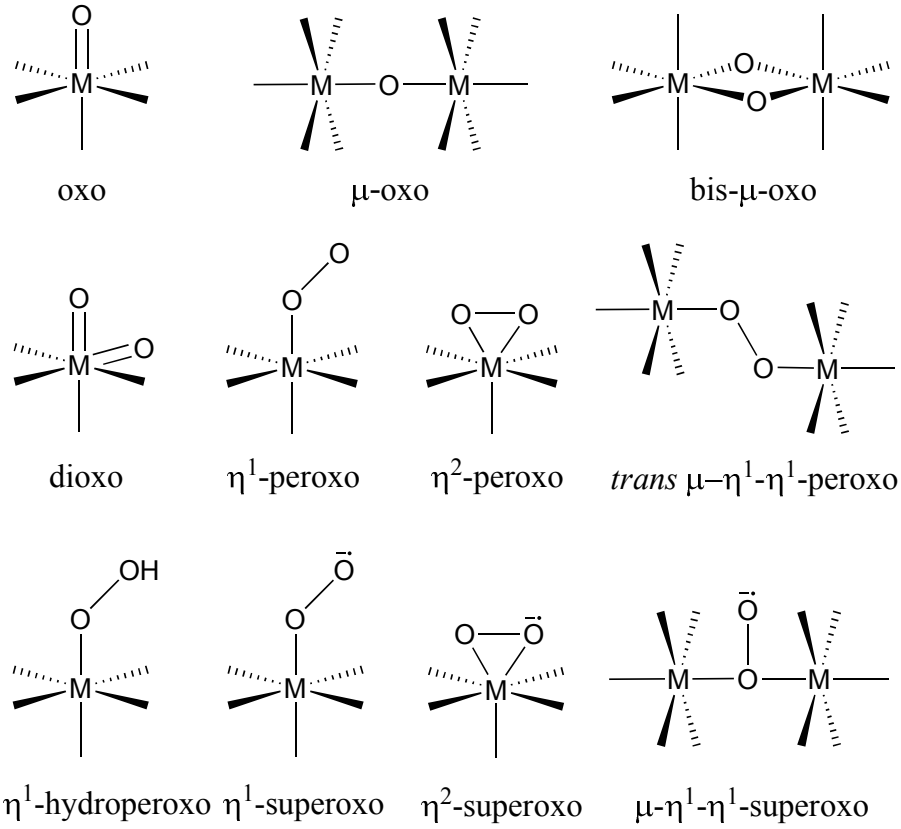

Figure 1.2.: Selected binding modes of oxygenic species to a metal center.[17]

For a brief general discussion, OAT is simplified discussed as "oxo"-transfer. In such cases, a distinction can be made between "primary" and "secondary" oxo-transfer reactions.[15,18]

Primary oxo transfer is a specification of Figure 1.1 to either

$$M^zO_nL_m + A \rightleftharpoons A{=}O + M^{z-2}O_{n-1}L_m \tag{1.1}$$

where one oxo-ligand is transferred to the acceptor molecule and the oxidation state of the metal center is reduced by two, or

$$(M^zO_nL_m)_2O + A \rightleftharpoons A{=}O + 2M^{z-1}O_nL_m. \tag{1.2}$$

In equation 1.2 the transferred oxygen originates from a μ-oxo bridged binuclear compound which leads to two monomolecular compounds where the metal centers oxidation state is reduced by one each. In both cases the number of ligands is not necessarily the same on both sides of the equation since the free coordination site at the reduced metal center is readily filled by another ligand. It is also possible that the oxidized species itself occupies the empty site at the metal center.[18]

As an example system for primary oxo transfer according to equation 1.1 one may consider a model system for molybdenum oxotransferases investigated by Schultz et al., stated in equation 1.3 where tBuL-NS is bis(4-tert-butylphenyl)-2-pyridyl-methanethiolat and X is for example Et_3P, Me_3N or Ph_2S.[19]

$$Mo^{VI}O_2(tBuL{-}NS)_2 + X \rightleftharpoons X{=}O + Mo^{IV}O(tBuL{-}NS)_2 \tag{1.3}$$

Although catalytic systems fulfilling equation 1.2 are rather uncommon, there do exist several examples, e.g. the work of Baird et al.[20] and Wasser et al..[21]

Secondary oxo transfer involves a ligand coordinating to a substituted metal center, followed by an oxygen atom transfer to one of the original ligands. In contrast to equation 1.1 the coordinating ligand here is not the acceptor species, making it an internal redox reaction.[18]

$$M^zO_nL_m + L' \rightleftharpoons M^{z-2}O_{n-1}L'^{z'}_{m-1}L' + L{=}O \tag{1.4}$$

This three types of oxo-transfer reaction are also called **metal-centered** since they directly involve an oxo ligand bound to the metal center. Another possibility of a **secondary** oxo transfer is that the oxygen atom is transferred from a ligand to an acceptor accompanied by both reduction of the ligand and the metal center.

Reactions of that type can be referred to as **ligand-centered**,[18] expressed via

$$M^z(LO_n)_m + A \rightleftharpoons M^{z-1}(LO_n)_{m-1}(LO_{n-1}) + A{=}O. \tag{1.5}$$

For secondary oxo transfer reactions, ligand-centered pathways are observed much more often than pathways where a metal-bound oxo ligand is involved. Examples for that are the systems published by Afshar et al.[22] and Goodwin et al.,[23] both of which employ a nitro-substituent as source of the transferred oxygen.

Generally, there are several factors that influence the usability of a system for OAT. First of all, a substrate (oxidant) is needed, in which a comparatively weak D-O bond is employed.[18] Such oxidants are e.g. H_2O_2 and *tert*-butylhydrogenperoxide (TBHP) to name the most prominent examples. The weakened bond between donor and donated oxygen atom can also be caused by coordination of the donor to a metal center. An example would be the coordination and subsequent activation of a side-on coordinated peroxo-moiety at a metal center as depicted in Figure 1.2.[24]

The second requirement is a "labile" metal center which makes transition metals and their ability to employ a broad range of oxidation states an obvious choice.[4] Additionally, the metal center has to have a vacant coordination site or at least a labile ligand to enable a coordination of the oxygenic species.[25]

Subsequently, the oxygenic species can be transferred to an acceptor species which makes oxygen atom transfer reactions a sequence of two reactions where in the first step the oxygen is transferred from the donor to the catalyst and in the second step from the catalyst to the acceptor. The catalyst is thus needed to "activate" the transferred oxygen for nucleophilic attack, which in case of transition metal catalysts happens due to the electropositivity of the metal center.[25] Examples of (transition metal catalyzed) oxygen atom transfer reactions are hydroxylation, sulfoxidation, epoxidation and various other reactions which involve a coupled oxidation/reduction depending on which process is the desired one e.g. the oxidation of phosphines or the reduction of perchlorate.[17,25,26]

1.3. Rhenium compounds in the catalysis of OAT-reactions

The first reference to catalytic activity of Re (metal) has been given shortly after the metals discovery, in 1926. X-ray studies showed traces of Re in MnO_2 which were later held accountable for the catalytic activity of MnO_2 in the decomposition of $KClO_3$.[27] In 1929 subsequently I. and W. Noddack filed a patent covering the usage of catalysts comprising Re-metal, Re-salts or Re-oxides for various oxidation reactions employing oxygen or air as oxidant.[28]

Nowadays Re (as metal) as well as Re-compounds gain more and more importance in catalysis. Its broad range of (stable) oxidation states and subsequently the variety and accessibility of stable compounds is a major benefit for that. Furthermore Re is, despite the limited resources, still cheaper as many other transition metals used regularly in catalysis as for example gold, platinum or rhodium.[29] There are only a few examples of rhenium catalysts yet which are used commercially, such as the organorhenium(VII) compound methyltrioxorhenium (MTO).[29–31] Generally there exist several organic transformations which are actively catalyzed by Re-compounds e.g. C-C coupling, hydrosilylation, hydrogenation, olefin metathesis and a variety of oxygen atom transfer reactions.[32] In fact, for OAT reactions, Re became one of the most studied elements over the years, where the oxidation states +V and +VII are of major interest. They are isoelectronic to the oxidation states +IV and +VI of molybdenum (and tungsten), the most extensive studied element when it comes to oxygen atom transfer catalysis.[17]

Among the first investigated catalytic applications of oxorhenium(V) complexes in OAT were the oxidation of carbon monoxide to carbon dioxide by Re(V)-oxo-hydrido-complexes[33] as well as the OAT from pyridine-N-oxide and derivatives to phospines which was reported and mechanistically investigated by Espenson and coworkers.[34–36]

Interestingly it has been stated that catalysts with only minor structural differences can undergo different catalytic pathways which also involve different postulated intermediates.[37] Also the catalytic oxidation of organic sulfides by oxorhenium(V) species has been investigated.[38]

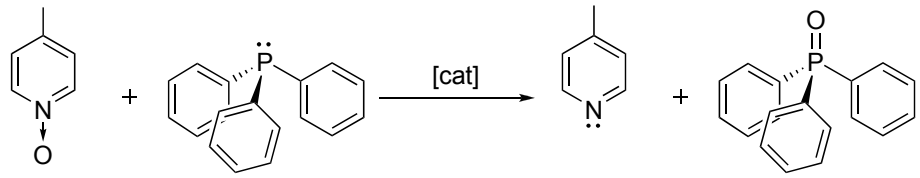

Figure 1.3.: Catalytic OAT from 4-methylpyridine-N-oxide to triphenylphosphine.[37]

Epoxidation of olefins

One of the first Re-compounds to be intensively investigated for its application in oxidation reactions was the Re(VII) compound methyltrioxorhenium (MTO). First synthesized by Beattie and Jones in 1979,[39] it took nearly ten years until a convenient synthesis had been found. In 1988, Herrmann and coworkers were able to develop a comparatively simple and reproducible synthesis for MTO from rhenium(VII)oxide and tetramethyltin which made the compound finally accessible for thorough investigation.[30] Up to now, MTO has been successfully employed as catalyst in a variety of transformations such as aldehyde olefination, olefin metathesis and the epoxidation of olefins by the use of hydrogen peroxide as oxidant.[40] The compound is soluble in most standard laboratory solvents as well as in aqueous media. Furthermore it is stable towards air and temperatures up to 300 °C, all qualities which make the handling of the compound convenient.[31] MTO reacts with H_2O_2 by the formation of a bisperoxo-complex as shown in Figure 1.4.[41]

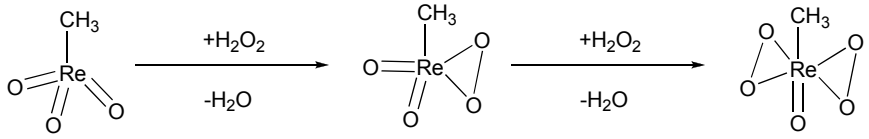

Figure 1.4.: Reaction of MTO with hydrogen peroxide.[41]

Both, the mono- and the bisperoxo-species have proven to be catalytically active in the epoxidation of olefins.[41] Despite the massive research efforts, an isolation and structural characterization of the monoperoxo-species was not successful up to now. The bisperoxo-species and adducts on the other hand have been characterized by single crystal X-ray and neutron diffraction.[41,42] The proposed catalytic epoxidation pathways for the mono- and bisperoxo-species are shown in Figure 1.5.

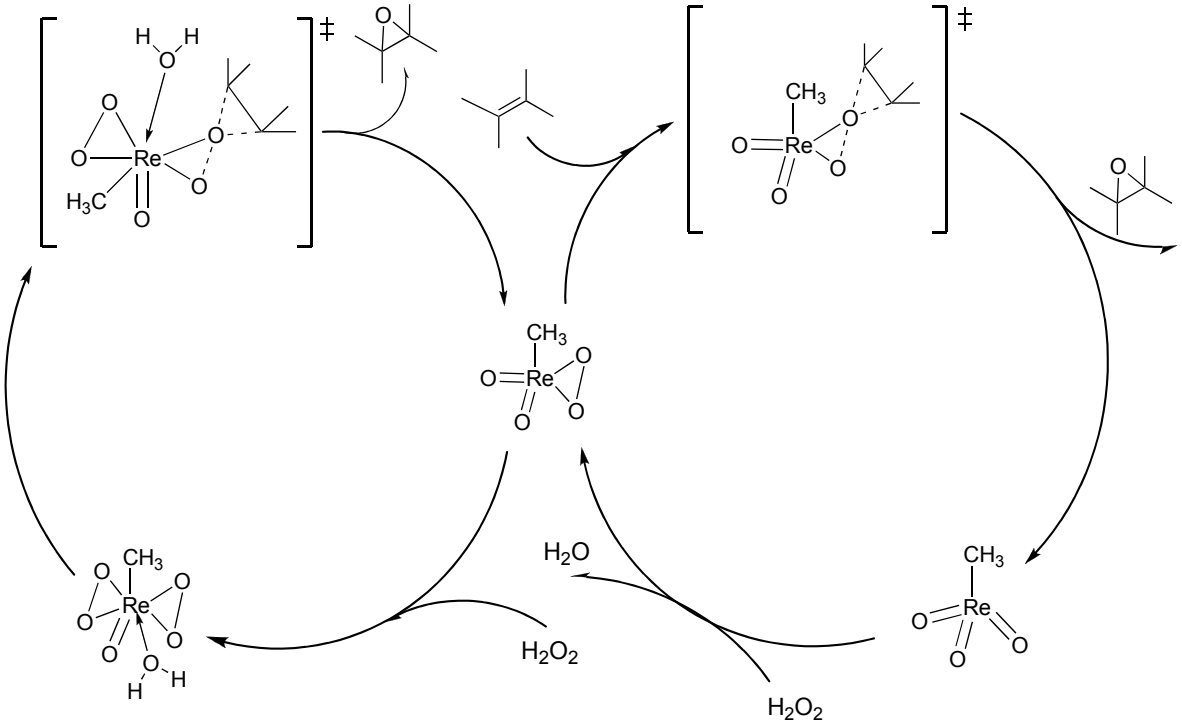

Figure 1.5.: Proposed catalytic cycles of MTO-catalyzed olefin epoxidation.[43]

It has been found that the predominant pathway depends on the concentration of hydrogen peroxide. For 85 %wt of H_2O_2 only the bisperoxo-complex takes actively part in the epoxidation whereas at 30 %wt of H_2O_2 also the monoperoxo-species is present.[43] Up to now, research interest in MTO and its catalysis remains high.[44,45]

Recently, an environmentally less harmful synthesis without the usage of the highly toxic tetramethyltin has been published.[46] Huge benefits of MTO as epoxidation catalyst are the ease of preparation, the broad range of feasible substrates like cycloalkenes, allylalcohols and n-alkenes as well as a broad activity range both in catalyst loading and reaction conditions.[47]

Nevertheless there do exist drawbacks as well, some directly related to the high activity of the catalyst. Under alkaline conditions, in the presence of hydrogen peroxide, MTO undergoes an irreversible degradation to inert perrhenate and methanol. This degradation can also be observed in aqueous media under ambient conditions.[48] Thus acidic conditions have to be employed to stabilize the catalytically active species which is in the case of sensitive substrates rather problematic.[49,50] It has been proven that sensitive epoxides are in several cases, especially under acidic conditions, catalytically hydrolyzed to the respective dioles or follow-up reaction products.[47,51,52] On the other hand, the use of water-free organic solvents facilitates in some cases a Re-chelation by dioles, which leads to the formation of deactivated diolates.[49]

The ring-opening formation of dioles has been attributed to the Lewis-acidity of the metal center in MTO.[47] Therefore first steps to overcome this and other unwanted follow-up reactions were made by the addition of tertiary nitrogen bases to inhibit the ring opening by the use of an H_2O_2-urea adduct. As a downside, a decrease in catalytic activity was the result.[53,54] In contrast to those initial publications, Sharpless and coworkers observed an increase in the epoxidation rates after adding pyridine in a defined quantity (12 mol % have been found ideal, whereas 1 mol % causes fast catalyst decomposition), especially in non-coordinating solvents.[55]

They subsequently enhanced their methods by using a mixture of various substituted pyridines to facilitate the difficult epoxidation of terminal alkenes.[56] Nowadays there exist a variety of nitrogen-containing Lewis base ligands.[40,57]

The stated disadvantages of MTO in epoxidation catalysis triggered the search for a less sensitive alternative system. In the case of rhenium, the attention turned to rhenium(V)-compounds which were at first investigated for their catalytic activity in several oxygen atom transfer reactions. Those were for example oxygen transfer from sulfoxides to phosphines and reduction of oxoanions as well as for sulfur atom transfer.[17,58,59]

Monooxorhenium(V)-compounds with various ligand systems were investigated for their capability of olefin epoxidation with differing success. Generally, the investigated ligands were bi- or tetradentate chelating ligands coordinating via O and N. The ligands are anionic (bidentate) and bisanionic (tetradentate) respectively. With bidentate ligands monosubstituted complexes of the type $[ReOCl_2L(EPh_3)]$ (E = P, As) and disubstituted complexes of the type $[ReOClL_2]$ were investigated. A comprehensive survey has been published very recently by B. Machura.[60] Here selected examples of such systems investigated in epoxidation catalysis are presented.

Several complexes with bi- and tetradentate Schiff base ligands coordinated to the $[ReOCl]^{2+}$ core were reported by Herrmann and coworkers capable to catalyze the epoxidation of cyclooctene (cyOct) to cyclooctane oxide (cyOxide) with TBHP as oxidant (cf. Figure 1.6).[61,62] After induction periods from 30-70 min epoxide yields around 60 % (conditions 1mol% cat, 50 °C, $CHCl_3$) were obtained. The catalysts employing tetradentate ligands decomposed after the reaction whereas the bidentate disubstituted complexes were reusable.[61,62] Mono- and disubstituted oxorhenium(V) compounds with bidentate pyridylalkoxide-ligands gave only epoxide yields around 30 % at comparable conditions.[63]

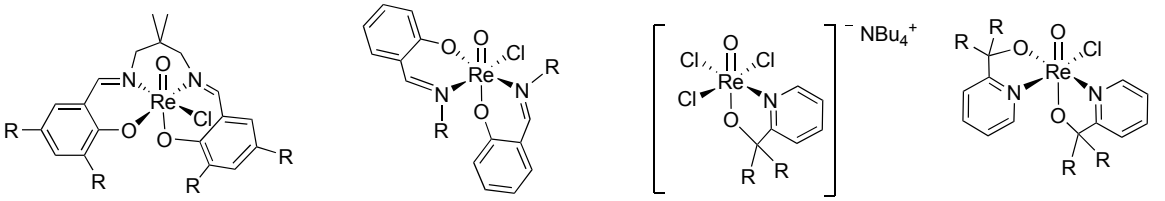

Figure 1.6.: Re(V)=O compounds for epoxidation of cyclooctene.[61–63]

Deloffre et al. synthesized [ReOMeL$_2$] compounds with bidentate picolinato-ligands,[64] which epoxidized various olefins albeit in two-phase systems (in homogeneous systems diol formation of 70% and more was observed).[64]

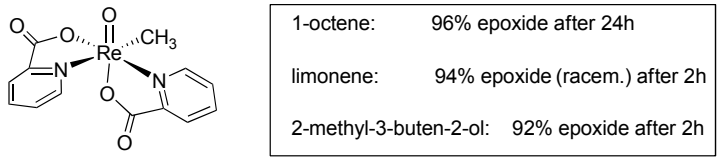

Figure 1.7.: Compound investigated by Deloffre et al..[64] Conditions: 1 mol% catalyst, 150 eq. H_2O_2 (10% in H_2O), biphasic system H_2O/CH_2Cl_2.

