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Synthesis and Catalytic Application of Monomeric Organomolybdenum Complexes

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To my family

With deep gratitude and love

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Abbreviations

Ac	acetyl
acac	acetylacetonate
BET	Brunauer-Emmett-Teller
bipy	2,2'-bipyridyl
bipym	bipyrimidine
[BMIM]NTF_2	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIM]PF_6	1-butyl-3-methylimidazolium hexafluorophosphate
Brij	1,3-diacetoxy-1,1,3,3-tetrabutyltin oxide polyethylene glycol dodecyl ether
Bu	butyl
Bz	benzyl
[C_8MIM] PF_6	1-octyl-3-methylimidazolium hexafluorophosphate
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cp`	substituted cyclopentadienyl ring
CP MAS NMR	Cross Polarization Magic Angle Spinning NMR
CTABr	Cetyltrimethylammonium Bromide
cy	cyclohexyl
δ	chemical shift (ppm)
d	doublet
DAB	1,4-diaza-1,3-butadiene
DME	dimethoxyethane
DMF	N, N'-dimethylformamide
DMSO	dimethylsulfoxide
EI	Electron Ionisation
Et	ethyl
EXAFS	Extended X-Ray Absorption Fine Structure
FAB	Fast-Atom Bombardment
GC	Gaschromatograghy
HMPA	hexamethylphosphorotriamide
Imz	imidazole
IR	Infrared Spectroscopy
L	Ligand
m	multiplet
m	meta

Me	methyl
MS	Mass Spectroscopy
Mes	2,4,6-trimethylbenzyl
MTO	methyltrioxorhenium (VII)
NMR	Nuclear Magnetic Ressonance Spectroscopy
μ	wave number (cm^{-1})
o	ortho
OTf	trifluoromethanesulfonate
Pe	pentane
Ph	phenyl
Pr	propyl
ppm	parts per million
py	pyridine
pz	pyrazolyl
q	quartet
Solv or S	solvent
sym	symmetric
R	alkyl or aryl
RT or r. t.	room temperature
RTIL	room temperature ionic liquids
s	singulet
t	triplet
tame	trisaminomethylethane
TBHP	*tert*-butylhydroperoxide
t-BuOH	*tert*-butanol
TEM	Transmission electron micrograph
TGA	Thermogravimetric analysis
THF	tetrahydrofurane
TlOEt	thalium ethoxide
TMAOH	tetramethylammonium hydroxide
TMS	tetramethylsilane
TOF	turnover number
Tp	hydridotris (1-pyrazolylborate)
Tp*	hydridotris (3, 5-dimethyl-1-pyrazolyl)borate)
X	halogen or methyl
XANES	X-ray Absorption Near Edge Structure
XRD	X-ray Diffraction

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1. Introduction

1.1. Introduction

Oxidation is an enormous field of great importance in nature and industry. It includes different process such as combustion, biological oxidation, production of specific organic and inorganic compounds, corrosion and degradation of material. Oxidation reactions can be performed stoichiometrically or catalytically. Transition metal catalysed oxidation is important both in biological and industrial processes. In biological processes, metalloenzyme reactions are essential for energy transformation and storage and for the biosynthesis and metabolism of biomolecules. In industrial processes, transition metal based catalysts are important tools in the production of millions of tons of oxygenated compounds per year. [1]

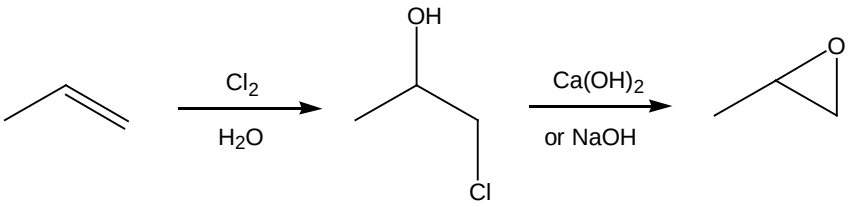
1.1.1. Epoxidation Catalysis

1.1.1.1 Epoxidation - Application and Industrial Processes

Epoxides, particular ethylene and propene oxides, are key raw material for a wide variety of chemicals (such as glycols, glycol ethers and alkanolamines) and they can be also be used as building blocks for polymers (polyesters and polyurethanes).

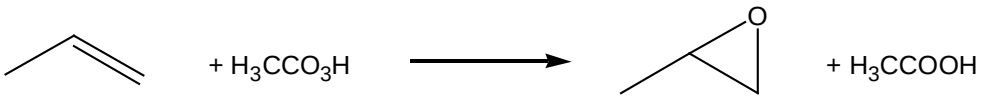
The simplest epoxide, ethylene epoxides, is produced commercially by vapor-phase oxidation of ethylene with air or oxygen over a silver catalyst, promoted by alkali metals and supported on a non-porous form of α-alumina. [2] This process was introduced by Union Carbide in 1937 and by Shell in 1958 to replace the practice of ethylene oxide production via the chlorohydrin process. However, this silver catalysed process can only be applied to olefins which do not possess C-H allylic bonds, such as ethylene, 1,3-butadiene and styrene. For all the other olefins, such as propene, low yields of the desired product are obtained, due to the competing oxidation of allylic C-H bonds, which leads to numerous by-products. [3] Propene oxide producers have traditionally employed the chlorohydrin route which comprises reacting propylene with hypochlorous acid to form propylene chlorohydrin and the dehydrochlorination of the propylene chlorohydrin to form propylenen oxide (Scheme 1.1).[4]

But these processes are currently being subjected to increasing environmental pressure, due to the use of expensive, toxic and corrosive chlorine as reagent and highly toxic by-products.



Scheme 1.1. The chlorohydrin route.

In light of the complexity and cost of the chlorohydrin route, the peracid route was developed.[4] This route involves the formation of a peracid, such as peracetic acid, through the reaction of hydrogen peroxide with the organic acid and the epoxidation of an olefin with the peracid (Scheme 1.2). The disadvantages of the peracid route, however, are also sufficient to preclude significant commercialization. The reagents are expensive, corrosive and non-regenerable, and the overall efficiency of the process is low.



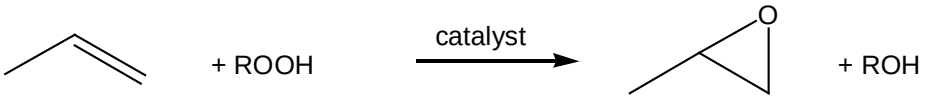
Scheme 1.2. The peracid route.

Subsequent attempts to develop olefin epoxidation systems included the use of hydrogen peroxide alone or in the presence of osmium tetraoxide, manganese dioxide, tungsten and molybdenum oxides. However, none of the systems was considered commercially feasible.[5] Hawkins was the first to report a metal-catalysed epoxidation with an alkyl hydroperoxide in the synthesis of cyclohexene oxide in 30 % yield using cumene hydroperoxide in combination with V_2O_5. [6] Subsequently, Brill described the use of *tert*-butyl hydroperoxide (TBHP) in the precence of catalytic amounts of hydrocarbon soluble acetyl acetonates of molybdenum, vanadium and chromium. [7]

The most important industrial epoxidation processes, based on high valent transition metal

catalysts in combination with alkyl hydroperoxides as the oxygen source, are the SHELL and the ARCO/HALCON processes for propene oxide synthesis.[8] HALCON [9] and Atlantic Richfield (ARCO) [10] independently developed processes for the production of epoxides using an alkyl hydroperoxide in the presence of homogeneous catalysts based on molybdenum, tungsten, titanium, columbium, tantalum, rhenium, selenium, chromium, zirconium, tellurium, uranium and vanadium. From the all the referred metals, molybdenum, tungsten and titanium are considered better options. The inventors suggested utilization of the molybdenum catalyst in the form of organic salts, oxides, chlorides, oxichlorides, fluorides, phosphates, sulfide and molybdic acid. Solubilization through organometallic modifications was also mentioned.

After the success of the two independently developed processes, ARCO and Halco formed a joint venture, the Oxirane Corporation, to exploit the technology for the manufacture of propylene epoxide using a molybdenum (VI) catalyst and organic hydroperoxides. Molybdenum catalysts gave the highest rate and selectivity when used with TBHP or ethylbenzene hydroperoxide (from molecular oxygen and ethylbenzene) (Scheme 1.3). *Tert*-butanol and 1-phenyl ethanol, which are obtained as by-products of the epoxidation process, are finally converted into the versatile bulk products methyl *tert*-butyl ether (MTBE, which can be used as an octane booster in gasoline) and styrene. [11]



Scheme 1.3. ARCO and Halcon process.

Nowadays, propylene oxide is produced industrially with an annual worldwide capacity of approximately 5 million tons by two major processes: the antiquated chlorohydrin process and the ARCO/Halcon process. The chlorohydrin process still accounts for 55% of the global propylenen oxide production. [12] However, in order to meet economical as well as ecological issues, alternative processes continue to be developed.

In the heterogeneous SHELL process, [13] TBHP is used in the presence of a Ti(IV)/SiO_2 catalyst for the epoxidation of propene. This catalyst has the advantage of being suitable for continuous fixed bed operation.

Despite the widespread use of transition metal compounds as catalysts, [14] stoichiometric reactions are nevertheless commonly used for the oxidation of fine chemicals. [15] The most widely used epoxidation reagent in research is meta-chloroperoxybenzoic acid (m-CPBA). [16] However, this features a number of problems resulting in the need for the development of new efficient catalysts.

Attention has been also paid to the industrial development of processes that use hydrogen peroxide as oxidant. Hydrogen peroxide had not been considered a good oxidant due to its high price and impossibility of selling or regenerating its by-product (water). [10] However, environmental pressure stimulates the search for environment friendly by-products, such as water. Enichem developed an integrated process for a variety of liquid phase oxidations, in which hydrogen peroxide is produced from water and methanol by the anthraquinone route and without separation is used as oxidant with a titanium-substituted silicate (TS-1) catalyst.[12] This process has been commercialised for other reactions but not for epoxidation of propylene. [3] Degussa is also developing an industrial process using a TS-1 catalyst and H_2O_2, but in this case, it has been especially developed to obtain propylene oxide. [17]

In spite of the importance of the processes with transition metal catalysts and organic hydroperoxides, the direct epoxidation of propene with molecular oxygen is still an attractive goal. Olin Corporation, for example, patented a process in which propylene is oxidized by O_2-enriched air. [18] In this process, the reactants (and some recycled by-products) are passed through a molten mixture of alkali metal nitrates, which function as reaction medium and catalyst. [19] However, despite considerable effort no economically viable process has been found.

1.1.1.2. Asymmetric Epoxidation

The need for optical pure pharmaceuticals, herbicides and insecticides as well as perfumes had a great influence on the development of enantioselective catalysis. In the production of pharmaceuticals and agrochemicals, chiral epoxides are of great importance as intermediates and are usually obtained from the asymmetric epoxidation of olefins. For example, 2- (2,4-difluorophenyl)-epoxyallyalcohol is an intermediate for the synthesis of the triazol fungicide.

Olefins with a hydroxyl substituent in the allylid position have a more reactive double bond, and the possibility of an additional coordination to the metal center of the catalyst by the hydroxyl group plays an important role in the stereodifferenciation of the double bond. In 1980 Sharpless and Katsuki developed the first method for the asymmetric epoxidation of allylic alcohols with TBHP, using a titanium(IV) catalyst. This asymmetric epoxidation technology affords high yields and enantiomeric selectivities with a broad range of allylic alcohol substrates, and has been widely applied in organic synthesis. [20]

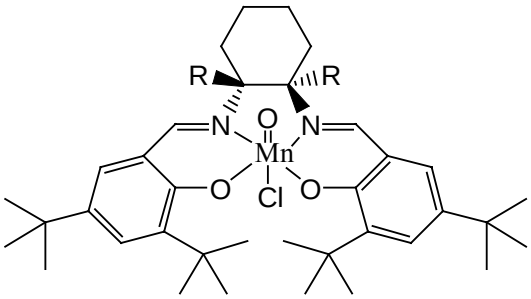
Recently it has been shown that chirally modified lithium and magnesium *tert*-butyl peroxide can be used for the epoxidation of electron deficient olefins, like chalcones, leading to yields of ca. 60 % and ees of 90 %. [21]

The catalytic system developed by Grove and Myers using the π –interaction of the substrate and aromatic substituent on the chiral Fe(III)-porphyrin complex can obtain 51 % optical induction with iodosylbenzol as oxidant,[22] but the synthesis of the chiral prophyrin ligand is very expensive.

It is noteworthy that neither the titanium (IV) tartrate catalyst nor other metal catalyst-alkylhydroperoxide reagents are effective for the asymmetric epoxidation of unfunctionalised olefins. The only system that affords high enantioselectivities is the manganese (III) chiral Schiff base complex/NaOCl combination developed by Jacobsen in 1990 (Scheme 1.4). [23]

With this system it is possible to achieve yield as high as 97% with ees of 98%. This system has already found an industrial application by ChiRex Inc. for the stereoselective HIV-

protease-inhibitor Crixivan (Merck & Co). [24] But this process is only applicable for the epoxidation of *cis*-olefins, due to the catalyst's geometry and the mechanism of oxo transfer.



Scheme 1.4. Jacobsen's epoxidation catalyst (active species)

1.1.2. MoO_2^{2+} Chemistry

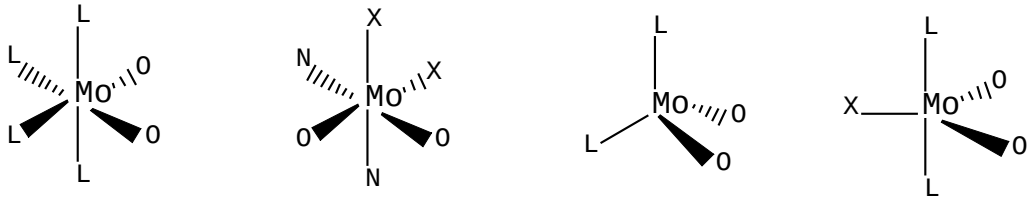
The enthusiasm shown in the coordination chemistry of molybdenum followed the discovery of molybdenum in a number of redox enzymes, [25] such as aldehyde oxidase, sulphite oxidase, xanthine oxidase, nitrate reductase and nitrogenase.

The chemistry of Mo(VI) is dominated by the molybdenum dioxochemistry, although in the last 20 years it was discovered S^{2-} and other ligands, such as selenides (Se^{2-}), peroxide (O_2^{2-}), imide (NR^{2-}), nitride (N^{3-}), alkylcarbide (RC^{3-}), hydrazide (R_2NN^{2-}) and hydroxylamide (R_2NO^-) are able to undergo chemistry related to that of the oxo ligand.

Since the last review published by Stiefel in 1987 [26] molybdenum oxide chemistry was not reviewed in a comprehensive way. For this reason, this part covers the literature of the last 17 years focused on the mononuclear dioxomolybdenum (VI) complexes.

1.1.2.1. Structural Aspects

The vast majority of the dioxomolybdenum complexes are six-coordinate and mostly with a distorted octahedral structure (**A**). In the octahedral structure, the two Mo-O_t (O_t = terminal oxygen) bonds are invariably *cis* to each other. The strong σ- and π- donor nature of the oxo ligands makes it favourable for them to avoid competing for the same *p* and *d* orbitals, maximizing the π-bonding to the metal.



A **B** **C** **D**

The structural results show that both the Mo-O_t distances and O_t-Mo-O_t angles lie in a narrow range except when the ligands forbid molybdenum to achieve the highly favourable *cis*-octahedral structure. Typical values for the O_t-Mo-O_t angles are around 109°,[27] while optimal values for Mo-O_t distances lie around 1.69±0.03Å.[27, 28] There are other features common to the octahedral complexes. Bonds *trans* to the dioxo group suffer a pronounced *trans* influence and are significantly longer than the corresponding bonds to the same donor type that are *cis* to the oxo group.

The general rule for the octahedral structures is that when given a choice, the weaker donor atoms are found trans to Mo-O_t since they do not compete for the empty *p* and *d* orbitals. An important exception for the molybdenum oxide complexes is what happens with the neutral adducts MoO_2Cl_2(tmen) (tmen = N, N, N', N'-tetramethylethylenediamine),[29] and $MoO_2Cl_2(\eta^2$-TMC) (TMC=1, 4, 8, 11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[30] These complexes exhibit the so –called "all-*cis*" geometry (**B**). These structures are very unusual because they contradict the previous rule, having a chloride donor atom trans to an oxygen of the dioxo group, with a longer Mo-Cl distance. This disposition might be due to steric problems, forcing the molecule to adopt this unusual configuration.