Early investigations of our group (Mösch-Zanetti and coworkers) were directed towards bidentate ketiminato-ligands where the respective mono- and disubstituted Re(V) compounds catalyzed the epoxidation of cyclooctene with TBHP without induction periods with conversions up to 60 %.[65,66] Subsequently our group developed pyrazole-phenolate ligands which also led to moderate formation of cyOxide from 44 to 64 % with TBHP.[67] Modification of such ligands with electron withdrawing substituents resulted in compounds which were able to catalyze cyclooctene epoxidation almost quantitative in short periods of time with TBHP and also in a system employing H_2O_2 as oxidant where they were able to convert up to 60 % of cyclooctene within one hour making them a promising starting point for the development of a potent Re(V) epoxidation catalyst (cf. Figure 1.9).[68]

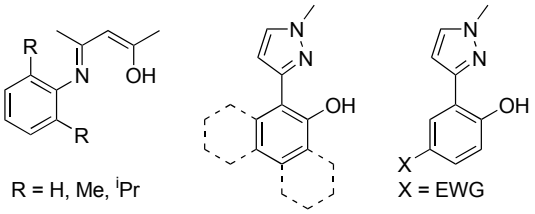

Figure 1.8.: Ligands for epoxidation catalysts investigated by Mösch-Zanetti and coworkers.[65–68]

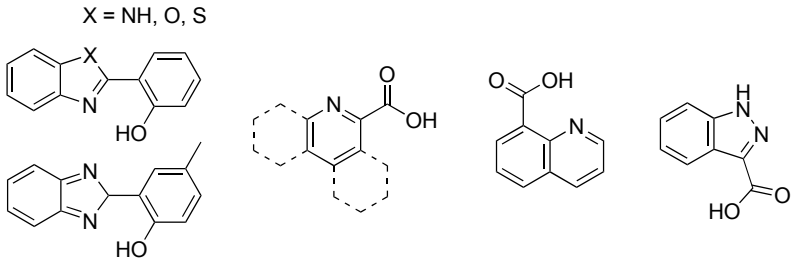

Figure 1.9.: Ligands for epoxidation catalysts investigated by Machura and coworkers.[69,70]

Machura and coworkers tested several oxorhenium(V)-complexes employing carboxylate- and phenolate-derived ligands with various substituents and obtained moderate conversions of cyclooctane.[69,70]

Perchlorate reduction

Many oxohalide species such as BrO_4^-, BrO_3^- and ClO^- are used as oxidants in OAT, therefore considered easily reducible.[18] A remarkable exception is the high stability of perchlorate, ClO_4^-, which is a kinetically stabilized and therefore non-labile anion.[71] Due to the kinetic nature of its inertness, a catalytic reduction of perchlorate should in principle be possible. The high stability, and therefore also biological persistence brought attention to perchlorate as a pollutant.[72] Perchlorate impacts human health negatively since it binds irreversibly to the thyroid gland which causes an inhibition of iodine uptake and subsequently an interference in hormone production.[73,74]

The adverse effects of perchlorate-ions led to the investigation of a possible catalytic reduction to harmless chloride-ions. In such a reaction perchlorate acts as an oxygen donor and is stepwise reduced according to Figure 1.10.

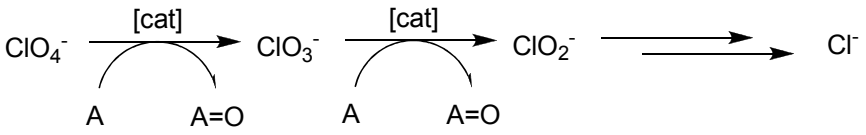

Figure 1.10.: Stepwise reduction of perchlorate via catalytic OAT, where A denotes an oxygen acceptor.

The first described homogeneous catalyzed perchlorate reduction used in-situ generated methylrhenium dioxide (MDO). The related catalytic system is nevertheless accompanied by several difficulties such as the maintenance of pH=0, the need for H_3PO_2 as oxygen acceptor and the irreversible oligomerization and subsequent deactivation of MDO with time and concentration.[75,76] Also MTO adsorbed onto Pd/C and H_2 as oxygen acceptor was investigated. The main advantage of the system is its heterogenity which allows the use of an aqueous system and a straightforward catalyst recovery. On the other hand the system contains Pd and is also sensible towards pH (acidic conditions with pH $<$ 3 are needed).[17,77]

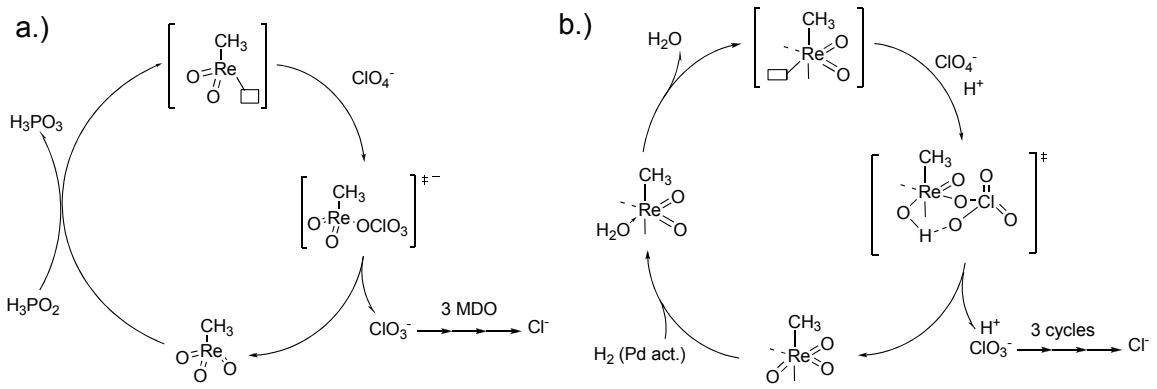

Figure 1.11.: Proposed catalytic cycles for ClO_4^--reduction with a.) MDO and b.) MTO adsorbed on Pd/C.

Much like for epoxidation reactions, also for perchlorate reduction Re(V) systems have been investigated. Abu-Omar and coworkers showed that three oxorhenium(V) compounds are active catalysts in perchlorate reduction with organic sulfides as oxygen acceptors.[26] They investigated a neutral and a cationic oxorhenium(V) complex with two bidentate oxazoline-phenolato ligands and an oxorhenium(V) compound employing a tetradentate Schiff base ligand (stereoisomeric to a compound previously published,[62] left complex in Figure 1.6), shown in Figure 1.12.[26]

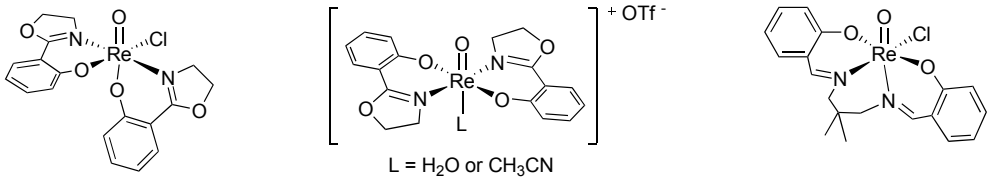

Figure 1.12.: Oxorhenium(V)-catalysts for perchlorate reduction.[26]

The neutral and cationic complexes with the oxazoline-based ligands were able to reduce perchlorate quantitative after four hours with Me_2S or Et_2S as oxygen acceptors and 62 and 69 % resp. after 48 hours with the tetradentate substituted compound and the same substrates. The catalytic reduction of perchlorate with the oxazoline-species has been investigated thoroughly by Abu-Omar and coworkers, especially concerning the mechanistics within the catalytic cycle. The cationic complex has been identified as the catalytically active species to which the neutral compound is transformed via chloride-abstraction.[78,79] The catalytic reduction of perchlorate with the tetradentate species has not been pursued further.

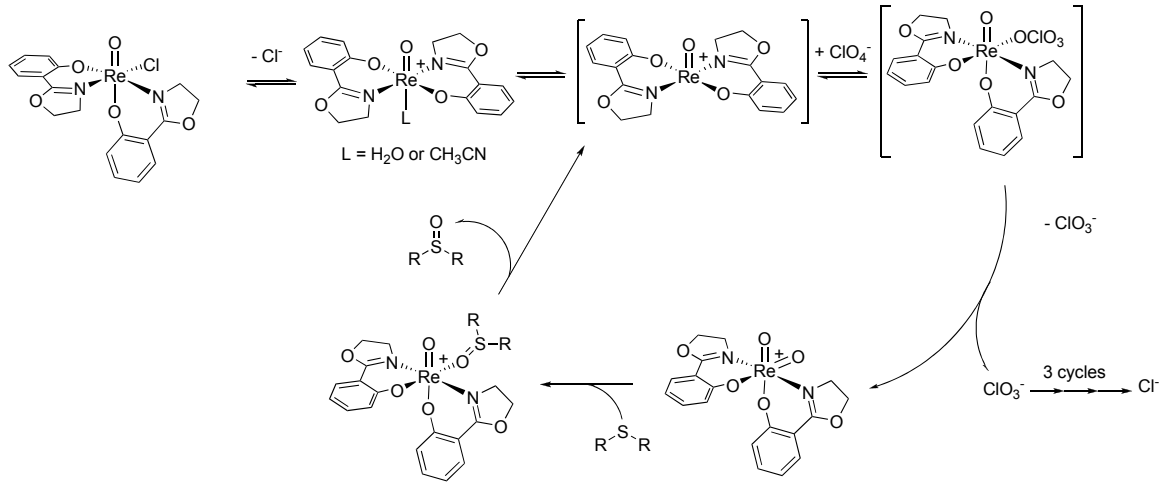

Figure 1.13.: Proposed catalytic cycle for the reduction of perchlorate with the neutral oxazoline-complex.[26,78,79]

The proposed cycle presented in Figure 1.13 reveals several isomeric rearrangements between symmetric and asymmetric species as well as the ligands arrangements with respect to each other.

The catalytically active tetradentate species is much less likely to undergo these rotations due to steric hindrance. Therefore it is questionable whether the same catalytic pathway is present. Furthermore, the group of Mösch-Zanetti also investigated the proposed mechanism of the perchlorate reduction employing bidentate coordinated catalysts with the goal to increase the reactivity and stability of the published system as well as the possibility to use more stable ligands, since the original oxazoline-based ligands are somewhat sensitive to ring-opening decomposition, especially in the presence of Cl^-.[79]

Within the scope of that investigation a coordination isomer of the compound reported by Abu-Omar and coworkers[26] could be identified as a second significant product within the catalyst synthesis.

This N,N-cis isomer as shown in Figure 1.14 (N,N-cis and N,N-trans denote the position of the equatorial coordinated N-atoms with respect to each other) exhibits significantly lower activity in the reduction of perchlorate than the reported compound which indicates the importance of a specific ligand coordination motif for optimal catalytic activity.[80]

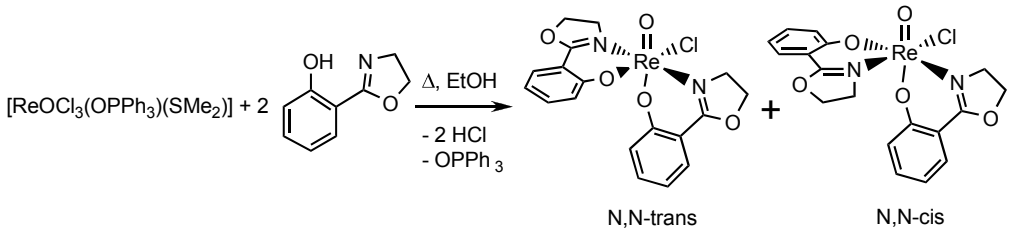

Figure 1.14.: Formation of two isomers in the synthesis of the oxazoline-precatalyst for perchlorate reduction (previously published N,N-trans complex[26] and stereoisomer N,N-cis[80]).

1.4. Tetradentate ligands and coordination isomerism

Different possible geometric ligand arrangements in coordination compounds lead to isomers. The isomerism can be of geometrical nature, which denotes the different possibilities of ligand coordination in heteroleptic compounds. Geometrical isomerism also occurs in homoleptic compounds with asymmetric ligands. The isomerism can also be of optical nature which occurs in both homo- and heteroleptic complexes employing multidentate ligands.[81]

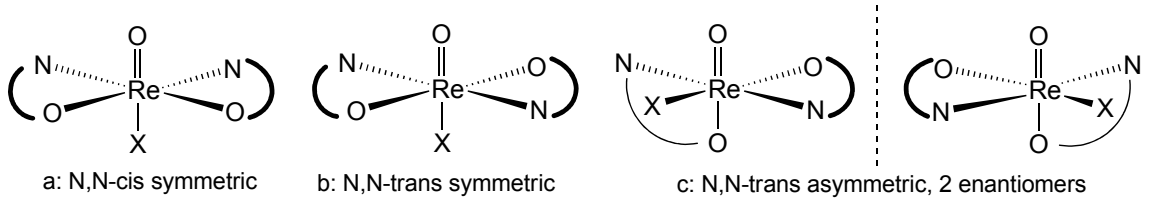

Figure 1.15.: Examples for geometrical (a-c) and optical (c) isomers.

[ReOXL] compounds with tetradentate ligands can coordinate in symmetric as well as asymmetric motifs as shown in Figure 1.16.

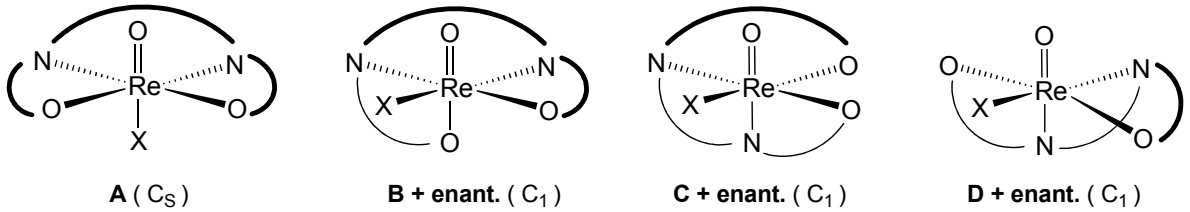

Figure 1.16.: Possible coordination patterns for tetradentate ligands and overall complex symmetry, given in brackets.

Depending on the ligand's flexibility, different complex geometries are preferred. In the case of a $[ReOX]^{2+}$-center, the strong *trans*-influence of the oxo-ligand plays a major role, dependent on the nature of the ligand X. If X is a halide or electron withdrawing group (EWG), all-equatorial coordination is disfavored due to the resulting *trans*-O=Re-X arrangement. Therefore, if the ligand has a high enough flexibility, asymmetric coordination motifs are favored whereas rigid ligands are only able to coordinate all-equatorial if at all. On the other hand, the influence of the oxo-ligand also disfavors the coordination of a neutral nitrogen trans to to it, leaving structure type **B** the most probable.

Tetradentate Schiff base ligands are long known and simple to prepare.[82–85] Examples of corresponding oxorhenium(V)-complexes which are catalytically active both in the epoxidation of olefins as well as in the reduction of perchlorate have been reported.[26,62] Since especially perchlorate reduction requires distinctive isomeric structures in the proposed catalytic cycle sketched in Figure 1.13, Schiff base ligands represent a good opportunity to investigate the effects of rearrangement hindrance.

Moreover, the straightforward synthesis via a condensation reaction allows an adjustment of the ligands rigidity by simply employing various diamines as bridging backbones and therefore the possibility to force the ligand into a specific geometric arrangement.

In accordance with the previous considerations, complexes of the type [ReOX(L)], where X is an EWG, employing tetradentate Schiff base ligands with flexible alkyl-backbones exhibit predominantly the asymmetric coordination motif **B**, Figure 1.16.[62,86–88] Only few examples of a symmetric arrangement (type **A**, Figure 1.16) of a flexible ligand exist.[89] Ligands employing a phenylene-backbone on the other hand would mark the opposite extreme, too rigid to coordinate in another way than all-equatorial. As backbones of intermediate rigidity, cycloalkyl-bridges would mark a good choice for several reasons. On the one hand the derived ligands contain a chiral center which allows for enantioselective catalysis and which has been shown in case of manganese-catalyzed epoxidation.[90–92] On the other hand they should exhibit a flexibility somewhere in between phenylene- and dimethylpropylene-bridged ligands and should therefore be able to employ all coordination motifs **A** - **D**, Figure 1.16. Structural examples for asymmetric as well as symmetric coordination exist.[92,93]

1.5. Scope of this work

Synthesis of Schiff base ligands with increasing rigidity was targeted to allow us the preparation of complexes with specific coordination patterns. The influence of the geometry on two different catalytic reactions, namely olefin epoxidation and perchlorate reduction, is to be investigated.

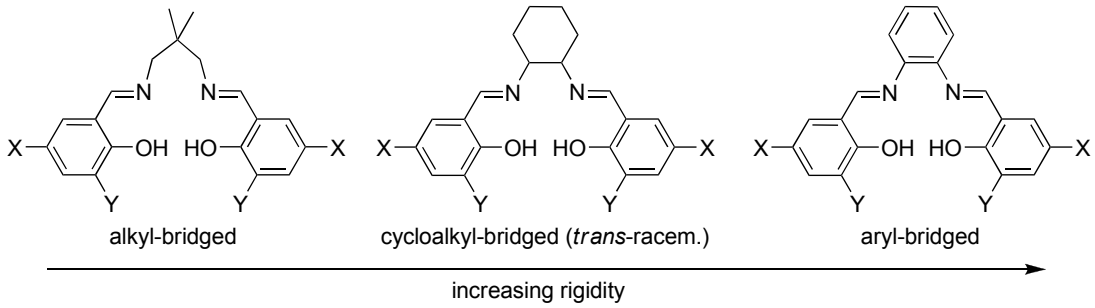

Figure 1.17.: Structures of the tetradentate Schiff base ligands used in this thesis. Used substituents were X=Y=H, X=NO_2, Y=H and X=Y=tBu.