Although complexes containing a MoO_2^{2+} core are generally six-coordinate, some four- or five- coordinate also exists (**C** and **D** structures). The *tetra*-coordinate compounds are tetrahedral or pseudo-tetrahedral and are related to MoO_4^{2-}, e.g., $MoO_2(OSiPh_3)_2$,[31] or MoO_2Cl_2 and MoO_2Br_2.[32] Examples of five-coordinate complexes are known. Holm and co-workers prepared the first example in the mid 80's, [33] and more examples are known today.[31, 34, 35] These complexes adopt a trigonal bipyramidal structure with the oxo ligands situated in the equatorial plane. Some five-coordinate complexes attain the preferred

octahedral structure forming a polymeric chain by intermolecular interactions between a terminal oxygen atom from one molecule and the metal center of the next molecule. [36]

1.1.2.2. Synthesis and Structures of MoO_2^{2+} Core Complexes

There are some readily available starting materials for the synthesis of dioxomolybdenum complexes with the MoO_2^{2+} core, e. g., $MoO_2(acac)_2$, which is easily prepared by the acidification of an aqueous ammonia solution of molybdic anhydride by adjusting the pH. [37] This method has been improved over the years.[38] Dioxomolybdenum complexes are readily prepared by ligand exchange. This reaction proceeds in THF or MeOH, sometimes with an amine, such as triethylamine, to assist the ionization of the incoming ligands. The free AcacH can be readily distilled off with the solvent under vacuum.

MoO_2X_2bipy, an important complex because of its use in the preparation of organometallic complexes, was prepared by the oxidation of $Mo(CO)_4$bipy with Br_2 or Cl_2 in EtOH-CH_2Cl_2.[39]

Another possible starting material for the preparation of this type of complexes are MoO_2Cl_2 and MoO_2Br_2. These two starting materials are much easier to use when transformed to solvent adducts, $MoO_2X_2L_2$ (X = THF, CH_3CN, DMF, DMSO). [40] When stored free of moisture they can be kept for a long period of time and they are much easier to handle than the flurry MoO_2Cl_2 or MoO_2Br_2.

Molybdates, [41] polymolybdates [42] or even MoO_3 [43] are also used in the preparation of complexes with the MoO_2^{2+} core.

A very uncommon method is the oxidation of molybdenum (IV) oxides, $MoOL_n$ (L_n = bi- or tridentate ligand), by trimethylamine N- oxide in DMF to give the dioxomolybdenum (VI) complexes. [44] This method is not very useful, but it mimics the oxidation process present in the molybdenum enzymes.

Using Na_2MoO_4 as starting material, potentiometric titrations can be made to prepare $[MoO_2L_2]^{2-}$ complexes (L = $(CH_3CH(O)CO_2)^{2-}$, lactate, or $^-O_2CCH_2CH(NH_2)CO_2^-$, aspartate, or pyridinyl alcohols). [45]

1.1.2.2.1. Solvent Adducts and Phosphoryl Ligands

As already mentioned, dissolving MoO_2X_2 (Cl, Br) in good donor solvents gives adducts with the general formular $MoO_2X_2L_2$ (X = THF, CH_3CN, DMF, DMSO, H_2O, dyglime). [40, 46]

A number of phosphine oxide complexes of Mo(VI) have been reported, structurally characterized examples include $[MoO_2X_2(OPPh_3)_2]$ (X = Cl or Br), $[MoO_2Cl_2(OPMePh_2)_2]$, $[MoO_2Br_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$, $[MoO_2Cl_2\{Ph_2P(O)(CH_2)_3P(O)Ph_2\}]$, $[MoO_2Cl_2\{(CH_2P(O)(CH_2CH_2OMe)_2)_2\}]$ $[MoO_2X_2(OPMe_3)_2]$ (X = Cl or Br) and $[MoO_2Br_2\{o\text{-}C_6H_4(P(O)Ph_2)_2\}] \cdot 2CH_2Cl_2$, which were prepared from the reaction of MoO_2Cl_2 with two molar equivalents of L or one molar equivalent of L–L afforded the six-coordinate $[MoO_2Cl_2L_2]$ or $[MoO_2Cl_2(L–L)]$, respectively. [47]

Ligands with phosphoryl and hydroxyl groups were also used. The reaction of the chiral ligands, (1S)-2-(diphenylphosphoryl-1-methylethanol and (1R)- 2- (diphenylphosphoryl-1 – methylethanol with MoO_2Cl_2 in dichloromethane produced adducts of the type $MoO_2Cl_2(HL)_2$. Complexes of the type MoO_2L_2 were obtained only in the presence of TlOEt.[48a] The same type of complex is achieved from the reaction of two equivalents of (S)-2-diphenylphosphinoyl-2'-hydroxy -1,1'-binaphtalene with MoO_2Cl_2 in THF in the presence of TlOEt. [48b]

Ligands, such as, 1,2-bis[bis(methoxyethyl)phosphino]ethane dioxide, diethyl (2-phenyl-2-oxoethyl) phosphonate or the chiral ligand with phosphoryl and carbonyl donor groups, the β-ketophosphonate (1R)-endo-(+)-3-(diethoxyphosphoryl) camphor, react with MoO_2Cl_2 in THF, yielding $MoO_2Cl_2L_2$ adducts. [49] The referred chiral ligand may act as a unidentate or a bidentate ligand, coordinated by two phosphoryl oxygens (P=O) or through the phosphoryl and carbonyl oxygens (P=O and C=O) respectively, to MoO_2Cl_2. [49c]

The reaction of $(RO)_2P(S)CH_2C(O)NEt_2$ (R = Et, Bu), with MoO_2Cl_2 in ethanol gave the adduct $MoO_2Cl_2L_2$. Crystallographic data showed that the ligand was bound by the oxygens of the carbonyl groups. [50] Comparing these donor groups, the thiophosphonate, phosphonate and the carbonyl groups, it may be concluded that the molybdenum(VI) center prefers to bind to a hard oxygen rather than to a soft sulfur atom and, given the preference to bind to a

phosphoryl rather to a carbonyl oxygen, it suggests that the phosphoryl oxygen is a harder center.

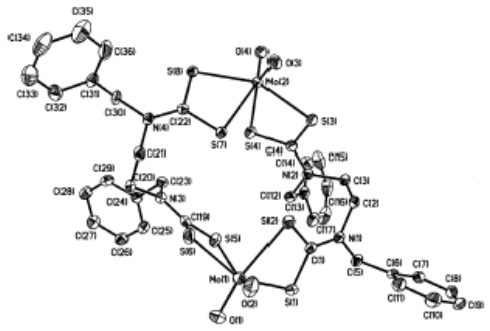
1.1.2.2.2. Sulfur and Sulfur-Nitrogen Ligands

The presence of the pterinic (pterin = 2-amino-4(1*H*)-pteridinone) co-factor in the active site of the molybdenum enzymes, [8] as well as the early discover that MoO_2L_2 complexes with dithiocarbamates as ligands were able to be reduced and oxidized by oxygens atom transfer reactions, emphasized the importance of ligands with S donor atoms. [51] This latter type of complexes (L = dithiocarbamate ligands, R_2dtc- (R = Et, *n*-Pr, *i*-Bu)) were prepared and thoroughly studied, especially in the mentioned oxygen atom transfer reactions. Recently Bargon et al. [52] used diethyl dithiocarbamate dioxomolybdenum complex as starting material to synthesize molybdenum disulfur complexes and employed them as sulfur-transfer agents for the episulfidation of alkenes.