Complexes of structure type **B**, Figure 1.16 employing Schiff base ligands with a dimethylpropyl-bridge as alkyl-bridge have been investigated as catalysts for olefin epoxidation and showed moderate activity.[62] Catalytic activity in the reduction of perchlorate has been reported for a compound stereoisomeric to one within Herrmann's investigation but of structure type **D**, Figure 1.16 by Abu-Omar and coworkers.[26] Since Abu-Omar and coworkers referenced the synthesis of their catalyst to the work of Herrmann and coworkers, one goal within this project was the verification of the catalysts structure. Due to that reasons, as an alkyl-bridge a dimethylpropyl-unit has been chosen.

The dimethylpropyl-derived ligands are expected to have the highest flexibility among the three investigated general ligand types. Therefore, in accordance with literature, a predominantly asymmetric coordination (structure types **B** - **D**, Figure 1.16) with $[ReOCl]^{2+}$ should occur since the trans-effect of the oxo ligand favors a *cis*-O=Re-Cl configuration.

In contrast ligands with a phenylene-backbone should only coordinate all-equatorial (structure type **A**, Figure 1.16) due to their rigidity, which would lead to complexes with a *trans*-O=Re-Cl moiety. The cyclohexyl-backbone has been chosen as species of intermediate rigidity. Furthermore the use of enantiopure ligands of that type allows potentially for enantioselective epoxidation.

A further goal of the project represents the investigation of electronic and steric changes in the ligand and their effects on the coordination motifs as well as the catalytic activity of the corresponding complexes. Therefore, the synthesis of ligands with electron withdrawing groups as well as sterically demanding substituents has been targeted. Whereas the electron withdrawing substituents are expected to increase the catalytic activity in epoxidation reactions, the bulky substituents might cause a preference of an all-equatorial ligand coordination. Furthermore the bulky substituents increase the corresponding complexes solubility in organic solvents.

Chapter 2: Results and discussion

2.1. Ligand synthesis

As described in chapter 1.5, the following ligands were prepared:

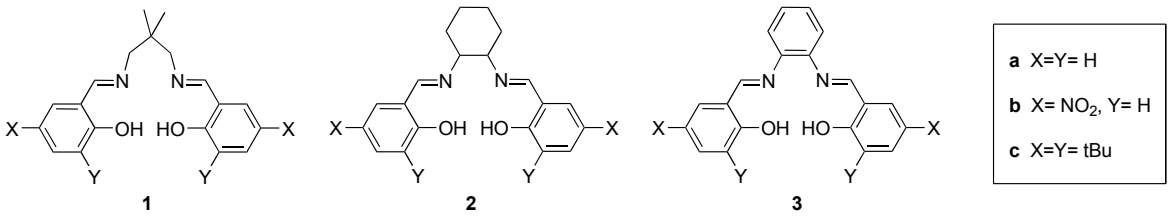

Figure 2.1.: Tetradentate Schiff base ligands investigated in the scope of this thesis.

Due to the widespread use of tetradentate Schiff base ligands in various fields of chemistry[82–85] there exist a variety of syntheses, all employing a condensation reaction between aldehydes and amines at various reaction conditions. All ligands shown in Figure 2.1 have previously been prepared,[94,95] with the exception of **1b**.

The preparation of ligands **1 a-c**, **2 a-c** and **3 a,c** was straightforward following published procedures[62,94,95] and obtained yields from 77 to 92 %. The known ligand's nature and purities have been confirmed by ^{1}H-NMR spectroscopy.

The use of a similar protocol for ligand **3 b** (solvent EtOH, two hours stirring at room temperature) was not successful and led to the formation of a dark orange solid which was identified by ^{1}H-NMR spectroscopy and EI-MS spectrometry as a putative asymmetric species where only one amine group reacts with the corresponding acetophenone (crude yield: 84 %).

The use of a published procedure[96] (stirring at room temperature for 24 hours) for the prepararation of ligand **3 b** led to the formation of an orange powder, insoluble in most organic solvents. ^{1}H-NMR spectroscopy and EI-MS spectrometry point towards the desired ligand accompanied by several unaccountable impurities. In the synthesis of **3 b**, the formation of side products did even occur for prolongued reaction times greater than 24 hours in significant quantities.

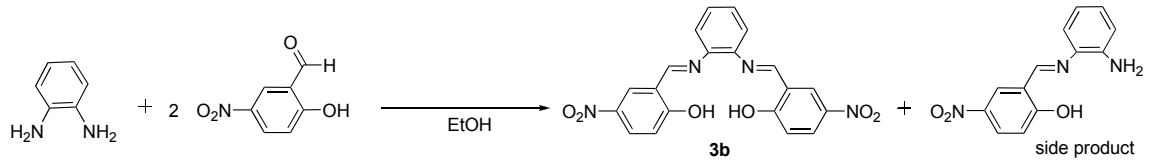

Figure 2.2.: Formation of monophenol side product within the synthesis of **3 b**

An acidic work up with hydrochloric acid 1N and subsequent washing with distilled water turned out to be a viable purification process since it removes the asymmetric diamine species as well as remaining diamine starting material via formation of the corresponding water soluble ammonium salt according to equation 2.1:

$$\mathrm{R{-}NH_2 + HCl \longrightarrow R{-}NH_3{}^+Cl^-} \tag{2.1}$$

A complete purification of ligand **3 b** was nevertheless not successful up to now but only a product in roughly 90 % purity was obtained.

The purification problems seem to be in accordance to previous observations since published ^{1}H-NMR spectroscopy data sets are inconsistent with our observations as well as to each other.[96,97] A comparison of published and observed ^{1}H-NMR shifts is given in the following table.

Table 2.1.: Comparison of published and observed spectral ^{1}H−NMR-data.

^{1}H-NMR shifts	solvent	-OH	-CH=N	Ar-H
Giannicchi et al.[96]	DMSO−d_6	10.17 (bs, 2H)	9.16 (s, 2H)	9.16-7.01 (m, 10H)
observed (crude **3 b**)	DMSO−d_6	13.85 (bs, 2H)	9.12 (s, 2H)	7.14-8.25 (m, 10H)
Sankareswari et al.[97]	$CDCl_3$[a]	13.10 (s, 2H)	8.57 (s, 2H)	6.99-7.40 (m, 10H)

[a] our product proved to be insoluble in $CDCl_3$

The undesired monophenol compound described above represents an interesting species on its own since it could be used as a tridentate ligand (Lane et al. reported a Re(V) species with a similar ligand[98]) or as possible starting material for the synthesis of asymmetric Schiff base ligands which would allow a very specific ligand modification. Whereas similar syntheses have been reported, they mostly lacked product purity and produced bis-products in the attempted synthesis of monosubstituted diimine.[99,100]

2.2. Complex synthesis

Synthesis of complexes employing a dimethylpropyl-bridged tetradentate ligand

For reasons of comparison, the synthesis of a previously described compound employing ligand **1 a** has been explored.[62] According to literature two equiv of ligand **1 a** (one equiv acts as base to neutralize the formed HCl) as well as one equiv of the metal precursor $[NBu_4][ReOCl_4]$[101] were dissolved in ethanol and heated to reflux temperature (cf. Figure 2.3).

After three hours of reaction time the reaction solution had turned deeply green and a green precipitate had formed. The precipitate was filtered off and washed with cold pentane (yield 78 %, assuming a monomeric compound of the type [ReOCl(**1 a**)]). The crude product was characterized by ^{1}H-NMR spectroscopy indicating the formation of a major asymmetric species (**I a**) as well as two additional products (subsequently identified as **I a'** and **IV**).

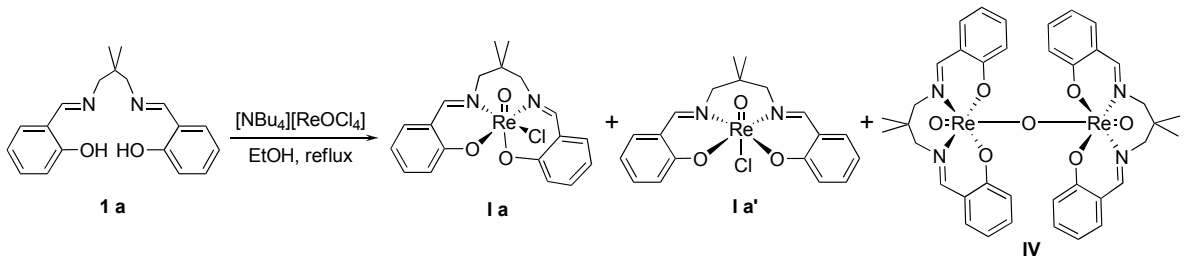

Figure 2.3.: Identified products **I a** and **IV** as well as putative isomer **I a'** in complex synthesis according to literature, total yield = 78 % (two isomers and dimer).

Recrystallization of the crude mixture from CH_2Cl_2 led to **I a** in the shape of green plate crystals suitable for single crystal X-ray diffraction analysis and identified the major isomer as the asymmetric coordinated monomeric complex published by Herrmann and coworkers (structure type **B**, Figure 1.16).

During the recrystallization also dark green rods formed which were identified as a μ-oxo bridged dimeric species **IV** by single crystal X-ray diffraction analysis. The dimer **IV** has been obtained in pure form only in small quantities, therefore a full characterization was not possible. Nevertheless, ^{1}H-NMR data is provided in the experimental section and in Figure 2.4 and can be assigned to the minor symmetric side product in the ^{1}H-NMR-spectrum of the crude material.

Since the major impurity in the crude ^{1}H-NMR spectrum shows only one set of resonances, comparable to the ^{1}H-NMR signals of the dimer **IV** it is most likely a complex with a symmetrically coordinated ligand (structure type **A**, Figure 1.16). Despite the fact that single crystals of **I a** were obtained, according to the literature procedure bulk **I a** and **I a'** could not be obtained. For this reason another synthetic procedure was explored.

A comparison of the ^{1}H-NMR-spectra (3.5 - 8.5 ppm) of pure **I a**, a mixture of **I a**/**I a'** and pure **IV** is provided in Figure 2.4 (Pure **I a** has been obtained within a different experiment, cf. Figure 2.5).

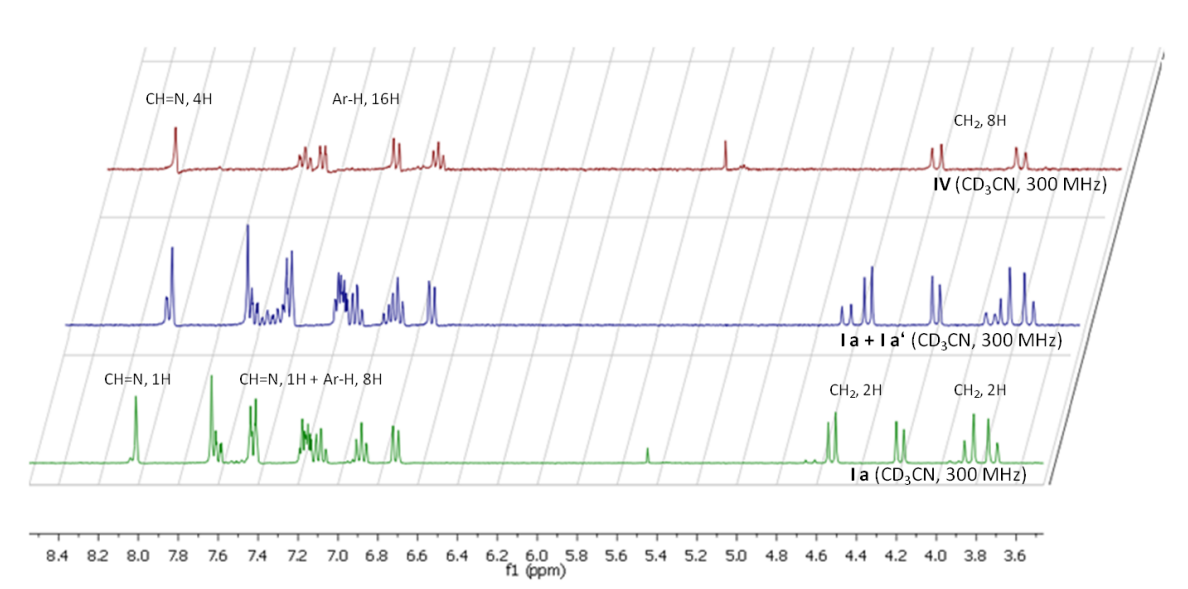

Figure 2.4.: Comparison of ^{1}H-NMR shifts of **I a**, **I a'** and **IV** between 8.5 and 3.5 ppm.

Due to a more convenient work up procedure, another precursor, $[ReOCl_3(OPPh_3)(SMe_2)]$[102,103] has been reacted with ligands **1 a-c**.

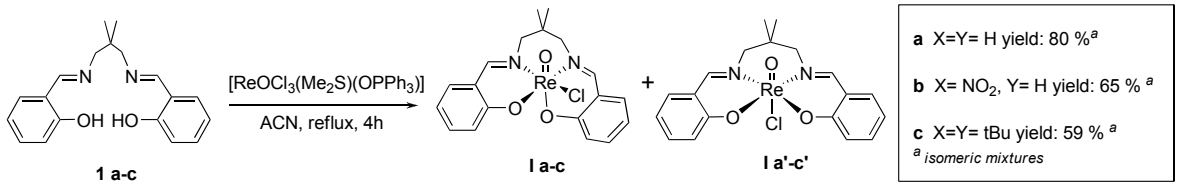

Figure 2.5.: Modified synthesis procedure for complexes employing dimethylpropyl-bridged ligands.

In the modified synthesis 2.1 equiv of the respective ligands **1 a-c** (one equiv acts as base to neutralize the formed HCl) were dissolved in acetonitrile. Subsequently one equiv of the metal precursor $[ReOCl_3(OPPh_3)(SMe_2)]$[102,103] was added and the reaction mixture heated to reflux temperature. After four hours of reaction time the reaction solution had turned deeply green.

Concentration of the reaction solution *in vacuo* and subsequent cooling to 5 °C led to a greenish (**I a**/**I a'** and **I b**/**I b'**) or brown (**I c**/**I c'**) crystalline precipitate which was filtered off and washed with cold pentane to give isomeric mixtures of **I a** and **I a'** (ratio 4:1), **I b** and **I b'** (ratio 3:1) as well as **I c** and **I c'** in overall yields of 59 to 80 % (cf. Figure 2.5). Isomeric pure **I a** and **I b** were obtained via recrystallization from acetonitrile in which they are slightly less soluble than the symmetric isomers in yields from 17 to 20 %. Compound **I c** could not be separated from the isomer **I c'** up to now in bulk. Furthermore pure **I a'** and **I b'** could not be obtained as they were always contaminated by residual **I a** and **I b**, respectively.

The influence of solvent on the isomeric ratios of **I a**/**I a'** and **I b**/**I b'**, respectively, was investigated. For this purpose the isomeric mixtures were dissolved in CD_3CN and $CDCl_3$, respectively. Recorded ^{1}H-NMR spectra confirmed that the ratio of the two isomers is solvent independent, therefore formation ratios have been calculated via integration of characteristic peaks. The initial formation ratios of the putative symmetric isomers are 20 % for **I a'** and 25 % for **I b'**, respectively.

To investigate the influence of reaction conditions, a sythesis of complex **I b** has been performed following the protocol above, but instead of heating to reflux temperature, the reaction mixture has been stirred for four days at room temperature. ^{1}H-NMR spectroscopy revealed the same initial isomeric ratio as observed in previous syntheses.

An attempted use of a base like Et_3N instead of the second equiv ligand was not successful and led to no complex formation (addition of Et_3N led to immediate darkening of the reaction solution, likely due to reactant decomposition).

Complexes **I a-c** were characterized by ^{1}H-NMR and EI-MS. In all spectra two imine proton resonances are apparent as well as two sets of aromatic protons. This is consistent with an asymmetric compound (structure types **B-D**, Figure 1.16). Compounds **I a** and **I c** have been previously described in literature.[62] Whereas ^{1}H-NMR spectroscopic data of **I c** is consistent with our data obtained in this work, we cannot confirm the described data for **I a**. Due to the similarity of our data, we are fairly confident that all three compounds we have synthesized exhibit the same type of structure.

Further evidence for structure type **B**, Figure 1.16, delivers a single crystal X-ray diffraction analysis of **I a** (vide infra). In none of our experiments we find any indication for the formation of a species that matches the literature described data for **I a**. Complex **I b** has additionally been characterized by ^{13}C-NMR.

It is interesting to note, that under the reaction conditions presented in Figure 2.5 the formation of the μ-oxo bridged dimeric species **IV** was not observed. Nevertheless, recrystallization of the isomeric mixtures from alcohols or chlorinated solvents as well as extensive contact to humidity (on air or in solution) caused decomposition of the compounds.

The formation of a μ-oxo bridged dimer derived from monomeric oxorhenium(V) Schiff base complexes has been previously described.[88,104] Whereas decomposition pathways by moist air were discussed,[105] van Bommel et al. suggest a mechanism via an alcoholate-complex with subsequent hydrolysis.[86] This is in accordance with our observations where we obtain dimer only in alcoholic solutions, but not in acetonitrile. Furthermore, the rare formation of complexes employing bidentate ligands has been observed predominantly in alcoholic solvents respectively for alkoxy-complexes.[104,106–108]

Abu Omar and coworkers published a compound referenced to the work of Herrmann and colleagues.[26,62] The structure as provided within their publication would be a stereoisomer of **I a** of structure type **D**, Figure 1.16. This stereoisomer could not be observed within our syntheses. Unfortunately no synthesis or characterization of their respective complex is provided within their publication.

Synthesis of complexes employing cyclohexyl-bridged ligands.

The introduction of cyclohexyl-bridged tetradentate Schiff base ligands, including the so called Jacobsen ligand (**2 c**)[90,91] has been investigated.

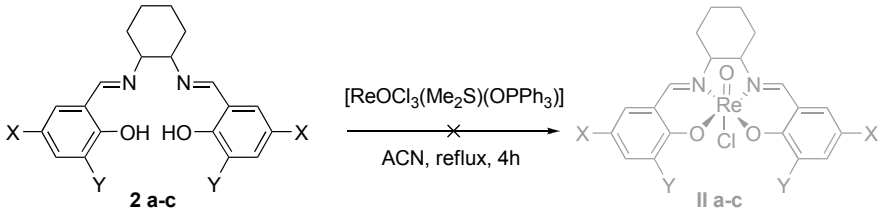

Figure 2.6.: Synthesis approach for complexes employing cyclohexyl-bridged ligands. Used substituents were X=Y=H, X=NO_2, Y=H and X=Y=tBu.