In order to mimic the catalytic oxidation reactions of the molybdenum enzymes, the complexes $[MoO_2(bdt)_2]^{2-}$ [44, 53] and $[MoO_2(mnt)_2]^{2-}$ (bdt^{2-} =1,2-benzenedithiolate, mnt^{2-} = 2,3-disulfanylmaleonitrile dianion (1,2-dicyanothethylenedithiolate)) were prepared by the oxidation of the Mo(IV)O species by trimethylamine N-oxide in DMF to give the desired dioxomolybdenum(VI) complexes. [54, 55]

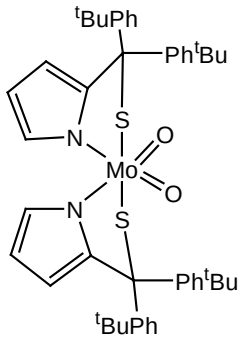
These complexes constitute reasonable structural models for the active site of DMSO reductase and *Pyrococcus furiosus* AOR (aldehyde ferredoxin oxidoreductase), and also serve as functional models for oxotransferase enzymes. It has been found that $[MoO_2(mnt)_2]^{2-}$ is capable of oxidizing hydrogensulfite to HSO_4^-, a reaction directly relevant to the function of sulfite oxidase.[54, 56] Furthermore, the reactions between $[MoO_2(mnt)_2]^{2-}$ with other oxygen acceptors $PPh_{3-x}Et_x$ (X = 0-3) was investigated. [57] Recently Kirk et al. [58] performed an electronic structure calculation at DFT level of theory on $[MoO_2(S_2C_2Me_2)(SCH_3)]^-$ as computational model of the oxidized SO site and the results strongly suggest that the two oxo ligands are highly inequivalent electronically and the propose of O-atom selection and activation are a direct function of the low-symmetry structure of the oxidized active site,

indicating a role of the ene-1,2-dithiolate in the sulfite oxidase in promoting OAT (oxygen atom transfer) reactivity via a kinetic trans effect. Treating $MoO_2(acac)_2$ with $Na_2(Bz_2endtc)$ (Bz_2endtc^{2-} = ((2 -dithiocarboxybenzylamino)ethyl)-benzylamino) methanedithioate), an unexpected novel dinuclear cis-dioxomolybdenum(VI) with a quadradentate dithiocarbamate complex [{$MoO_2(Bz_2endtc)$}2] (**1**) bridged by Bz_2endtc^{2-} was obtained. [59]



1

Holm and co-workers prepared complexes with bulky ligands to study oxygen atom transfer reactions. The use of bulky ligands prevents the formation of molybdenum(V) species undesirable in these kind of studies. Examples of these ligands are bis(*p-tert*-butylphenyl)-2-pyridyl-methanethiol (**2**), 2,6-bis(2,2-diphenyl-2-mercaptoethanyl)pyridine) (**3**), which formed the first reported penta-coordinated molybdenum (VI) complex mentioned in the literature, and diphenyl-2-pyridylmethanethiol, as well as methyl ester derivative of 2-mercaptomicotinic acid (CH_3nicSH).[8, 60, 61, 62]



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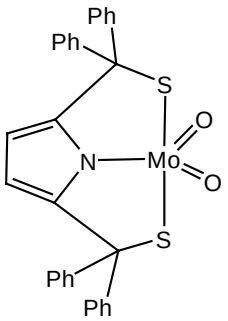


3

These complexes were prepared from the reaction of $MoO_2(acac)_2$ with the respective thiol or from their lithium salt in methanol. Related complexes with the hydroxyl group in place of sulfur, such as diphenyl-2-pyridylmethanol and bis(4-tert-butylphenyl)-2-pyridylmethanol, were also prepared. [60, 61]

The tetradentate MeS_4^{2-} (MeS_4H_2 = $HSC_6H_4SCH(Me)CH_2$-SC_6H_4SH), a ligand with only sulfur donor atoms, was also used in the preparation of dioxomolybdenum complexes. [63]

Organic molecules with sulfur and nitrogen donor atoms were widely used as ligands in this chemistry. Among these ligands are the tetradentate $[(SH)CH(Me)CH_2N(Me)CH_2]_2$ and N, N' –bis(mercaptophenyl)-2,3-diaminobutane, [64] the tridentate $HN(CH_2CH_2S)_2$, [10] as well as the bidentate *t*-$BuNSPh^-$ and pyrimidine-2-thiol. [65] These ligands react with $MoO_2(acac)_2$ yielding repectively, complexes of the type MoO_2L, $MoO_2L(solv)$ and MoO_2L_2.

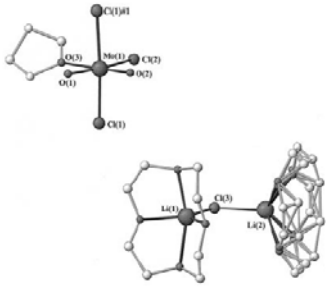
A new class of asymmetric N-capped (dianionic/trianionic) tripodal proligands , e.g. 2-[N-(2-mercaptoethyl)-N-(2-pyridylmethyl)]amino-4-methylphenol, 2-[bis(2-mercaptoethyl) aminomethyl] pyridine, N,N-bis(2-mercaptoethyl)benzylamine which possess pendant arms with N_2O_S, N_2S_2 or NOS_2 donor groups and with different chelate ring has been prepared by the reacting of $MoO_2(acac)_2$ with corresponding ligands to obtained five or six-coordinated complexes. [66]

1.1.2.2.3. Oxygen Donor Ligands

These ligands may appear with different functionalities, such as alcohols, carboxylic acids, salicylic acid (a combination of a carboxylic acid and a hydroxyl group), etc.

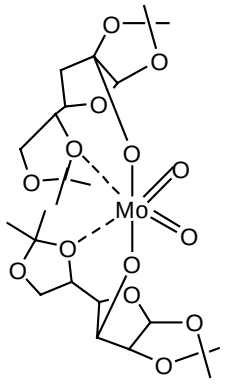
Alkoxides are widely used as ligands. $MoO_2(OR)_2L_2$ complexes (OR^- = alkoxide; L = CH_3CN, py, 1/2 bipy) can be prepared by treatment of MoO_2Cl_2 with lithium alkoxide in acetonitrile at low temperature ca. -10°C), followed by addition of L. [67] When MoO_2(O*t*-Bu)$_2$ was employed as a starting material and treated with the Li salt of 2-propenylphenolate, which was prepared in situ in the presence of the crown ether, this led to the isolation of $[Li(12\text{-crown-}4)_2][MoO_2(PO)_3]$ (**4**), which represents a rare example of a five-coordinate

dioxomolybdenum(VI) complex as well as being the first example among these complexes with a squarepyramidal ligand arrangement. [68]



4

Another example is the oxomolybdenum complex formed by the reaction of the lithium salt of the chiral sugar 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose with MoO_2Cl_2 suspended in diethyl ether (**5**). Despite its sensitivity to moisture, it was possible to obtain its structure which is pseudo-octahedral with two *cis*-terminal oxo ligands, two *trans* alkoxide bonds and weak *cis* contacts. The phenanthroline adduct of this complex was also obtained and structurally characterized. [69]



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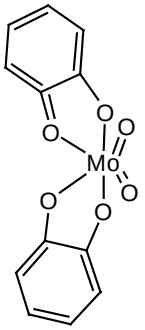
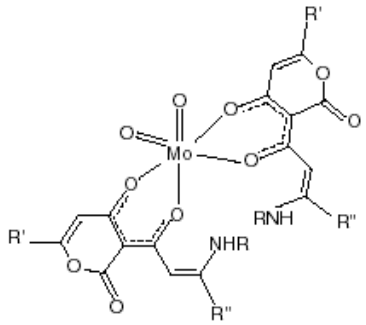


6

Glycolato and S-lactato complexes containing the dioxomolybdenum(VI) moiety have also been synthesized for studies on the role of the a-hydroxycarboxylato anion in the iron molybdenum cofactor of nitrogenase. The ligands in these complexes, $K_2[MoO_2(glyc)_2]\cdot H_2O$ (H_2glyc = glycolic acid) and $\{Na_2[MoO_2(S\text{-lact})_2]\}_3 \cdot 13\ H_2O$ (H_2lact = lactic acid) chelate through their a-alkoxyl and a-carboxyl oxygen atoms.[70]

Another type of ligands are those with at least one hydroxyl and one carbonyl group, α-hydroxylketones or even oxalic acid. The reaction of these ligands with $MoO_2(acac)_2$ or MoO_2Cl_2 yields complexes of the type MoO_2L_2, such as $MoO_2(c\text{-}C_7H_5O_2)_2$ (**6**), or even binuclear complexes of the type $(MoO_2Cl_2)_2L$ may be formed, such as $(MoO_2Cl_2)_2(c\text{-}C_6Cl_2O_4)$ or $(MoO_2Cl_2)_2(C_2O_4)$.[71] Mononuclear molybdenum(VI) $[MoO_2L_2]$ complexes have been prepared by the reaction of $MoO_2(acac)_2$ with the appropriate β'-hydroxy-β-enaminones (HL) (**7**).[72] The Ligand L is coordinated in a didentate fashion to molybdenum through two oxygen atoms and not through the nitrogen atom.