Thus, a slight excess (2.1 equiv) of the respective ligands **2 a-c** was reacted with $[ReOCl_3(OPPh_3)(SMe_2)]$[102,103] in acetonitrile. With **2 a** or **2 b** insoluble brown residues were obtained that could not be characterized.

The formation of the possibly dimeric insoluble products in the attempted syntheses of **II a** and **II b** is in accordance to previous publications, where the only characterization is given by IR-bands of Re=O and Re-O-Re as well as elemental analyses.[88,105,109] The published IR-bands[109] for a dimer employing ligand **2 a** occur in the IR-spectrum of our synthesis product as well (provided in the appendix). On this basis the formation of μ-oxo bridged dimers is suggested, even if a clear identification of the distinctive Re=O and Re-O-Re bands is due to several unaccounted bands in our compounds IR-spectra not unequivocal possible.

In a complex synthesis employing ligand **2 c**, also known as Jacobsen's ligand,[90,91] the resulting dark brown reaction solution was concentrated *in vacuo* and subsequently stored at 5 °C. After several days, a mixture of green and brown crystals had formed (subsequently denoted fraction one; yield 31 %, assuming a monomeric compound of the type [ReOCl(**2 c**)]). The solid was filtered off and washed with cold pentane. The still dark solution was again stored at 5 °C for several days, whereupon dark brown crystals formed (subsequently denoted fraction two; yield 34 %, assuming a monomeric compound of the type [ReOCl(**2 c**)]).

In an attempt to seperate the isomers obtained in the second crystalline fraction, a recrystallization from Et_2O/ACN has been performed and gave a small quantity of dark orange crystals of the symmetric monomer **II c** suitable for single crystal X-ray diffraction analysis. Despite the fact that single crystals of **II c** were obtained, bulk **II c** and **II c'** could not be obtained.

Fractions one and two have been characterized by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum of fraction one (cf. Figure 2.7a) shows two symmetric compounds with one set of resonances each (putative dimers **V** and **VI**).The ^{1}H-NMR spectrum of fraction two showed also two products. One compound shows two sets of resonances which can be assigned to an asymmetric coordinated compound (**II c'**) and therefore necessarily monomeric (likely structure type **B**).

The second product (symmetric monomer **II c**) exhibits an unusual ^{1}H-NMR spectrum since the imine protons as well as alkyl-protons show two sets of resonances whereas the aromatic protons show only one set of resonances. EI-MS measurements of both fractions showed a $[ReOL]^{+}$-peak with correct isotope pattern but no observable $[M]^{+}$-peak. A ^{1}H-NMR spectrum of the recrystallization product of fraction two still showed the two isomers initially found.

The ^{1}H-NMR spectra of fractions one and two in the aromatic region (9 to 6.6 ppm), containing two compounds each, with coloration of the distinctive signals are provided in Figure 2.7.

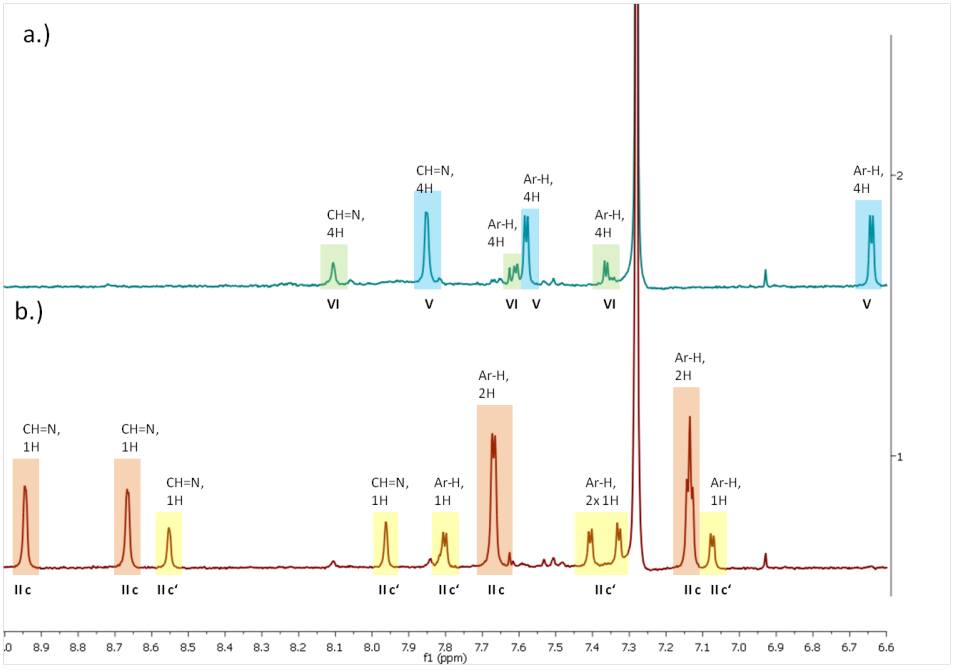

Figure 2.7.: a.) ^{1}H-NMR spectrum of fraction one (green, blue: minor symmetric compounds **V** and **VI**); **b.)** ^{1}H-NMR spectrum of fraction two (red: major symmetric isomer **II c**, yellow: asymmetric isomer **II c'**).

The resonances observed for compound **II c** are unexpected since single crystal X-ray diffraction analysis identified the compound as symmetric complex of structure type **A**, Figure 1.16.

A possible explanation can be given by a distorted coordination of the ligand caused by the strain of the cyclohexyl-bridge. Two resonance sets are reported for a symmetric cationic complex with an unsubstituted cyclohexyl-bridged Schiff base ligand,[109] but in contrast to our observations also the aromatic protons are reported to show two sets of resonances. A clarification for the single set of resonances for the aromatic protons of our compound **II c** cannot be given at this point and has to be investigated further.

The formation of two additional symmetric products in fraction one can be explained by two dimeric compounds with a $[O{=}Re{-}O{-}Re{=}O]^{4+}$-core. This is possible due to the use of a racemic chiral ligand which allows in principle the formation of equivalent (R,R)/(R,R), (S,S)/(S,S) dimers (subsequently denoted as **V**) and a (R,R)/(S,S) dimer, subsequently denoted **VI**. Figure 2.8 shows a summary of identified (**II c**) and putative (**II c'**, **V** and **VI**) complexes employing ligand **2 c**.

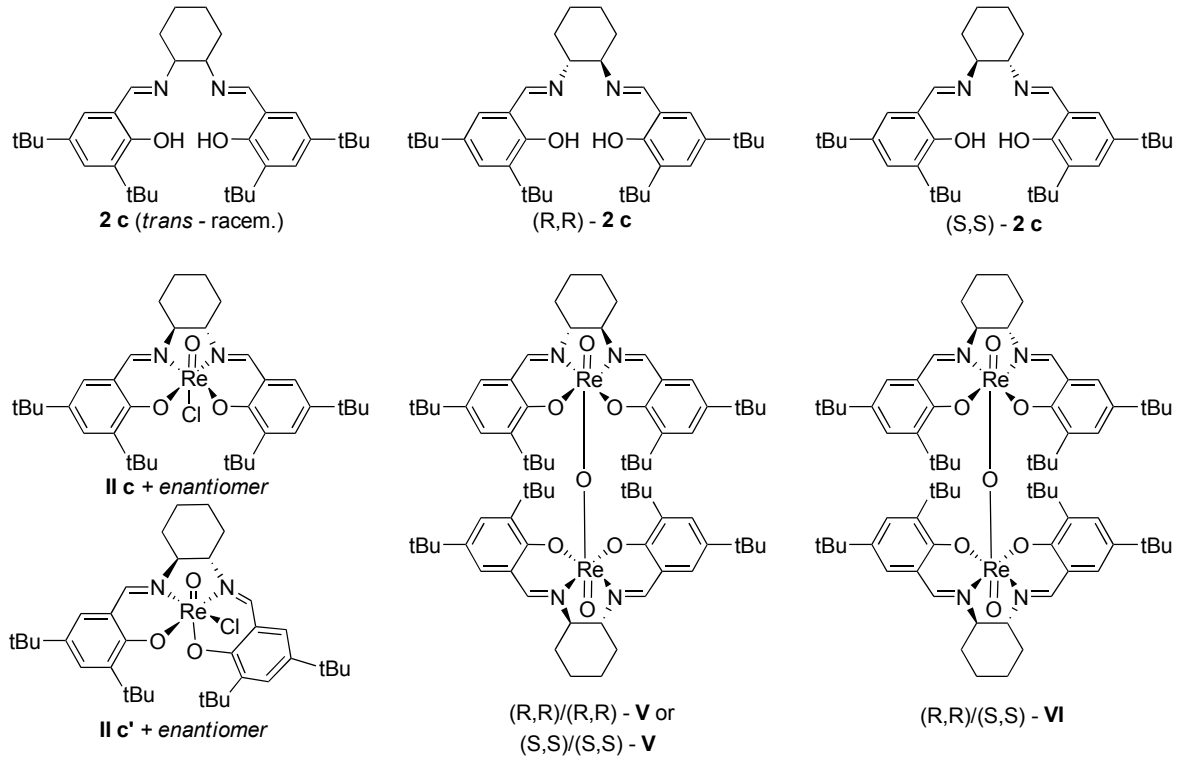

Figure 2.8.: Enantiomers of ligand **2 c**, compound **II c** and the putative compounds **II c'**, **V** and **VI**.

The investigation of the compounds as well as the catalytic activites of complexes employing cyclohexyl-derived Schiff base ligands has not been pursued further due to severe problems with product characterization as well as isolation.

Synthesis of complexes employing phenylene-bridged ligands

For the synthesis of these complexes, the same procedure as described previously has been used.

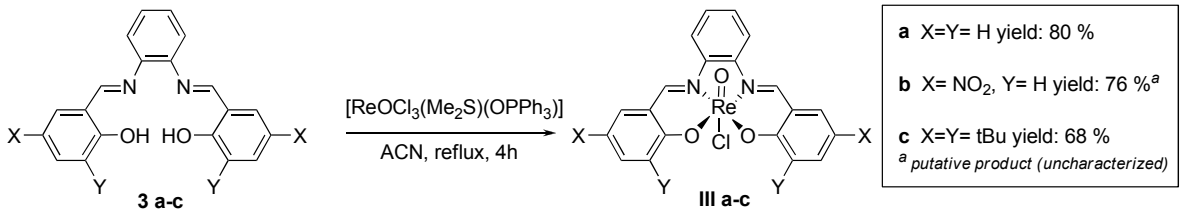

Figure 2.9.: Synthesis of symmetric complexes employing phenylene-bridged tetradentate Schiff base ligands.

A slight excess (2.1 equiv) of the respective ligand **3 a-c** (one equiv acts as base to neutralize the formed HCl) was dissolved or suspended (**3 b**) in acetonitrile. Subsequently one equiv of the metal precursor $[ReOCl_3(OPPh_3)(SMe_2)]$[102,103] was added and the reaction mixture heated to reflux temperature. After four hours of reaction time the reaction solution had turned dark red-brownish and a brown precipitate formed when ligands **3 a** or **3 b** were used. The precipitates were filtered of and washed with cold pentane to give **III a** and the putative product **III b** in yields from 76 to 80 %. Compound **III b** is insoluble in most standard laboratory solvents and only very little soluble in DMSO or DMF, preventing the recording of meaningful NMR-data.

The dark red solution resulting in the synthesis of **III c** was concentrated *in vacuo* and subsequently stored for several days at 5 °C until **III c** formed as dark red crystals in a yield of 68 %.

A similar approach with the still deeply brown reaction solution from the synthesis of **III a** led to dark red crystals of **III a**, suitable for single crystal X-ray diffraction analysis (vide infra). Despite the fact that all syntheses have been performed at atmospheric conditions with laboratory grade solvents (no additional drying operations were performed), all complexes were stored in a desiccator.

Compound **III c** has been fully characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy, EI-MS spectrometry and elemental analysis. Compound **III a** has been characterized by ^{1}H-NMR spectroscopy and EI-MS spectrometry. The ^{1}H-NMR spectra of **III a** and **III c** showed only one set of resonances for all imine and aromatic protons pointing towards symmetric compounds of structure type **A**. The published ^{1}H-NMR spectroscopic data of compound **III a** cannot be confirmed,[98] since two sets of proton resonances are described. Single crystal X-ray diffraction analysis confirmed compound **III a** as symmetric complex of structure type **A**, Figure 1.16. In the syntheses employing phenylene-bridged ligands, no isomer or dimer formation was observed.

Despite the fact that meaningful NMR-data could not be obtained for compound **III b**, EI-MS data points to the complex formation as a peak with the correct isotope pattern for the $[ReOL]^{+}$-fragment is observable.

Experiments using our the precursor $[NBu_4][ReOCl_4]$ did not lead to complex formation.

Complexes **III a-c** can be assigned to structure type **A**, Figure 1.16 and therefore mark rare examples of symmetric oxorhenium(V) complexes employing a *trans*-$[OReCl]^{2+}$ moiety, accessible in bulk. The missing isomer formation matches with expectations since an asymmetric coordination of the rigid phenylene-bridged ligands is not possible.

2.3. Molecular structures

Molecular structure of [ReOCl(1 a)] (I a)

The molecular structure of **I a** has been determined due to significant deviations of observed from published[62] NMR-data. The X-ray diffraction analysis confirmed the compound as [ReOCl(1 a)]. The complex shows the asymmetric arrangement of structure type **B**, Figure 1.16, as observed in the monoclinic modification of this compound.[62] Whereas the Re-Ligand bond lengths are similar, the Re=O and Re-Cl bond lengths are elongated in the triclinic modification [e.g. Re-Cl published 2.390(1) Å, Re-Cl observed 2.4142(5) Å]. The molecular view is given in Figure 2.10, selected bond lengths are given in Table 2.2, a full summary of refinement parameters is provided in the appendix.

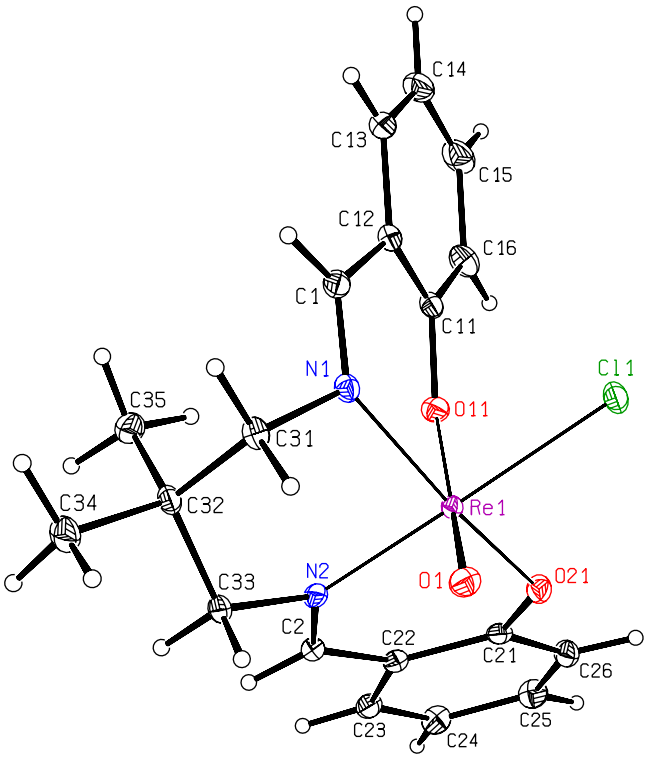

Figure 2.10.: ORTEP[110] plot of **III a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50 % probability level. The H atoms are drawn with arbitrary radii.

Molecular structure of [ReOCl(2 c)] (II c)

The X-ray diffraction analysis of **II c** confirmed the compound as [ReOCl(2 c)]. The tetradentate ligand occupies an equatorial plane in the octahedral surrounding of the Re atom, the complex exhibits structure type **A**, Figure 1.16. The Re(=O)Cl group together with the coordinating O atoms are disordered over two orientations [site occupation factors of 0.5985(11) and 0.4015(11)]. The cyclohexane ring is also disordered over two orientations corresponding to the R,R- and to the S,S-enantiomers [s.o.f.s of 0.651(7) and 0.349(7)], respectively. Since the space group is P -1 the substance is a racemate. The molecular view is given in Figure 2.11, selected bond lengths are given in Table 2.2, a full summary of refinement parameters is provided in the appendix.

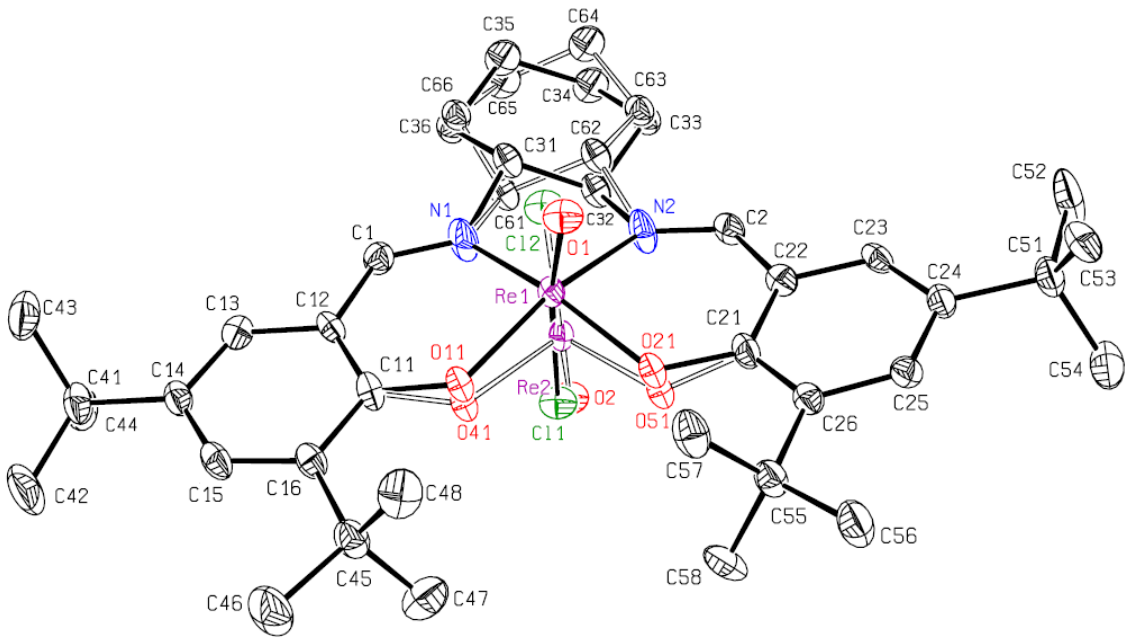

Figure 2.11.: ORTEP[110] plot of **IIc** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50 % probability level. The bonds to atoms with site occupation factors less than 0.5 [e.g. 0.4015(11)] are plotted with open bonds. The H atoms were omitted for clarity reasons.