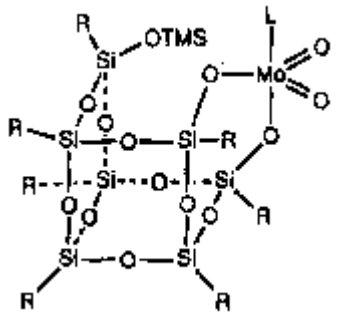


7

Also known in the literature, the ligands 3-hydroxypyridin-2-one and 1,2-dimethyl-3-hydroxypyridin-4-one reacted with molybdates giving the same type of complexes as the previous examples.[73] They follow the same pattern as the other complexes, with trans hydroxylate and cis carbonyl groups around the molybdenum center.

The salicylate ligand (sal = $C_6H_4(O)(CO_2)^{2-}$), and other dihydroxybenzonic acids were also used as ligands. Their reaction with $MoO_3{\cdot}nH_2O$ or molybdates in water affords MoO_2L_2 complexes bonded by the deprotonated phenol and carboxylate oxygen atoms, [74a] or by the two deprotomated hydroxyl groups. [74b]

Other carboxylic acid were used as ligands such as, $Ph_2C(S)CO_2H$, [75] or $Ph_2C(O)CO_2H$, [76] which adopt the same coordination pattern, with the formation of a five-membered ring with the molybdenum atom.



(R = c-C_6H_{11}, L = C_5H_5N or Ph_3PO)

8

Ligands containing the siloxy group attracted interest as models for silica. An interesting example was obtained by the reaction of MoO_2Cl_2 with the thalium-stabilized R-$Si_7O_9(OTMS)(OTl)_2$ (R=*c*-C_6H_{11}) resulting in the formation of a tetra-coordinated molybdenum(VI) dioxo complex (**8**). [77]

Hydroxamic acids have also been used as ligands in this chemistry. The reaction of acetohydroxamic acid and 2-hydroxyphenyl-hydroxamic acid with $MoO_2(dedtc)_2$ ($dedtc^-$ = N, N'-diethyl dithiocarbamate) and $MoO_2(acac)_2$ affords the hydroxamato/hydorximato $\{MoO_2[MeC(O)NH(O)][MeC(O)N(O)]\}^-$, $\{MoO_2[C_6H_4C(O)NH(O)][C_6H_4C(O)N(O)]\}^-$ complexes, respectively. [78]

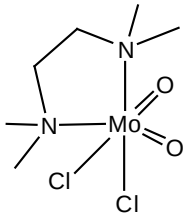
The use of sterically demanding R_3SiO- ligands such as triphenylsiloxy in place of trimethylsiloxy, increases the solubility and crystability of the product, also increases the air stability and prevents the possible oligomerization through the siloxy group. The reaction of silver molybdate with triphenylsilyl chloride in DME and a small amount of acetonitrile gives the tetra-coordinated complex $MoO_2(OSiPh_3)_2$ which reacts at low temperature with PPH_3, affording the penta-coordinate $MoO_2(OSiPh_3)_2(PPh_3)$, which was the first structural characterized triphenylphosphine derivate of the MoO_2^{2+} core.[6]

1.1.2.2.4. Nitrogen Donor Ligands

One of the first molybdenum oxide complexes to be characterized was MoO_2Br_2bipy. [79] Since then, more complexes related to this one have been structurally characterized, such as

MoO_2Cl_2(phenanthroline), [80] Two more structures of this family have been presented in the following years, MoO_2Cl_2(4, 4'-dimethyl-2,2'-bipyridine) [12] and MoO_2Br_2 [(4, 4'-di(tert-butyl)-2, 2'-bipyridine)]. [81]

Amine has been widely used as ligands in the dioxomolybdenum chemistry, especially in molecules with other functional groups. A complex with only amine group was obtained from the reaction of tmen (tmen = N, N, N', N',-tetramethylethylenediamine) with MoO_2Cl_2 suspended in CH_2Cl_2 (**9**). [8] This structure is very unusual because it shows an all *cis*-disposition of the ligands around the metal center.



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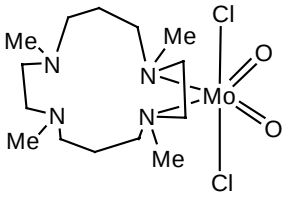


10

Marocycles were also used in the preparation of dioxomolybdenum complexes. [82] Reacting 1, 4, 8, 12- tetraazacyclopentadecane, ([15]aneN_4), and 1, 4, 8, 11- tetramethyl- 1, 4, 8, 11-tetraaza-cyclopentadecane (TMC), with MoO_2Cl_2, complex [MoO_2[15]aneN_4-H]Cl and the neutral adduct MoO_2Cl_2(η^2-TMC) (**10**) are obtained. [6] This last example shows the unusual all-*cis* octahedral geometry. The reaction of the macrocycle 7, 16-dihydro-6, 8, 15, 17-tetramethyldibenzo [*b, i*][1, 4, 8, 11]-tetraazacyclotetrade-cine with $MoO_2(acac)_2$ only substitutes one of the acac- ligands. [83]

The small macrocycle 1, 4, 7-triazacyclononane (L) was used to prepare a variety of molybdenum complexes from the oxidation state 0 to VI. The molybdenum(VI) complex $[LMoO_2Br]^+$ was prepared from $[MoL(CO)_3Br]^+$ in concentrated HNO_3. [84]

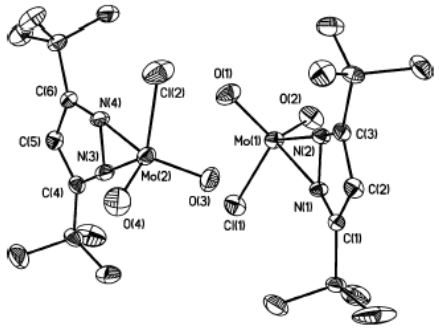
$[(Me_3tacn)MoO_2(OMe)]^+$ (**11**), $[(t\text{-}Bu_3tach)MoO_2(OH)]^+$ and $[(Me_3tacn)MoO_2(OH)]^+$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclonane, *t*-Bu_3tach = 1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane) can be obtained when trigonal complexes [(Me_3tacn)MoO3] or [(*t*-Bu_3tacn)MoO_3] is alkylated with MeOTf , or protonated with HOTf. [85]

11 **12**

The tris(pyrazolyl)borate N-donor ligands have rendered a significant impact in the field of producing a variety Mo(VI) complexes, e.g. complex (**12**). [18, 86, 87] The role of these tripodal ligands as functional models for various facets of enzyme structures and reactivities is believed to arise from their capability to block one face of the metal site and control the reactivity of the other. [18, 88] On the other hand, development of mononuclear complexes with unlinked pyrazolate ligands is often hampered by their preference to build up bridging structures. [89] Recently, mononuclear pyrazolate complexes have been prepared by the introduction of sterically demanding groups in 3- and 5-positions featuring unusual η^2-coordiantion of the heterocycle. [90] The hydrotris(3, 5-dimethyl-1-pyrazolyl)borate (L) and other related molecules, e.g., hydrotris(3-isopropyl-1-pyrazol-1-yl)borate and hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl) borate, [88] have also been used as ligands in the dioxomolybdenum coordination chemistry. These ligands are of sufficient size to occupy one side of the complex preventing the undesired formation of the unreactive μ-oxo-bridged molybdenum (V) species in the catalytic cycle of the oxidation of PPh_3 to $OPPh_3$. Reacting these ligands with MoO_2Br_2 and MoO_2Cl_2 or one of their solvent adducts, leads to the formation of $LMoO_2X$ (X= Cl, Br). [88] A variety of co-ligands were used by a metathesis reaction with NaZ (Z = $^-$OMe,$^-$SPh, $^-$OPh) to prepare complexes with the general formulae $LMoO_2Z$. The complex $[HB(Me_2pz)_3]MoO_2(NCS)$ was obtained from the reaction of this ligand with $(Et_4N)_2[MoO_2(NCS)_4]$ in dry dimethylformamide. [18] Treatment of $[MoO_2Cl_2]$ with one equivalents of potassium 3, 5-di-tert-butylpyrazolate (pzK) in toluenen at room temperature afforded five-coordinated $[MoO_2Cl(\eta^2\text{-pz})]$, whose crystal structure provides the first structural evidence of a η^2-coordinated pyrazolate ligands at a $[MoO_2]^{2+}$ core (**13**).[91]

The anionic $[PPh_4]_2[MoO_2(NCS)_4]$ and the neutral $MoO_2(CNS)_2$bipy are remarkable agents in oxygen atom transfer reactions. The first was prepared from the reaction of Na_2MoO_4 with KNCS in an acidic medium, followed by cationic exchange under phase transfer conditions.[92] Treatment with bipy led to the second complex. [93]

The lithium benzamidine $PhC(NSiMe_3)_2Li$ reacts with MoO_2Cl_2, yielding $MoO_2[PhC(NSiMe_3)_2]_2$. [94]



13

Schiff bases and other imines have been widely used as ligands in the dioxomolybdenum chemistry. Examples are the N, N'-bis(*t*-butyl)-1,4-diaza-1,3-butadiene,[5b] and the great variety of MoO_2Cl_2 and MoO_2Br_2 adducts described with different 1,4-diaza-1.3-butadiene derivatives.