Molecular structure of [ReOCl(3 a)] (III a)

The X-ray diffraction analysis of **III a** confirmed the compound as the solvent-free complex [ReOCl(3 a)]. The octahedral coordination of the Re atom is built by the square-planar environment of the tetradentate ligand [Re-O 1.980(4)-1.981(4)Å, Re-N 2.060(5)Å] and the trans oriented oxo and chloro ligands which are disordered [site occupation factors of 0.5780(11) and 0.4220(11)] over the two possible locations [Re=O 1.753(17)-1.754(17)Å, Re-Cl 2.506(5)Å, 2.481(7)Å] as observed in the chloroform solvate.[98] Due to the space filling conditions the Re atoms as well as the coordinating adjacent atoms are disordered, too. The compound is of structure type **A**, Figure 1.16. The Re-Ligand bond lengths in the solvent free compound are similar to the chloroform-solvate, but the Re=O bond length is shortened [Re=O published 2.568(1) Å, Re=O observed 2.506(5) Å] whereas the Re-Cl bond is elongated [Re-Cl published 1.665(3) Å, Re-Cl observed 1.753(17) Å]. The molecular view is given in Figure 2.12, selected bond lengths are given in Table 2.2, a full summary of refinement parameters is provided in the appendix.

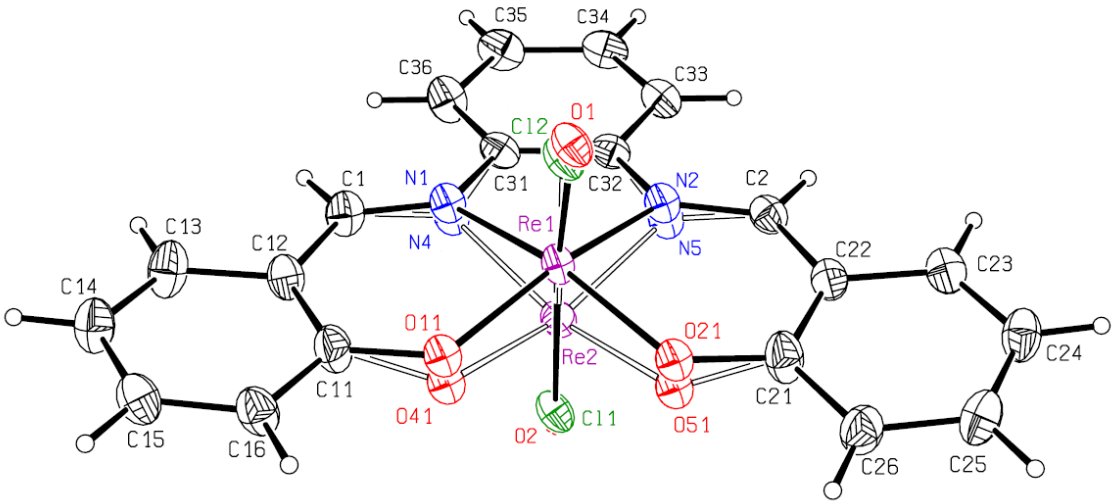

Figure 2.12.: ORTEP[110] plot of **III a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50 % probability level. The H atoms are drawn with arbitrary radii. Bonds to atoms with site occupation factors less than 0.5 [e.g. 0.4220(11)] are plotted with open bonds.

Molecular structure of [{ReO(1 a)}$_2$(μ-O)] (IV)

The crystal structure analysis of **IV** confirmed the compound as [{ReO(1 a)}$_2$(μ-O)] methylenchloride solvate (1:4). The molecules are almost centrosymmetric but show significant deviations (e.g. the bonds C32-C34 and C62-C64 are both directed parallel to Re1-O1); the Re-O-Re bridge is slightly bent [177.16(13)°]. The solvent-free Re-complex crystallizes in P21/c with the bridging O atom at an inversion centre.[111] The molecular view is given in Figure 2.13, selected bond lengths are given in Table 2.2, a full summary of refinement parameters is provided in the appendix.

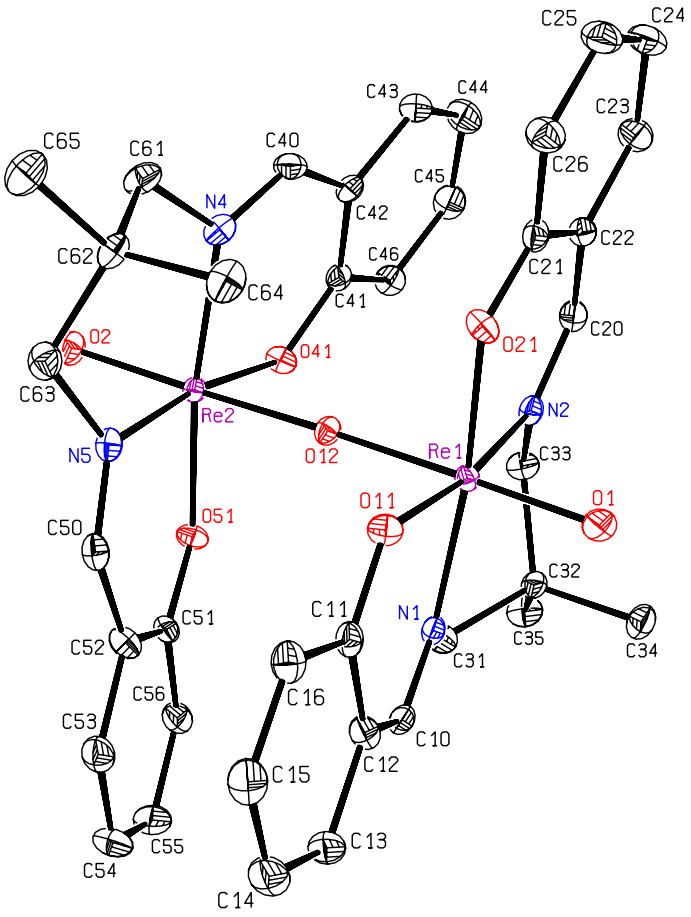

Figure 2.13.: ORTEP[110] plot of **IV** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50 % probability level. The H atoms and solvate molecules were omitted for clarity reasons.

Table 2.2 shows a comparison of selected bond lengths of the complexes **I a**, **II c**, **III a** and **IV**. For complexes **II c** and **III a** the bonds to atoms with higher site occupation factors are tabulated, for complex **IV** the bond lenghts for one half-unit are given exemplarily.

Table 2.2.: Comparison of selected bond lengths in complexes **I a**, **II c**, **III a** and **IV** in Å.

	I a	**II c**	**III a**	**IV**
Re-O1	1.6888(16)	1.664(9)	1.753(17)	1.708(2)
Re-O11	1.9803(16)	1.983(4)	1.981(4)	2.0203(19)
Re-O21	2.0071(15)	1.993(4)	1.980(4)	2.015(2)
Re-N1	2.0924(18)	2.014(4)	2.060(5)	2.110(2)
Re-N2	2.0923(18)	2.077(4)	2.060(5)	2.116(2)
Re-Cl1	2.4142(5)	2.538(5)	2.506(5)	-
Re-O12	-	-	-	1.920(2)

As depicted in Table 2.2, the Re-Cl bond is elongated in the symmetric complexes **II c** and **III a** (structure type **A**, Figure 1.16) in comparison to the asymmetric complex **I a** (structure type **B**, Figure 1.16). In complex **III a** the Re=O bond length is elongated as well.

Furthermore the O=Re-Cl bond angle shows significant deviations from 180° in the molecules of structure type **A**, Figure 1.16. The O=Re-Cl bond angles are 171.7(3)° and 169.2(10)° for **II c** (two disordered molecules) as well as 172.9(6)° and 174.2(9)° for **III a** (two disordered molecules). This is in agreement with the favorable *cis*-O=Re-Cl arrangement as well as the higher rigidity of phenylene-bridged ligands.

2.4. Olefin epoxidation catalysis

The complexes **I a**, **I b**, an isomeric mixture of **I c**/**I c'** as well as complexes **III a-c** have been tested as catalysts in the epoxidation of *cis*-cyclooctene (cyOct) with tert-butylhydrogenperoxide (TBHP, 5.5 M in decane) and hydrogen peroxide (H_2O_2, 30 % in H_2O), respectively, as oxidants.

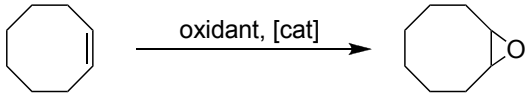

Figure 2.14.: Test-reaction for epoxidation catalysis.

The chosen standard conditions were 1 mol % catalyst, 3 equiv of oxidant, in $CHCl_3$ at 50 °C. The results of the epoxidation experiments with TBHP are summarized in Table 2.3.

Table 2.3.: Epoxide yields after one and six hours of reaction time.[a]

catalyst	epoxide yield [%] t = 1h	epoxide yield [%] t = 6h	published yield[62] t = 10h
I a	17	50	60
I b	26	51	-
I c + I c'	13	41	59
III a	12	12	-
III b	64	65	-
III c	26	56	-
3 b	-	6	-

[a] Conditions: 1 mol % catalyst, 3 equiv TBHP, $CHCl_3$, 50 °C.

Catalysis experiments have been performed by the use of a Heidolph parallel synthesizer. Aliquots of the reaction mixture have been withdrawn after time intervals of one hour, three hours and six hours by the use of a microliter pipette.

The samples have subsequently been quenched with a mixture of MnO_2 and dry $MgSO_4$, diluted with ethyl acetate and centrifuged. Aliquots of those dilutions have been transferred into GC-vials and again diluted with ethyl acetate. Conversions have been monitored via GC-MS measurements, where the respective quantities of cyOct and cyOxide were determined via integration of the peak areas and subsequent normalization against an internal standard (mesitylene). Since **III b** remains uncharacterized, a control experiment with the free ligand **3 b** has been performed.

In contrast to previous observations with bidentate pyrazolate-based ligands,[68] a comparison of catalysts **I a** and **I b** activities showed that the utilization of electron withdrawing substituents at the ligand only lead to a negligible performance increase. The conversion rates of catalysts **I a** and **I c** are within error margins consistent with literature.[62]

Surprising is the low catalytic activity of catalyst **III a** in comparison to its substituted analogues. A possible explanation therefore can be given by follow-up reactions which are in accordance with observed mass balance values of 90 % after one hour resp. 70 % after six hours. These values correspond to a 10-30 % loss of GC-detectable substance. Whereas catalyst **III b** shows a high conversion after a short period, the overall performance of catalysts **III b** and **III c** is of similar order of magnitude. Since the exact composition of catalyst **III b** is unclear, the results have to be handled with precaution. Nevertheless, a control experiment without rhenium but employing the free ligand **3 b** showed only minute conversions whith TBHP (< 10 %) substantiating the formation of a catalytically active species (mono- or dimeric) within the synthesis of compound **III b**. Epoxidation experiments employing hydrogen peroxide as oxidant showed only minute conversions to cyclooctane oxide (**I a-c** < 10 %, **III a-c** no conversion).

Diagrams showing the catalytic conversions as well as the mass balance of the catalysis experiments with **III a** and **III b** and TBHP as oxidant are provided in the following figures 2.15 and 2.16. Similar diagrams for catalysts **I a-c** and **III c** are provided in the appendix.

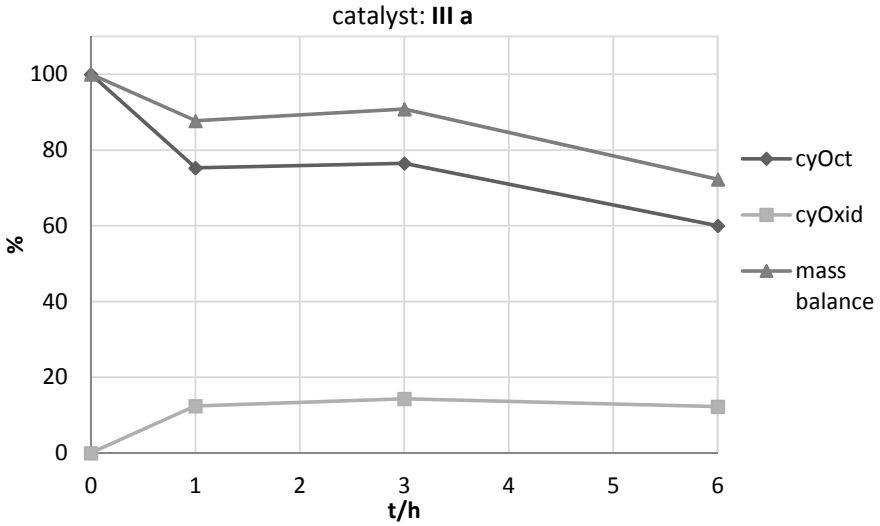

Figure 2.15.: Conversion and mass balance in cyOct epoxidation with **III a**, standard conditions.

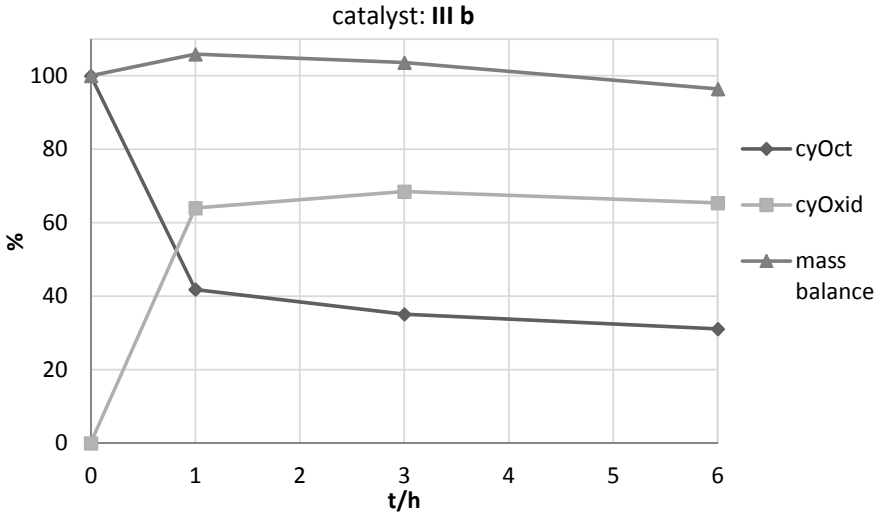

Figure 2.16.: Conversion and mass balance in cyOct epoxidation with **III b**, standard conditions.

The substituted phenylene-bridged complexes **III b** and **III c** led to higher epoxide yields than their more flexible alkyl-bridged counterparts **I b** and **I c**, probably due to the different structure type. A satisfying explanation for the unexpected low activity of complex **III a** in comparison to all other tested compounds cannot be provided yet and has to be investigated in detail.

2.5. Perchlorate reduction experiments

Compounds **I a**, **I b**, and **III a-c** have been tested as catalysts for the reduction of perchlorate with an organic sulfide as oxygen acceptor (cf. Figure 2.17). The reactions were performed in an NMR tube under the following conditions: 0.003 M catalyst, 0.092 M $LiClO_4$ and 0.5 M diphenylsulfide in a mixture of CD_3CN/D_2O (95:5 v/v) at room temperature. A control experiment without catalyst has been included in the series. After 48 hours a ^{1}H-NMR spectrum of each reaction mixture was recorded. Subsequently the yield of formed diphenylsulfoxide has been determined via integration of the respective peak areas (Ph_2S in CD_3CN δ: 7.24-7.33 (m, 10H) ppm and Ph_2S=O in CD_3CN δ: 7.65-7.75 (m, 4H), 7.43-7.53 (m, 6H) ppm).

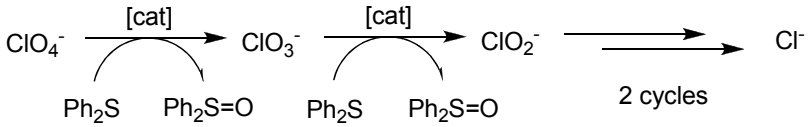

Figure 2.17.: Catalytic reduction of perchlorate with Ph_2S as oxygen acceptor.

As excess of disulfide was used, the conversions were calculated based on the limiting amount of perchlorate. Table 2.4 summarizes the calculated results of the reduction experiments.

Table 2.4.: Catalytic reduction of ClO_4^- employing compounds **I a**, **I b** and **III a-c** as catalysts.

catalyst	Ph_2S conversion [%]	$LiClO_4$ reduction [%]
I a	3.8	5.2
I b	15.9	21.6
III a	-	-
III b[a]	-	-
III c	17.4	23.6

[a] insoluble in CD_3CN/D_2O (95:5 v/v)

As an example, the ^{1}H-NMR spectrum of a sample of the catalytic reaction using **III c** in CD_3CN/D_2O (95:5 v/v) is given in Figure 2.18.

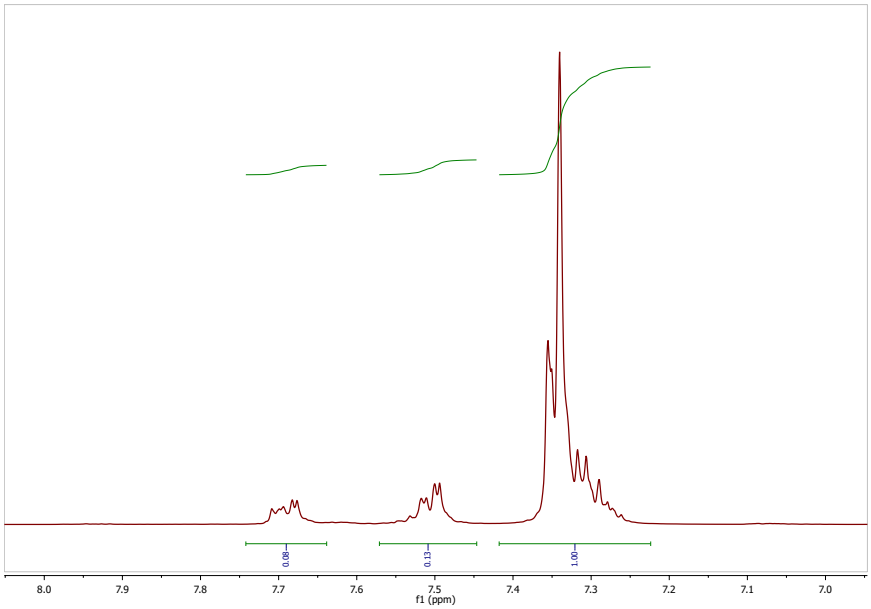

Figure 2.18.: ^{1}H-NMR of the perchlorate reduction experiment with **III c** as catalyst.