1.1.2.2.5. Ligands with two or three Different Donor Atoms

Ligands with the imine group together with other functionalities especially with other donor atoms, such as oxygen and sulfur, are also present in the literature. The importance of ligands with different donor atoms comes from extended X-ray absorption fine structure (EXAFS) results, which showed that sulfur and nitrogen or oxygen might be present in the coordination sphere of the molybdenum enzymes. [95]

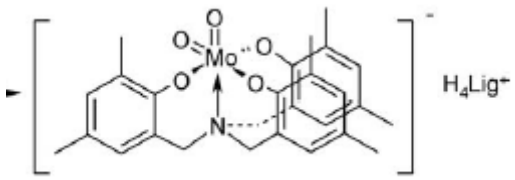
Tridentate Schiff base ligands, such as H_2sal-OHYBA (*o*-$HOC_6H_4CH{=}NC_6H_4OH$), N-2-hydroxy-1-naphthyliden-(2-mercaptoaniline) or $ClC_6H_3(OH)CH{=}NC(Me)(CH_2OH)_2$, react with $MoO_2(acac)_2$, yielding MoO_2L(solv) type complexes. [96]

The Schiff base ligands derived from the methylene-bis(salicylaldehyde) and dithio-bis(salicylaldehyde) and the ligand $SADH_4$ ($SADH_4$ = $[HOC_6H_4=NN=C(OH)]_2CH_2$) react in a one or two equivalents stoichiometry with $MoO_2(acac)_2$ in refluxing methanol and complexes of the type $[(MoO_2)_2L]$ are formed. [97]

Ligands containing the Schiff base semi-carbazide (-C=N-N=C-) group have been prepared and used in the molybdenum dioxide coordination chemistry. Bidentate ligands such as $dpcH_2$ ($dpcH_2$ = $C_6H_5(H)NNC(O)(H)NNC_6H_5$) or $dptcH_2$ ($dptcH_2$ = $C_6H_5(H)NNC(S)(H)NNC_6H_5$), reacted with $MoO_2(acac)_2$ affording MoO_2LL' complexes (L=dpc(-1), dptc(-2); L' = dpcH (-1), dptcH (-1)). [98]

$MoO_2(acac)_2$ reacts with tridentate ligands such as *o*-$C_6H_4(OH)CH=NN=C(OH)C_5H_5N$, *o*-$C_6H_4(SH)CMe=NN=C(SH)NhCPh_3$ to give complexes of the type MoO_2L or $MoO_2L(Solv)$, (Solv = MeOH, H_2O, py). [12, 99] The MoO_2L type complexes have the referred oligomeric/ polymeric structure. This oligomeric structure is destroyed in the presence of donor solvents.

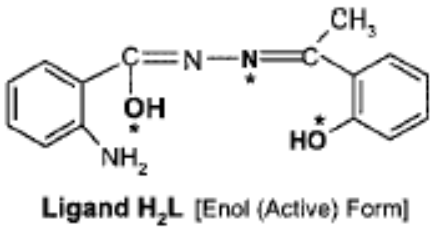
Amino diol ligands were used in the preparation of dioxomolybdenum complexes. The bidentate 2-aminophenol, the tridentate enantiomerically pure ligands, and other tetradentate ligands, react with $MoO_2(acac)_2$ yielding complexes of general formula MoO_2L_2 for the bidentate ligand and MoO_2L for the other cases. [100] Addition of two equivalents of tris(2-hydroxy-3,5-dimethylbenzyl)amine (H_3Lig) to the solution of $MoO_2(acac)_2$ in MeOH results in the formation of anionic complex $LigH_4$ $[MoO_2Lig]$ (**14**), which is the first example of structurally characterized ionic atrane complexes. [101]



14

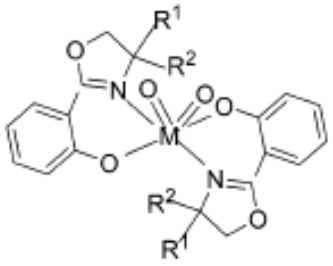
Also, the photo stabilizer Tunivin P, 2-(2'-hydroxyl-5'-methylphenyl) benzotriazole was reacted with $MoO_2(acac)_2$ yielding $MoO_2(acac)L$, rather than the disubstituted complexe. [102]

Recently Ghosh et al. [11] reported a five-coordinate complex MoO_2L, where H_2L is the ONO donor ligand 2-hydroxyacetophenone hydrazone of 2-aminobenzoyl hydrazine (**15**) and which is quite interesting with respect to coordination chemistry because penta-coordinated Mo(VI) complexes, in general, are rare [103] and those with an ONO donor environment are rarer still. The vacant position is found to act as a substrate-binding site, and six-coordinate adducts, like $[MoO_2L(Py)]$ and $[MoO_2L(Imz)]$, are easily formed by the attachment of pyridine or imidazole to this position. MoO_2L is found to mimic the active center of oxo transfer molybdoenzymes and hence is of interest in bioinorganic chemistry.



Ligand H_2L [Enol (Active) Form]

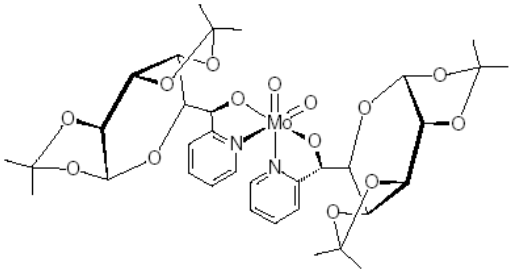
15



16

The chemistry of oxazoline-based ligands is of interest due to their use as chirality-transfer auxiliaries in combination with several transition metals in a wide range of asymmetric catalytic reactions. Several molybdenum(VI) complexes bearing 2-(2'-hydroxyphenyl) oxazolines have been reported in the literature. [104, 105] They were obtained by the reaction of their molybdenum acetylacetonates with corresponding ligand in absolute alcohol. (4'R)-2-(4'-ethyl-3', 4'-dihydroxazlo-2'-yl) phenolato and (4'S)-2-(4'-isopropyl-3', 4'-dihydroxazlo-2'-yl) phenolato were used as ligand to prepare the first dioxomolybdenum (VI) complexes containing chiral oxazoline ligands (**16),** which are obtained as mixtures of three diastereomers due to the ligand and metal chirality. [105]

The C_2-symmetric bis(oxazolines), prepared from readily available amino alcohols [106] can be used as chiral chelating ligand reacting with MoO_2Cl_2 in THF to obtain the complex of the type MoO_2Cl_2L (L = bis(oxazoline)). [107]



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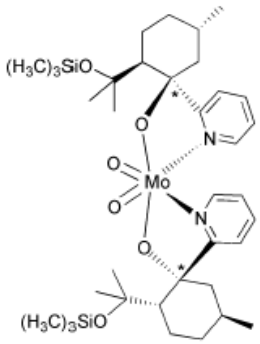
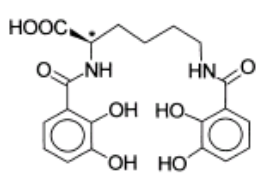