Abu Omar and coworkers published a catalyst for perchlorate reduction employing ligand **1 a** with a diphenylsulfoxide yield of 57 % after 38 hours.[26] The sulfoxide yield by the use of compound **I a** is lower compared to this published result. Since our group recently discovered significant reactivity differences of stereoisomers of oxorhenium(V) compounds, a possible explanation would be the use of a different geometric isomer. The compound previously published by Abu-Omar and coworkers (structure type **D**, Figure 1.16) as well as **I a** (structure type **B**, Figure 1.16) are depicted in Figure 2.19.

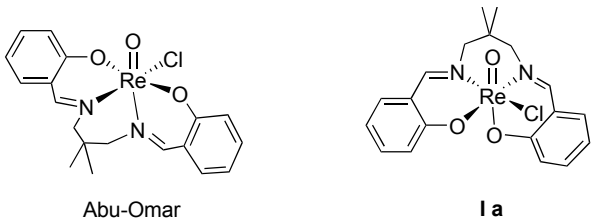

Figure 2.19.: Catalyst published by Abu Omar and coworkers[26] and compound **I a**.

Nevertheless, a substantiated explanation for their significantly higher sulfoxide yield cannot be given at this point. It was also somewhat unexpected that the amount of catalyst as published did not dissolve completely in the reaction solvent during the experiment.

The nitro-substituted compound **I b** has significantly higher activity in the reduction of perchlorate, indicating that a ligand modification with electron withdrawing groups provides a reactivity increase of the distinctive catalyst. The inactivity of the respective phenylene-bridged nitro-substituted compound could be a consequence of its almost complete insolubility in the chosen reaction medium.

Our finding, that the complex employing a di-*tert*-butyl-substituted phenylene-bridged ligand (**III c**) showed significant activity in the reduction of perchlorate is in contrast to our expectations. As a consequence it is highly likely, that a reduction of perchlorate catalyzed by complexes with tetradentate ligands employs a different mechanism than the one proposed for oxazoline-based compounds, since a formation of asymmetric intermediates in general and the formation of a *cis*-dioxo species is not possible in our case (cf. Figure 2.20).[78,79]

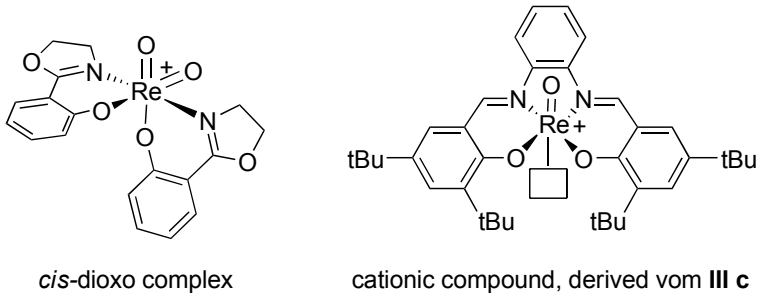

Figure 2.20.: Oxazoline-based cationic *cis*-dioxorhenium species and a cationic species derived from **III c**.

2.6. Conclusion and outlook

The targeted synthesis of rhenium(V)oxo complexes with specific geometries has been achieved by using tetradentate Schiff base ligands featuring different rigidities. A modification of published synthetic procedures reduced the formation of μ-oxo bridged dimeric species. Whereas alkyl-bridged ligands coordinate predominantly asymmetric (synthesized complexes **I a-c**), the formation of a second, symmetric isomer (**I a'-c'**) could be observed in varying quantities. This is in contrast to previous publications.[62] Isolation of pure (**I a'-c'**) has been futile. Phenylene-bridged complexes, in contrast, coordinate only all-equatorial (synthesized complexes **III a-c**) and mark therefore rare examples of symmetric oxorhenium(V) complexes employing a *trans*-$[OReCl]^{2+}$ moiety. A synthesis using a cyclohexyl-bridged ligand was only successful with ligand **2 c** and led to the formation of two monomeric compounds (symmetric **II c** and asymmetric **II c'**). The formation of dimeric species was also observed within this synthesis. Syntheses with ligands **2 a** and **2 b** only led to uncharacterized, probably dimeric compounds.

The new compounds **I b** and **III b, c** as well as the known complexes **I a** and **III a** have been tested in the epoxidation of cyclooctene and the reduction of perchlorate. None of them showed significant catalytic activity in epoxidation reactions with H_2O_2 as oxidant. Nevertheless, epoxide formation was observed by the use of TBHP as oxidant in moderate yields. Interestingly, the substituted phenylene bridged complexes **III b** and **III c** led to higher epoxide yields than the more flexible alkyl-bridged compounds **I b** and **I c**, probably due to the different structure type. A use of compound **III a** as catalyst in the epoxidation of cyclooctene only led to minor epoxide yields. Complex **III a** showed an unexpected low activity in comparison to all other tested compounds, a satisfying explanation therefore cannot be provided yet and has to be investigated in detail.

Similar results in the reduction of perchlorate as published for a compound stereoisomeric to **I a** (cf. Figure 2.19), could not be achieved by the use of **I a**.[26] It furthermore remains unclear which compound has been used by Abu-Omar and coworkers since they referenced their compound to a complex first published by Herrmann and coworkers, which corresponds to **I a**.[62] Interestingly, the published conditions for the catalytic experiments did not lead to a complete dissolution of the catalyst.[26] The quantities of reduced perchlorate in a catalysis using **I b** or **III c** were significantly higher than the quantities observed for **I a** but still remain below published values.[26] For complex **III b** no conversion could be observed which is likely a consequence to its total insolubility in the reaction medium.

The surprisingly high catalytic activity of compound **III c** is in contrast to our expectations and strongly suggests a mechanism different to the published one (for complexes employing oxazoline-based ligands).[78,79]

Summing up, especially symmetric monomeric compounds of structure type **A** (all-equatorial ligand coordination) are promising versatile catalysts for OAT-reactions. Therefore a further investigation especially of alkyl- and cyclohexyl-bridged symmetric compounds would be a worthy field of research.

Chapter 3: Experimental section

3.1. General

All experiments were performed under atmospheric conditions with standard laboratory equipment at the Institute of Chemistry, University of Graz, Schuberstraße 1 unless specified otherwise. Used chemicals and solvents were commercially available and have been used without further purification or drying operations.

The used Re-precursors $[NBu_4][ReOCl_4]$[101] and $[ReOCl_3(OPPh_3)(SMe_2)]$[103] were synthesized following published routes.

^{1}H- and ^{13}C-NMR spectra have been recorded with a Bruker Optics instrument (300 MHz). Chemical shifts are denoted in ppm and referenced to residual solvent protons. Peak multiplicity is denoted as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quadruplet (q) and multiplet (m). Used deuterated solvents are specified at the distinctive data sets.

Electron impact mass spectroscopy measurements (EI-MS) have been performed with a mass spectrometer type Agilent 5973 MSD with push rod. Results are denoted as cationic mass peaks, unit is the according ions mass/charge ratio. Infrared spectroscopy measurements have been performed using a Bruker Optics ALPHA fourier transform infrared-spectrometer (FT-IR) with an attenuated total reflection (ATR) diamond probe head.

Gas chromatography mass spectroscopy measurements (GC-MS) have been performed with a gas chromatograph type Agilent 7890 A (column type Agilent 19091J-433), coupled to a mass spectrometer type Agilent 5975 C.

Elemental analyses (C,H,N) were carried out by the Microanalytical Laboratory, Department of Chemistry, University of Vienna.

3.2. X-ray crystal structure analysis

Structure determination of complexes **I a**, **II c**, **III a** and **IV** via X-Ray diffraction analysis has been performed on a Bruker-AXS Smart Apex CCD diffractometer. All the measurements were performed using graphite-monochromatized Mo K-α radiation at 100K. The structures were solved by direct methods (SHELXS-97)[112,113] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[112,113] Experimental details on the single crystal X-ray diffraction analysis of the distinctive complexes are provided in the appendix.

3.3. Ligand synthesis

General

The ligands **1 a-c, 2 a-c** and **3 a-c** were synthesized according to known procedures with slight modifications.[62] Two equivalents of the respective 2-hydroxybenzaldehyde derivative have been dissolved in ethanol. Subequently one equivalent of the diamine has been added and the reaction mixture stirred for several hours.

After reduction of the solvent to a small volume *in vacuo*, the desired product was obtained by filtration and subsequent washing with a small amount of cold ethanol in yields from 77 to 92 %.

The ^{1}H-NMR shifts of the respective ligands matched published values (with the exception of **3 b** as discussed previously) and are given for reasons of comparison only.[94,95,97,114] The new compound **1b** has been fully characterized.

Proton NMR spectrum of 1 a

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 13.56 (s, 2H, OH), 8.34 (s, 2H, CH=N), 7.32 (t, 2H, Ar-H), 7.28-7.25 (dd, 2H, Ar-H), 6.97 (d, 2H, Ar-H), 6.91-6.86 (td, 2H, Ar-H), 3.50 (s, 4H, CH_2), 1.08 (s, 6H, CH_3) ppm.

Synthesis of 1 b

According to the general procedure, 2-hydroxy-5-nitrobenzaldehyde (2.0 equivalents, 365 mg, 2.20 mmol) and 2,2-dimethyl-1,3-propane-diamine (1.0 equivalent, 113 mg, 1.10 mmol) were mixed in 10 mL of ethanol and stirred for two hours at room temperature to give **1 b** (339 mg, 77 %) as yellow powder.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 14.66 (s, 2H, OH), 8.43 (s, 2H, CH=N), 8.28-8.21 (m, 4H, Ar-H), 7.02 (d, 2H, Ar-H), 3.58 (s, 4H, CH_2), 1.14 (s, 6H, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 168.19, 165.12, 139.51, 128.43, 128.14, 118.73, 117.20 (Ar and CH=N), 67.27(CH_2), 36.54 (q-C), 24.31(CH_3) ppm.

EI-MS: m/z 400 [M^+]

Anal. calcd. for $C_{19}H_{20}N_4O_6$ (400.39): C 57.00, H 5.03, N 13.99; found: C 56.74, H 5.13, N 13.89 %.

Proton NMR spectrum of 1 c

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 13.85 (s, 2H, OH), 8.36 (s, 2H, CH=N), 7.39 (d, 2H, Ar-H), 7.10 (d, 2H, Ar-H), 3.48 (s, 4H, CH_2), 1.46 (s, 18H, tBu) 1.31 (s, 18H, tBu), 1.10 (s, 6H, CH_3) ppm.

Proton NMR spectrum of 2 a

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 13.32 (s, 2H, OH), 8.26 (s, 2H, CH=N), 7.27-7.21 (m, 2H, Ar-H), 7.15 (dd, 2H, Ar-H), 6.89 (d, 2H, Ar-H), 6.79 (td, 2H, Ar-H), 3.34-3.30 (m, 2H, CH), 1.97-1.87 (m, 4H, CH_2), 1.78-1.67 (m, 2H, CH_2), 1.54-1.44 (m, 2H, CH_2) ppm.

Proton NMR spectrum of 2 b

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 14.29 (bs, 2H, OH), 8.35 (s, 2H, CH=N), 8.15 (m, 4H, Ar-H), 6.96 (m, 2H, Ar-H), 3.46 (m, 2H, CH), 2.04-1.48 (m, 8H, CH_2) ppm.

Proton NMR spectrum of 2 c

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 13.71 (s, 2H, OH), 8.30 (s, 2H, CH=N), 7.29 (d, 2H, Ar-H), 6.98 (d, 2H, Ar-H), 3.33-3.30 (m, 2H, CH), 1.96-1.86 (m, 4H, CH_2), 1.78-1.68 (m, 2H, CH_2), 1.55-1.41 (m, 2H, CH_2), 1.41 (s, 18H, tBu) 1.23 (s, 18H, tBu) ppm.

Proton NMR spectrum of 3 a

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 13.06 (s, 2H, OH), 8.64 (s, 2H, CH=N), 7.40-7.34 (m, 6H, Ar-H), 7.27-7.23 (m, 2H, Ar-H), 7.06 (d, 2H, Ar-H), 6.93 (td, 2H, Ar-H) ppm.

Proton NMR spectrum of 3 b

^{1}H-NMR (DMSO-d^6, 300 MHz) δ: 13.85 (s, 2H, OH), 9.12 (s, 2H, CH=N), 8.23 (dd, 2H, Ar-H), 7.74-7.71 (m, 3H, Ar-H), 7.34-7.31 (m, 3H, Ar-H), 7.16 (d, 2H, Ar-H) ppm.

Proton NMR spectrum of 3 c

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 13.55 (s, 2H, OH), 8.67 (s, 2H, CH=N), 7.44 (d, 2H, Ar-H), 7.34-7.29 (m, 2H, Ar-H), 7.27-7.22 (m, 4H, Ar-H), 1.44 (s, 18H, tBu) 1.33 (s, 18H, tBu) ppm.

3.4. Synthesis of coordination compounds

General procedure

For the synthesis of the coordination compounds 2.1 equivalents of the respective ligand (**1-3 a-c**) have been dissolved in acetonitrile. Subsequently one equivalent of the rhenium precursor [$ReOCl_3(OPPh_3)(SMe_2)$] has been added and the reaction mixture stirred for four hours at reflux temperature. Formed precipitate has been filtered and washed with cold pentane. Recrystallization from acetonitrile gave overall yields of 59 to 80 %.

The ^{1}H-NMR shifts of the known compound **I c** are in accordance to previous publications and are given for reasons of comparison only. The known compounds **I a** and **III a** exhibit a different ^{1}H-NMR spectrum than previously published,[62,98] the observed ^{1}H-NMR shifts are given subsequently. The dimer **IV** has been characterized by ^{1}H-NMR spectroscopy. For the not isolated compounds **I a'**, **I b'**, **II c** and **II c'**, ^{1}H-NMR shifts are provided. A characterization of **III b** was not successful up to now. The new compounds **I b** and **III c** have been fully characterized (with the exception of an elemental analysis for **I b**).

Synthesis of [ReOCl(1 a)] (I a)

According to the general procedure, **1 a** (2.1 equivalents, 50 mg, 0.17 mmol) and [$ReOCl_3(OPPh_3)(SMe_2)$] (1.0 equivalent, 50 mg, 0.08 mmol) were mixed in 25 mL of ACN and stirred for four hours at reflux temperature. The resulting green solution has been reduced *in vacuo* and stored for several days at 5 °C whereupon a mixture of **I a** and **I a'** in a ratio of 4:1 as deep green crystals was obtained. (36 mg, 80 %) Pure **I a** has been obtained by recrystallization from ACN (8 mg, 17 %).

I a : ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.84 (s, 1H, CH=N), 7.59 (m, 1H, Ar-H), 7.46 (s, 1H, CH=N), 7.44 (m, 1H, Ar-H), 7.31-7.24 (m, 2H, Ar-H), 7.16 (m, 1H, Ar-H), 7.05 (m, 1H, Ar-H), 6.93 (m, 1H, Ar-H), 6.82 (t, 1H, Ar-H), 4.45-4.34 (dd, 2H, CH_2), 3.74 (m, 2H, CH_2), 1.16 (s, 3H, CH_3), 0.92 (s, 3H, CH_3) ppm.

Literature data is inconsistent with the here reported data (see discussion on page 27).[62]

^{1}H-NMR (CD_3CN, 300 MHz) δ: 8.01 (s, 1H, CH=N), 7.63 (s, 1H, CH=N), 7.61 (m, 1H, Ar-H), 7.42 (m, 2H, Ar-H), 7.18-7.15 (m, 2H, Ar-H), 7.09 (td, 1H, Ar-H), 6.88 (t, 1H, Ar-H), 6.72 (d, 1H, Ar-H), 4.53 (d,1H, CH_2), 4.18 (d, 1H, CH_2), 3.86-3.69 (dd, 2H, CH_2), 1.11 (s, 3H, CH_3), 0.82 (s, 3H, CH_3) ppm.

EI-MS: m/z 546 [M^+], 511 [M^+-Cl]

*Upon substraction of the resonances for compound **I a**, the following chemical shifts can be assigned to the symmetric isomer **I a'**.*

I a' : ^{1}H-NMR (CD_3CN, 300 MHz) δ: 8.04 (s, 2H, CH=N), 7.54 (m, 2H, Ar-H), 7.46 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 6.63 (t, 2H, Ar-H), 4.63 (d, 2H, CH_2), 3.91 (d, 2H, CH_2, 1.27 (s, 3H, CH_3), 0.82 (s, 3H, CH_3) ppm.

Synthesis of [{ReO(1 a)}$_2$(μ-O)] (IV)

Following a published procedure,[62] **1 a** (2.0 equivalents, 155 mg) and [NBu_4][$ReOCl_4$] (1.0 equivalents, 147 mg) have been dissolved in 10 mL of ethanol and stirred for three hours at reflux temperature. The resulting green precipitate was filtered off and washed with cold pentane to obtain a mixture of **I a**, **I a'** and **IV** as a green crystalline powder (93 mg, 68 % calc. with respect to the monomers molecular weight). Recrystallization from CH_2Cl_2 resulted in green crystalline plates (**I a**) accompanied by large dark green rods (**IV**) both suitable for single crystal X-ray diffraction analysis.

*Crystal picking led to pure compound **IV** in a quantity suitable for ^{1}H-NMR spectroscopy.*

IV : ^{1}H-NMR (CD_3CN, 300 MHz) δ: 8.20 (s, 4H, CH=N), 7.55 (m, 4H, Ar-H), 7.45 (m, 4H, Ar-H), 7.10 (d, 4H, Ar-H), 6.89 (t, 4H, Ar-H), 4.39 (d, 4H, CH_2), 3.97 (d, 4H, CH_2, 1.14 (s, 6H, CH_3), 1.03 (s, 6H, CH_3) ppm.

Synthesis of [ReOCl(1 b)] (I b)

According to the general procedure, **1 b** (2.1 equivalents, 64 mg, 0.17 mmol) and [$ReOCl_3(OPPh_3)(SMe_2)$] (1.0 equivalent, 50 mg, 0.08 mmol) were dissolved in 25 mL of ACN and stirred for four hours at reflux temperature.

The resulting bright green solution was reduced *in vacuo* and stored for several days at 5 °C whereupon a mixture of **I b** and **I b'** in a ratio of 3:1 (33 mg, 65 %) was obtained as dark green crystals. Pure **I b** was obtained by recrystallization from ACN (10 mg, 20 %).

I b : ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 8.43 (dd, 1H, Ar-H), 8.31 (d, 1H, Ar-H), 8.25 (d, 1H, Ar-H), 7.97 (dd, 1H, Ar-H), 7.81 (s, 1H, CH=N), 7.49 (s, 1H, CH=N), 7.45 (d, 1H, Ar-H), 6.86 (d, 1H, Ar-H), 4.43 (q, 1H, CH_2), 4.00-3.86 (dd, 2H, CH_2), 1.25 (s, 3H, CH_3), 0.88 (s, 3H, CH_3) ppm.

^{13}C-NMR (DMSO-d^6, 75 MHz, Cq obscured) δ: 189.04, 165.73, 139.77, 133.37, 130.73, 124.36, 122.21, 118.49 (CH=N, Ar), 35.72, 25.68 (CH_2), 24.22, 22.98 (CH_3) ppm.

EI-MS: m/z 636 [M^+], 601 [M^+-Cl]

*Upon substraction of the resonances for compound **I b**, the following chemical shifts can be assigned to the symmetric isomer **I b'**.*

I b' : ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 8.57 (d, 1H, Ar-H), 8.42 (m, 2H, Ar-H), 8.37 (s, 2H, CH=N), 7.99 (d, 1H, Ar-H), 7.13 (d, 2H, Ar-H), 4.56 (d, 2H, CH_2), 4.09 (d, 2H, CH_2, 1.36 (s, 3H, CH_3), 1.27 (s, 3H, CH_3) ppm.

Synthesis of [ReOCl(1 c)] (I c)

According to the general procedure, **1 c** (2.1 equivalents, 86 mg, 0.17 mmol) and [$ReOCl_3(OPPh_3)(SMe_2)$] (1.0 equivalent, 50 mg, 0.08 mmol) were dissolved in 25 mL of ACN and stirred for four hours at reflux temperature. The resulting brownish solution was reduced *in vacuo* and stored for several days at 5 °C whereupon a mixture of **I c** and **I c'** (33 mg, 59 %) was obtained as a brown microcrystalline powder.

I c : ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.76 (s, 1H, CH=N), 7.67 (d, 1H, Ar-H), 7.42 (s, 1H, CH=N), 7.21 (d, 1H, Ar-H) 7.13 (d, 1H, Ar-H), 7.00 (d, 1H, Ar-H), 4.38 (dd, 2H, CH_2), 3.59 (dd, 2H, CH_2), 1.55 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$), 1.12 (s, 9H, $C(CH_3)_3$), 1.11 (s, 3H, CH_3), 0.89 (s, 3H, CH_3) ppm.

EI-MS: m/z 771 [M^+], 736 [M^+-Cl]

These data are consistent to literature.[62]

Synthesis of [ReOCl(2 c)] (II c)

According to the general procedure, **2 c** (2.1 equivalents, 88 mg, 0.17 mmol) and $[ReOCl_3(OPPh_3)(SMe_2)]$ (1.0 equivalent, 50 mg, 0.08 mmol) were mixed in 25 mL of ACN and stirred for four hours at reflux temperature. The resulting dark brown solution was concentrated *in vacuo* and stored for two weeks at 5 °C whereupon a mixture of **V** and **VI** was obtained as green-brownish microcrystalline powder (19 mg, 31 %). The residual dark solution was again stored for one week at 5 °C to obtain a mixture of **II c** and **II c'** as dark brown crystals (21 mg, 34 %). Recrystallization of the second fraction from Et_2O/ACN gave orange crystalline plates of **II c** suitable for single crystal X-ray diffraction analysis.

II c: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 8.92 (s, 1H, CH=N), 8.65 (s, 1H, CH=N), 7.65 (d, 2H, Ar-H), 7.12 (t, 2H, Ar-H), 4.32 (t, 1H, CH), 3.68 (t, 1H, CH), 2.09 (m, 2H, CH_2), 1.43-1.81 (m, 6H, CH_2), 1.55 (s, 9H, $C(CH_3)_3$), 1.54 (s, 9H, $C(CH_3)_3$), 1.31 (s, 18H, $C(CH_3)_3$) ppm.

EI-MS: m/z 748 [M^+-Cl]

*Upon substraction of the resonances for compound **II c**, the following chemical shifts can be assigned to the symmetric isomer **II c'**.*

II c': ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 8.53 (s, 1H, CH=N), 7.94 (s, 1H, CH=N), 7.78 (d, 1H, Ar-H), 7.39 (d, 1H, Ar-H), 7.31 (d, 1H, Ar-H), 7.05 (d, 1H, Ar-H), 4.03 (t, 1H, CH), 3.05 (t, 1H, CH), 2.88 (dd, 2H, CH_2), 2.71 (dd, 2H, CH_2), 2.57 (m, 2H, CH_2), 2.09 (m, 2H, CH_2), 1.63 (s, 9H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 1.26 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$) ppm.

Synthesis of [ReOCl(3 a)] (III a)

According to the general procedure, **3 a** (2.1 equivalents, 54 mg, 0.17 mmol) and $[ReOCl_3(OPPh_3)(SMe_2)]$ (1.0 equivalent, 50 mg, 0.08 mmol) were dissolved in 25 mL of ACN and stirred for four hours at reflux temperature. The formed precipitate was filtered off and washed with cold pentane to give **III a** (35 mg, 80 %) as a red brownish powder. Concentration of the remaining reaction solution *in vacuo* and subsequent crystallization at 5 °C for several days gave dark red crystals suitable for single crystal X-ray diffraction analysis.

^{1}H-NMR (DMSO-d^6, 300 MHz) δ: 10.28 (s, 2H, CH=N), 8.48 (m, 2H, Ar-H), 8.05 (d, 2H, Ar-H), 7.87 (t, 2H, Ar-H), 7.74 (m, 2H, Ar-H), 7.42 (d, 2H, Ar-H), 7.18 (t, 2H, Ar-H) ppm.

Literature data is inconsistent with the here reported data (see discussion on page 34).[98]

EI-MS: m/z 552 [M^+], 517 [M^+-Cl]

Synthesis of [ReOCl(3 c)] (III c)

According to the general procedure, **3 c** (2.1 equivalents, 92 mg, 0.17 mmol) and $[ReOCl_3(OPPh_3)(SMe_2)]$ (1.0 equivalent, 50 mg, 0.08 mmol) were dissolved in 25 mL of ACN and stirred for four hours at reflux temperature. The resulting dark red solution was concentrated *in vacuo* and stored for several days at 5 °C to give **III c** (42 mg, 68 %) as dark red crystals.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.71 (s, 2H, CH=N), 7.92 (m, 2H, Ar-H), 7.78 (d, 2H, Ar-H), 7.48 (m, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 1.59 (s, 18H, $C(CH_3)_3$), 1.36 (s, 18H, $C(CH_3)_3$) ppm.

^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 164.84, 158.70, 142.88, 140.43, 137.31, 128.30, 127.43, 126.90, 119.93, 118.47 (Ar and CH=N), 35.25, 34.30 (q-C), 31.60, 29.55 ($C(CH_3)_3$) ppm.

EI-MS: m/z 776 [M^+], 741 [M^+-Cl]

Anal. calcd. for $C_{36}H_{46}ClN_2O_3Re$ (776.42): C 55.69, H 5.97, N 3.61; found: C 55.62, H 5.61, N 3.58 %.

3.5. Typical catalytic experiments

Catalytic epoxidation of cyclooctene

Epoxidation experiments were performed by the use of a Heidolph parallel synthesizer. The used conditions were: 1 mol % catalyst, 3 equiv. TBHP in 0.5 mL of $CHCl_3$ at 50 °C. Aliquot samples were withdrawn in given intervals and quenched with a mixture of MnO_2 and dry $MgSO_4$. The samples were subsequently diluted with ethyl acetate and analyzed with GC-MS. Substrate conversions and epoxide yields were calculated via integration of the peak areas and normalization to an internal standard (mesitylene).

Catalytic reduction of perchlorate

The reactions were performed in NMR tubes under the following conditions: 0.003 M catalyst, 0.092 M $LiClO_4$ and 0.5 M diphenylsulfide in a mixture of CD_3CN/D_2O (95:5 v/v) at room temperature. A control experiment without catalyst has been included in the series. After 48 hours an ^{1}H-NMR spectrum of each reaction mixture was recorded. The yield of formed diphenylsulfoxide has been determined via integration of the respective peak areas.

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Appendix A: Curriculum Vitae

Name	Niklas Zwettler
Address	Ruckerlberggürtel 19, 8010 Graz
Telephone	+43 676 964 92 66
E-Mail	niklas.zwettler@gmx.at
Marital status	unmarried
Date of birth	30.03.1988
Nationality	Austrian

Education

Oct. 2012 - present	Technical University of Graz, Master program "Chemistry"
Oct. 2010 - present	University of Graz, Bachelor program "Physics"
Oct. 2008 - June 2012	Technical University of Graz, Bachelor program "Chemistry" - graduated
Sept. 2002 - June 2007	Higher Technical College Kapfenberg, Subject area "Plastics and environmental engineering" - graduated with honors
Sept. 1998 - July 2002	Academic high school Bruck an der Mur
Sept. 1994 - July 1998	Primary school Körnerstraße I in Bruck an der Mur

Practical experience

Jan. 2008 - Sept. 2008	Bohler Forging GmbH & Co KG, Kapfenberg - Assistant to the project manager
Oct. 2008 - Mar. 2014	Bohler Forging GmbH & Co KG, Kapfenberg (part time) - REACH coordinator and environmental management
Aug. 2013 - Sept. 2013	Danish Technological Institute - Material sciences, IAESTE Trainee program
Nov. 2013 - Jun. 2014	University of Graz - Institute of Chemistry, Project work for master thesis - Inorganic Chemistry dept.

Military service (mandatory)

July 2007 - Dec. 2007	Discharge as "Gefreiter", equivalent to a PFC

Extracurricular activities

May 2011 - present	Students council for the subject area Physics - vice president
July 2014 - present	Faculty council, Faculty of Natural sciences, University of Graz - vice president
Oct. 2011 - June 2013	University council, Austrian National Union of Students at the University of Graz - representative

Additional skills

Languages	German: native speaker English: expert (written and spoken) equivalent C1 Russian: basic knowledge equivalent A1
IT skills	Windows, Linux, Office, C++ (working knowledge), Mathematica, ChemDraw

Appendix B: Supplementary Data

Experimental details on the X-ray diffraction analysis of I a

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH2 groups were refined with common isotropic displacement parameters for the same group and idealized geometry with approximately tetrahedral angles and C-H distances of 0.99 Å. The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms H1 and H2 were put at the external bisectors of the C-C-N angles at C-H distances of 0.95 Å and a common isotropic displacement parameter was refined for these H atoms. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C-C bond, and C-H distances of 0.98 Å. For 244 parameters final R indices of R1 = 0.0157 and wR^2 = 0.0409 (GOF = 1.220) were obtained. The largest peak in a difference Fourier map was 1.444e$Å^{-3}$.

Experimental details on the X-ray diffraction analysis of II c

The Re(=O)Cl group together with the co-ordinating O atoms are disordered over two orientations and were refined with site occupation factors [0.5985(11) and 0.4015(11), resp.] summing up to 1. The cyclohexane ring was also disordered over two orientations and was refined with s.o.f.s of 0.651(7) and 0.349(7), respectively. The same anisotropic displacement parameters were used for O and Cl in the Re(=O)Cl group, for the disordered O atoms, and for equivalent C atoms of the cyclohexane ring due to the

correlations of the displacement parameters. The equivalent bonds in these disordered parts were restrained to have the same lengths. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any additional constraints. The structure contains solvent accessible voids of approx. 72Å^3 in the centre of the unit cell. As the refinement of a disordered acetonitrile molecule resulted in a site occupation factor of only 0.121(12) the solvent molecule was entirely omitted. Since twinning was detected a twin matrix (-1 0 0 / 0 -1 0 / 0 0 1) was applied and a scale factor was refined [0.0123(4)] between the two unequal components. The H atoms of the tertiary C-H groups were refined with one common isotropic displacement parameter and all X-C-H angles equal at a C-H distance of 1.00 Å. The H atoms of the CH_2 groups of the cyclohexane ring were refined with a common isotropic displacement parameter and idealized geometry with approximately tetrahedral angles and C-H distances of 0.99 Å. The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl ring. The H atoms H1 and H2 were put at the external bisectors of the N=C-C angles at a C-H distance of 0.95 Å and a common isotropic displacement parameter was refined for these H atoms. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same tert-butyl group and idealized geometries with tetrahedral angles, enabling rotation around the C-C bond, and C-H distances of 0.98 Å. For 421 parameters final R indices of R1 = 0.0451 and wR2 = 0.0911 (GOF = 1.146) were obtained. The largest peak in a difference Fourier map was 0.798eÅ^{-3}.

Experimental details on the X-ray diffraction analysis of III a

Anisotropic displacement parameters were used for O and Cl in this Re(=O)Cl group and for the co-ordinating N and O atoms due to the correlations of the displacement parameters. The equivalent bonds in this disordered fragment were restrained to have the same lengths. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints.

Since twinning was detected, a twin matrix (-1 0 0 / 0 -1 0 / 0 0 1) was applied and a scale factor was refined [0.0166(5)] between the two unequal components. The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms H1 and H2 were put at the external bisectors of the C-C-N angles at C-H distances of 0.95 Å and a common isotropic displacement parameter was refined for these H atoms. For 252 parameters final R indices of R1 = 0.0483 and wR^2 = 0.1130 (GOF = 1.342) were obtained. The largest peak in a difference Fourier map was 1.385e$Å^{-3}$.

Experimental details on the X-ray diffraction analysis of IV

Non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The absolute configuration of **IV** was established by anomalous dispersion effects in the diffraction measurements on the crystal. Since racemic twinning was detected a twin matrix (-1 0 0 / 0 -1 0 / 0 0 -1) was applied and a scale factor was refined [0.203(3)] between the two unequal components. By this single additional parameter, the R-factor R1 reduced from 0.0195 to 0.0168. The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms bonded to a C atom of a C=N double bond were put at the external bisectors of the C-C=N angles at C-H distances of 0.95 Å and refined with a common isotropic displacement parameter. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C-H distances of 0.99 Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C-C bond, and C-H distances of 0.98 Å. For 590 parameters final R indices of R1 = 0.0168 and wR2 = 0.0405 (GOF = 1.055) were obtained. The largest peak in a difference Fourier map was 1.494e$Å^{-3}$.

Structure determination summary for compounds I a, II c, III a and IV

Table B.1.: Crystal structure and structure refinement for **I a** and **II c** in Å.

	I a	**II c**
Empirical Formula	$C_{19}H_{20}ClN_2O_3Re$	$C_{36}H_{52}ClN_2O_3Re$
Formula weight	546.02	782.45
Crystal description	block, green	needle, orange
Crystal system, space group	triclinic, P -1	triclinic, P -1
a [Å]	9.2407(4)	11.9835(8)
b [Å]	9.9456(4)	12.9480(9)
c [Å]	10.6146(5)	13.1585(9)
α [°]	107.7452(13)	70.315(2)
β [°]	92.9271(15)	81.226(2)
γ [°]	98.8156(13)	72.538(2)
V [Å^3]	913.17(7)	1830.8(2)
Z	2	2
F(000)	528	796
μ [mm^{-1}]	6.821	3.426
Unit cell determination [°]	$2.86 < \Theta < 36.02$	$2.50 < \Theta < 25.51$
Temperature [K]	100	100
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Radiation, λ [Å]	MoK_α, 0.71073	MoK_α, 0.71073
Scan type	χ and ω	χ and ω
Θ range for data collection [°]	2.84 to 30.00	2.27 to 26.00
Reflections collected	31060	12947
Unique	5305	7159
Significant unique [I>2σ(I)]	5255	5751
R(int), R(sigma)	0.0300, 0.0170	0.0292, 0.0695
Completeness to Θ= 30.0°[%]	99.9	99.6
Data/parameters/restraints	5305/244/0	7159/421/19
Goodness-of-fit on F^2	1.220	1.146
Final R indices [I>2σ(I)]	R1=0.0157, wR2=0.0408	R1=0.0451, wR2=0.0867
Largest difference peak [eÅ^{-3}]	1.444	0.798
Largest hole [eÅ^{-3}]	-1.369	-1.080

Table B.2.: Crystal structure and structure refinement for **III a** and **IV** in Å.

	III a	**IV**
Empirical Formula	$C_{20}H_{14}ClN_2O_3Re$	$C_{38}H_{40}N_4O_7Re{\cdot}4\,CH_2Cl_2$
Formula weight	551.982	1376.84
Crystal description	block, red	plate, green
Crystal system, space group	monoclinic, I 2/a	monoclinic, P 2_1
a [Å]	18.6593(12)	9.4353(4)
b [Å]	7.7594(5)	18.7105(7)
c [Å]	24.089(2)	13.4607(5)
β [°]	100.5060(11)	90.7434(13)
V [Å^3]	3429.3(4)	2376.14(16)
Z	8	2
F(000)	2112	1340
μ [mm^{-1}]	7.268	5.593
Unit cell determination [°]	$2.55 < \Theta < 30.73$	$2.84 < \Theta < 30.82$
Temperature [K]	100	100
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Radiation, λ [Å]	MoK$_\alpha$, 0.71073	MoK$_\alpha$, 0.71073
Scan type	χ and ω	χ and ω
Θ range for data collection [°]	2.55 to 30.00	2.42 to 30.00
Reflections collected	9995	27279
Unique	4951	13701
Significant unique [I>2σ(I)]	4268	13451
R(int), R(sigma)	0.0169, 0.0536	0.0204, 0.0360
Completeness to Θ= 30.0°[%]	99.0	99.8
Data/parameters/restraints	4951/252/13	13701/590/1
Goodness-of-fit on F^2	1.342	1.055
Final R indices [I>2σ(I)]	R1=0.0483, wR2=0.1113	R1=0.0168, wR2=0.0403
Largest difference peak [eÅ^{-3}]	1.385	1.494
Largest hole [eÅ^{-3}]	-1.680	-1.468

^{1}H-NMR spectra of the perchlorate reduction experiments facilitating compounds I a and I b

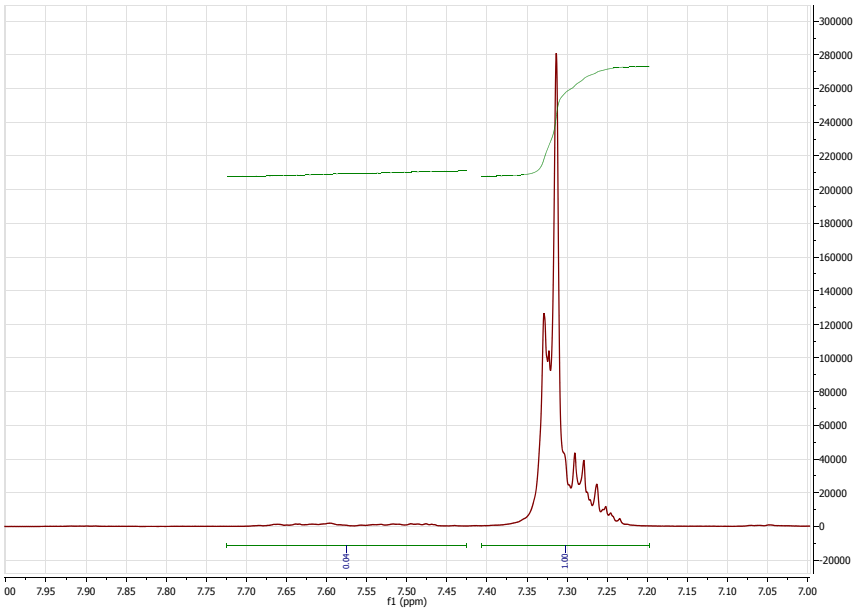

Figure B.1.: ^{1}H-NMR of the perchlorate reduction experiment with **I a** as catalyst.