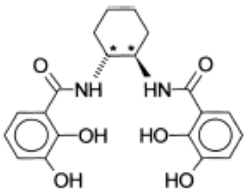
18

2'-Pyridyl alcohols, which are readily accessible in a broad range by the reaction of 2-lithiopyridine with either symmetrical or unsymmetrical ketones, [108] were also used to prepare dioxomolybdenum complex of the type of $MoO_2X(Solv)L$ (L= (2'-pyridyl)alcoholate) from MoO_2Cl_2 in THF [107] or of the type of MoO_2L_2 with $MoO_2(acac)_2$ or ammonium heptamolybdate as starting material. [109] Using the monoterpenes (+)-camphor, (-)-camphor, (±)-fenchone, (-)-fenchone, and (-)-menthone enantiomerically pure 2'-pyridinyl alcoholates can be obtained and can be applied as chiral N,O-Ligands in molybdenum (VI) complexes, e.g. compound (**17**). [110a] Some other chiral pyridyl alcoholate ligands, such as (1R, 2S, 5S)-8- trimethylsilyloxy-1- (2-pyridyl) has been also used to get the complexes of the type of $MoO_2X(Solv)L$ and the type of MoO_2L_2 (**18**). [110b]

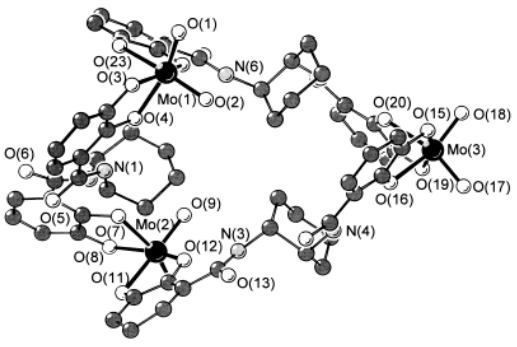
Schiff bases derived from salicylaldehyde and aminoalcohols bearing both alcoholic and phenolic hydroxyl groups and also one neutral nitrogen donor (CH=N imino group) can be used as multidentate ligands in dioxomolybdenum chemistry. [99a, 111]



Azotochelin



H_4-(1*R*,2*R*)-dachcam



19

The reaction of a solution of H_4-(1R, 2R)-dachcam, the analogue of the L-lysine derivative azotochelin, in DMSO with an aqueous solution of sodium or potassium molybdate in a 1:1 ration resulted in the formation of orange trinuclear complex $[\{MoO_2((1R, 2R)\text{-dachcam})\}_3]^{6-}$ (**19**), which be can a model complex to confirm the preferred configuration of the molybdenum complex of the naturally occurring L-lysine derivative azotochelin in aqueous solution. [112]

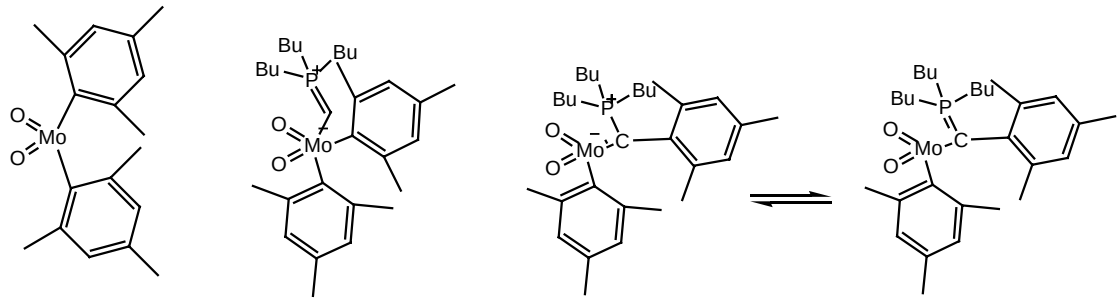
1.1.2.2.6. Organometallic Derivatives

An organometallic dioxomolybdenum complex was among the first organometallic complex synthesized. Over time stabilization of mononuclear dioxomolybdenum complexes by formation of an M-C bond has been achieved with different types of organic ligands. In this text, the review of the literature of monomeric organometallic dioxomolybdenum complexes will be divided in two sections. The first will focus on dioxomolybdenum (VI) complexes with Mo-C σ bonds and the second on dioxomolybdenum (VI) complexes with cyclopentadienyl ligands, a class of ligands which can form Mo-C π or σ bonds. These compounds have been extensively studied, particularly with respect to their metal oxides [113] and is estimated to be present in more than 80% of all known transition metal organometallic complexes. [114]

Dioxomolybdenum (VI) complexes with Mo-C σ bonds

Dioxomolybdenum (VI) complexes with Mo-C σ bonds have been known since 1975, when Heyn and Hoffmann reported the preparation of $MoO_2(mes)_2$ (**20**) from $MoO_2Cl_2 \cdot 2THF$ and the Grignard reagent (mes)MgX. [115]

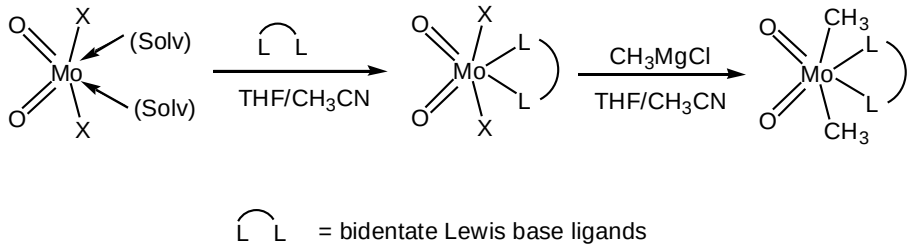
Arzoumanian et al. treated the $MoO_2(mes)_2$ complex with the phosphonium ylide Bu_3PCH_2 and obtained the complexes $MoO_2(mes)C(mes)(PBu_3)$ [116] and $MoO_2(mes)_2C(PBu_3)$ (**21**).[117] For $MoO_2(mes)C(mes)(PBu_3)$ (**22**) the crystallographic data suggest a hybrid of two mesomeric forms, which differ in the connection of the metal to the ylide group. The predominant form seems to be the carbine complex, which in terms of classification positions these complexes at the boundary between σ and π Mo-C bonds.



20 **21** **22**

Three years after the work of Heyn and Hoffmann, the interest in stable organometallic molybdenum complexes arose during the development of models for reactive intermediates of the enzyme nitrogenase.[118] The long term stability (under exclusion of water and oxygen) of the first model complexes of the type $RMoO_2Br(bipy)$ (R = Me, Et)[118] stimulated the search for analogous compounds. In subsequent papers Schrauzer et al. reported the synthesis of a series of complexes with the general formula $MoO_2R_2(bipy)$ (R = Me,[119] *neo*-Pe,[120] Bz,[121] Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, Cy [122] and Ph [123]) and focused mainly on the study of their stability. The methyl derivative was found to be a remarkably stable compound to temperature, decomposing only above 230° C. [119] The most thermally sensitive compounds are those with hydrogen bonds in the β position, such as the ethyl derivative, due to favoring of the β-elimination pathway for Mo-C cleavage, or those with bulky ligands, such as the cyclohexyl derivative, due to Mo-C labilization through steric effects. These alkyl derivatives [122] were obtained by the reaction of $MoO_2X_2(bipy)$ with the correspondent Grignard reagent. The difficulty in obtaining some of the alkyl derivatives necessitated the addition of an aerobic hydrolytic step to the original synthetic pathway. These complexes are isostructural with the other octahedral complexes described previously, with *cis*- MoO_2, the alkyl groups *trans* to each other and the bipy *trans* to the dioxo group. Other derivatives of this type were synthesized by the group of Teruel, like $MoO_2(o\text{-}CH_2C_6H_4Me)_2bipy$,[124] and the structurally characterized $\{HB[3,5(CH_3)\text{-}C_3HN_2]_3\}Mo(O)_2R$ (L= tris (3,5-dimethyl-pyrazol-1-yl)hydroborate) which can be prepared from the reaction of $[HB(3, 5\text{-}Me_2pz)_3]MoO_2Cl$ with trimethyl aluminium. [125]

Compounds of the type $Tp^*MoO_2CH_3$ (Tp^* = hydridotris (3,5-dimethyl-1-pyrazolyl)borate) could not be obtained by the reaction of the precursors Tp^*MoO_2Cl with the correspondent Grignard reagent,[126] but were instead obtained using the alkylation agent $AlMe_3$.[125b] Using the same alkylating reagent, Kaufmann detected by ^{1}H-NMR the formation of the complex $MoO_2Me_2(HMPA)_2$ after mixing MoO_2Cl_2, $AlMe_3$ and labeled HMPA at low temperature.[127]



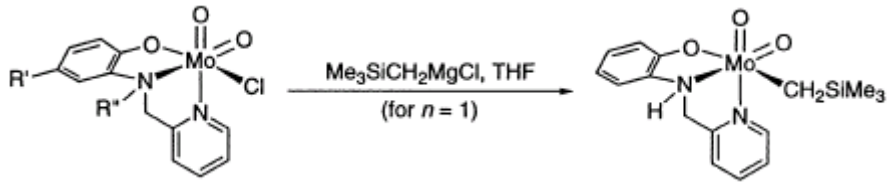
Scheme 1.5. Synthesis of the complexes of the type $MoO_2Me_2L_2$

$MoO_2Me_2L_2$ complexes with a large variety of bidentate ligands (L_2) were prepared in our laboratorirs.[128] These alkyl derivatives can be obtained by alkylation with MeMgX of the halogenated compounds $MoO_2X_2L_2$, which are easily accessible from the solvent adducts $MoO_2X_2(Solv)_2$ (Scheme 1.5). An ethyl derivative was also obtained.