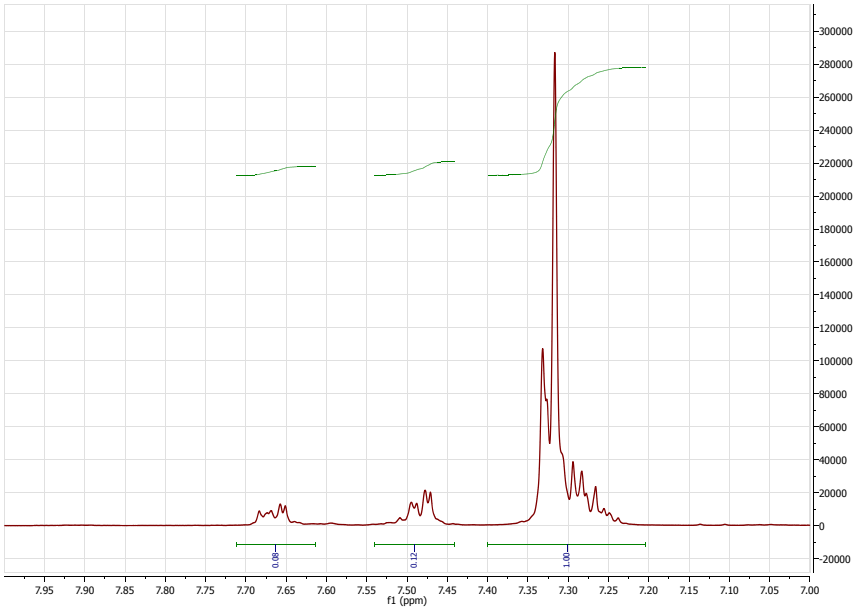

Figure B.2.: ^{1}H-NMR of the perchlorate reduction experiment with **I b** as catalyst.

^{1}H-NMR spectra of the perchlorate reduction experiments facilitating compounds III a and III b

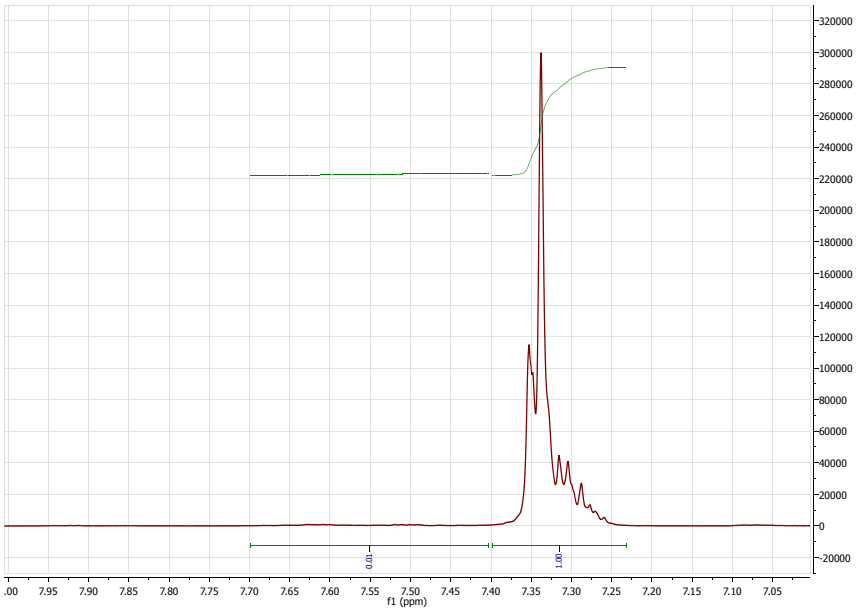

Figure B.3.: ^{1}H-NMR of the perchlorate reduction experiment with **III a** as catalyst.

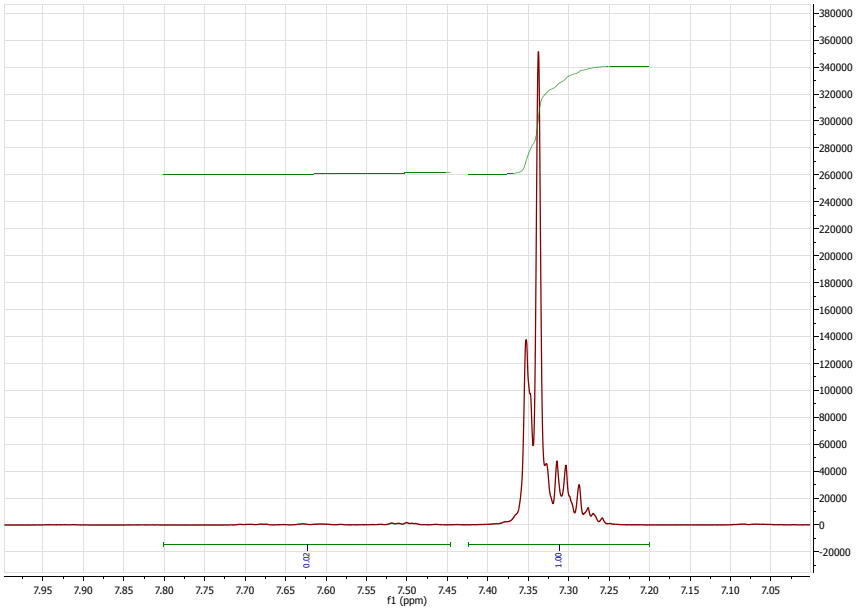

Figure B.4.: ^{1}H-NMR of the perchlorate reduction experiment with **III b** as catalyst.

Catalytic conversions of I a-c and III c

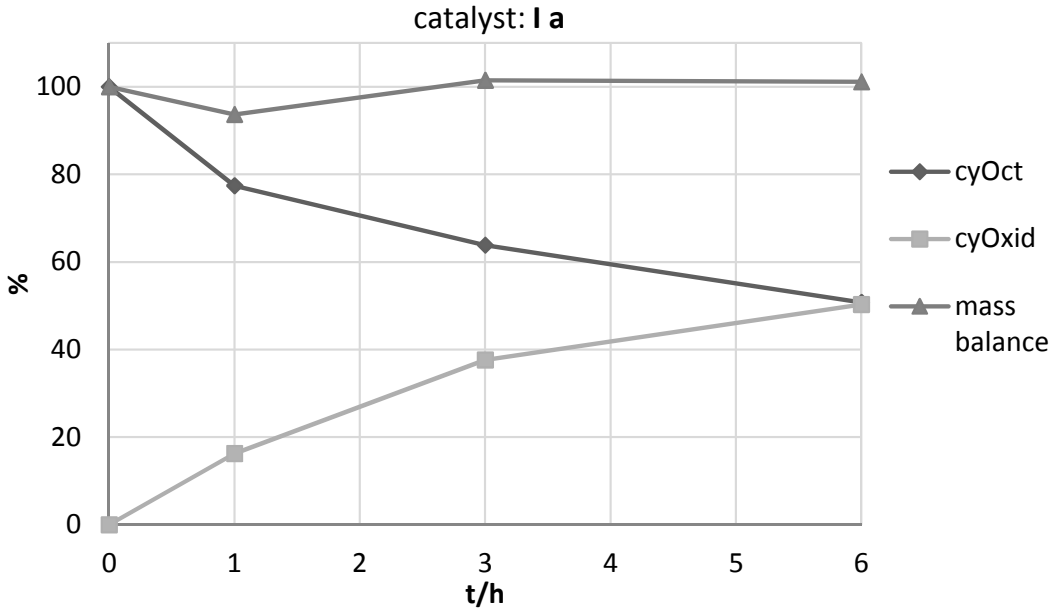

Figure B.5.: Conversion and mass balance in cyOct epoxidation with **I a**, standard conditions.

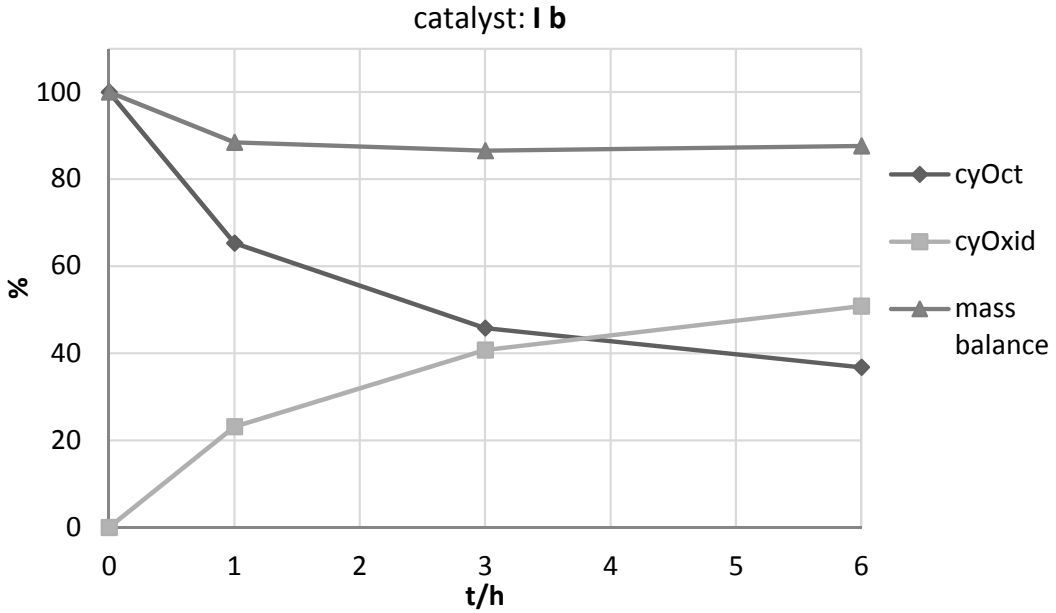

Figure B.6.: Conversion and mass balance in cyOct epoxidation with **I b**, standard conditions.

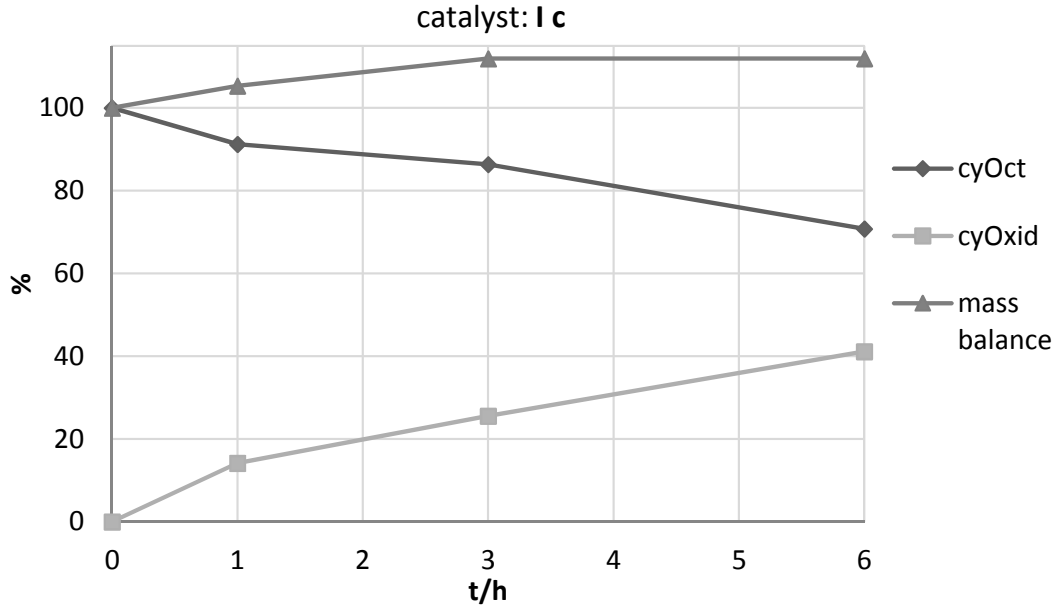

Figure B.7.: Conversion and mass balance in cyOct epoxidation with **I c**, standard conditions.

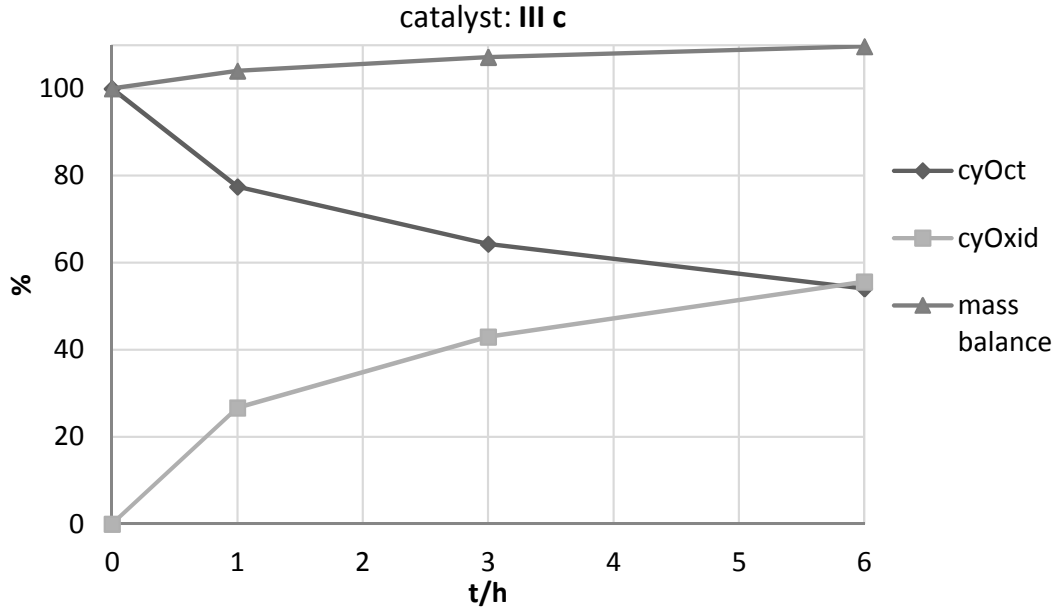

Figure B.8.: Conversion and mass balance in cyOct epoxidation with **III c**, standard conditions.

IR-spectra

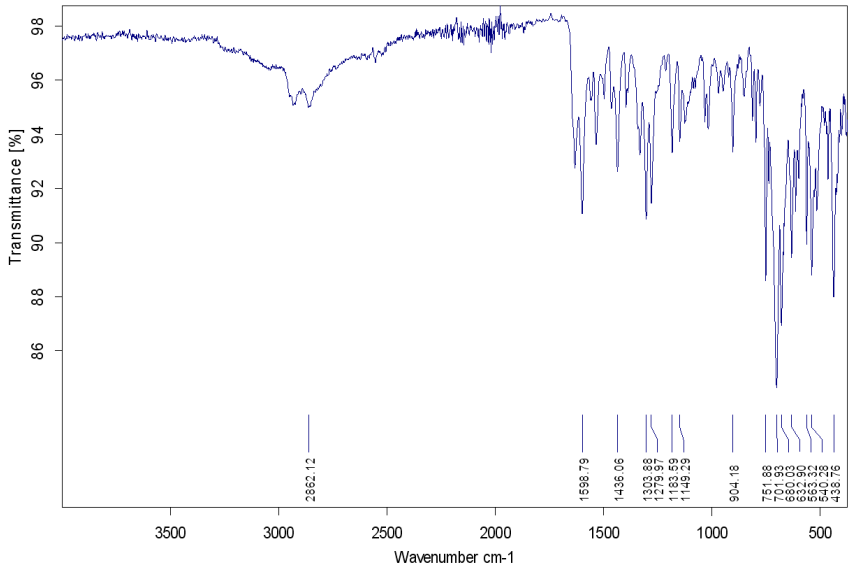

Figure B.9.: IR-spectrum of the product in an attempted synthesis of [ReOCl(2 a)].

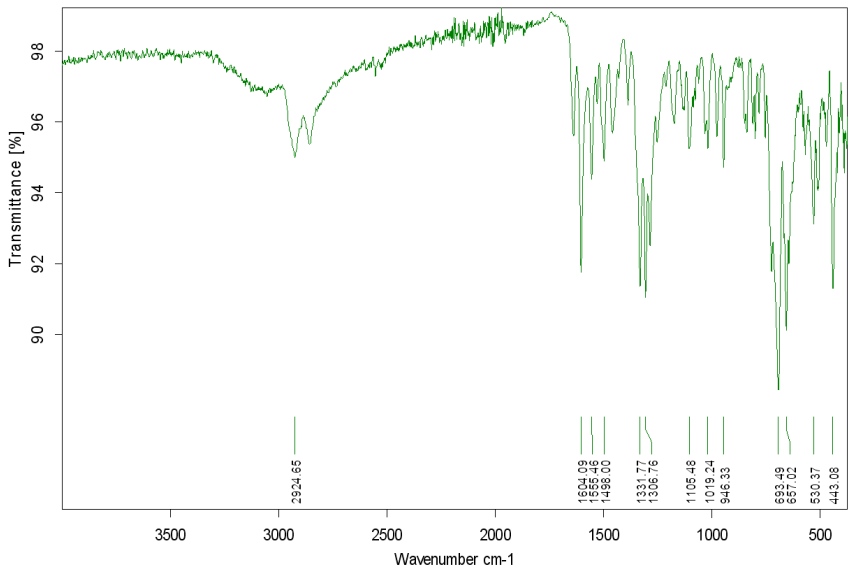

Figure B.10.: IR-spectrum of the product in an attempted synthesis of [ReOCl(2 b)].

EIDESSTATTLICHE ERKLÄRUNG

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