The bidentate ligands are of different types and have different substituents, but have in common a 1,4 diazabutadiene core. These ligands provided access to more soluble complexes than the unsubstituted bipyridyl (bipy) ligand previously used by Schruazer.[128a] No matter what type of ligand used, these complexes display a distorted octahedral geometry with the oxygen atoms in the trans position to the organic N-donor ligands in the equatiorial plane and the methyl groups in trans position, as observed in the halogenated precursors, which makes the more complexes suitable for spectroscopic characterization and sufficiently stable to be handled in air for brief periods of time.[128a]

Ng and Lee et al. [129] synthesized the complex $MoO_2(L_3)(CH_2SiMe)$ with a tridentate ligand (L_3) by treating $MoO_2(L_3)Cl$ or $[MoO_2(L_3)]_2O$ with the Gridnard reagents Me_3SiCH_2MgCl. (Scheme 1.6) Attempts to treat the starting compound with other Grignard reagents RMgX (R=Me, Et, $C_6H_4{}^tBu$-4) or with sodium alkoxides and thiolates were not successful. The

starting compounds were obtained by reaction of the ligand with $MoO_2Cl_2(DME)$ or $MoO_2(acac)_2$.



Scheme 1.6. The synthesis of $MoO_2(L_3)(CH_2SiMe)$ according to Ng et al..

Dioxomolybdenum (VI) Complexes with a Cyclopentadienyl Ligands

$CpMoO_2Cl$, the first dioxomolybdenum organomtallic compound, was obtained by Cousins and Green in small yield by air oxidation of the π-allyl complex $CpMo(CO)_2(\pi\text{-}C_3H_5)$ in the presence of HCl. [130] Later, the same authors found that this and other oxo-, oxochloro and oxobromcyclopentadienylmolybdenum complexes could be obtained by oxidation under various conditions of $CpMo(CO)_2(\pi\text{-}C_3H_5)$, $[CpMo(CO)_3]_2$ and $CpMo(CO)_3H$. [107] Among the obtained complexes two monomuclear dioxo complexes were obtained, namely $CpMoO_2Cl$ [131a] and $CpMoO_2Br$.[131b] Both compounds are stable under nitrogen atmosphere and decompose slowly in air. The obtained yields are generally quite low and the synthetic pathways unspecific for the dioxo complex. Although not depicited, for simplicity reasons, the oxidation of the carbonyl complexes originates several different types of oxo complexes (monomeric and dimeric complexes). These synthetic difficulties have probably hinderd the development of this chemistry, postponing its further development until the late 1980's.

Motivated by the developments in the chemistry of diverse high oxidation state organometallic complexes and by the discovery that the introduction of Cp* instead of Cp products in high oxidation state compounds, which are more tractable, Faller and Ma were able to synthesize the Cp^*MoO_2Cl complex by oxidation of the carbonyl complex $[Cp^*Mo(CO)_2]_2$ with O_2 in chloroform to a μ-oxo bridged dimer and subsequent treatment of this dimer with PCl_5.[132] X-ray crystallography showed that the complex presents the expected mononuclear piano-stool structure. The complex is thermally stably and can be

handled easily in dry air. The bromide derivative was also obtained but is much more unstable than the chloride derivative.

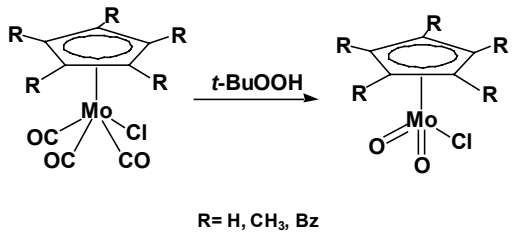
In the same year Legzdins and collaborators proposed a more general synthetic route to compounds of the type Cp'MoO_2R (Cp' = Cp, Cp*, R = Me, CH_2SiMe_3) by exposure of the dialkyl nitrosyl complexes Cp'$(NO)_2R_2$ to water and molecular oxygen. [133]

The compound Cp*MoO_2Cl was also obtained by hydrolysis of Cp*$MoCl_4$ under basic conditions in the presence of air and a reaction time of ca. 30 minutes. According to the authors, shorter reaction times originate a mixture of Cp*MoO_2Cl and Cp*$MoOCl_2$, and a longer reaction times or excess base originate a μ-oxo bridged dimer. [134] Using the same reaction type the compound [η^5-C_5(i-Pr)$_4$H]MoO_2Cl was also obtained. [135]

Inspired by the work of Cousins and Green, [131a] Trost and Bergman synthesized the complex Cp*MoO_2Cl by light-induced oxidation of Cp*$Mo(CO)_3Cl$ with O_2 in toluene. The authors confirmed the air stability of the compounds but referred its decomposition in solution upon exposure to the atmosphere. [136] The same method also afforded the compound [η^5-$C_5Ph_4Ph(OMe)_2$]MoO_2OR (R = Me, Et, Pr, *t*-Bu). [137]

As an alternative to the synthesis presented by Faller and Ma, which was less suitable for large scale synthesis, Bottomley and co-workers synthesized Cp*MoO_2Cl by oxidation of $[CpMo(CO)_2]_2$ with the powerful oxidant H_2O_2/HCl in chloroform.[138] It was reported that the decomposition of Cp*MoO_2Cl is accelerated by light and inhibited in dry oxygen.

Recently, a simple entry to (η^5-C_5R_5)MoO_2Cl (R = H, CH_3(Me), $CH_2C_5H_5$(Bz)) was developed by our group.[139] The compounds can be readily prepared from the parent carbonyls (η^5-C_5R_5)$Mo(CO)_3Cl$ upon reaction with TBHP in CH_2Cl_2 at room temperature (Scheme 1.7).



Scheme 1.7. Synthetic pathway of (η^5-C_5R_5)MoO_2Cl by our group.

1.1.3. Catalytic Applications of Dioxomolybdenum(VI) Complexes

Dioxomolybdenum(VI) complexes of the general formulas $MoO_2R_2L_2$, MoO_2CpX and $MoO_2L(Solv)$ (X = Cl, Br, CH_2R) are stable in room temperature and can be handled also in the air. They can be used as a catalyst for oxidations, for example in the olefin-epoxidation in connection with a suitable oxidant such as *tert*-butylhydroperoxide (TBHP).

1.1.3.1. An overview on the literature works

Dioxomolybdenum(VI)–complexes are important catalysts as well as catalyst-precursors for oxygen-transfer-reactions in chemical and biological system. [77, 103c, 140] Polymer complexes of the composition MoX_2O_2 are known for more than 100 years. [141] Special interest in Mo(VI)-oxo-komplexes arose especially in the late 1960's, when ARCO and Halcon published patents on the olefin-epoxidation through Mo(VI)-complexes in homogeneous phase. [9, 10a] In the following years investigations of the reaction mechanism were carried out to explain their high reactivity. The intensive debate over the mechanism originated mainly from the results presented by teams of Mimoun and Sharpless. [142] The mechanism question could not be solved finally in the spite of numerous theoretical and experimental work until today.

The industrial ARCO-Halcon-process worked with *tert*-butylhydroperoxide (TBHP) as an Oxidant. Although TBHP shows numerous advantages, it did not stop in the past years the development of hydroperoxide (H_2O_2) in place of TBHP as an oxidant, with water as by-product totally friendly for the environment instead of *tert*-butanol (out of TBHP). [3] Examples for newly developed catalysts are methyltrioxorhenium (VII) (MTO) [143] that was well examined mainly by the groups of Herrmann, Sharpless and Espenson and modified Mo(VI) system described by Sundermeyer, Kiefer et al. [144] However all these systems unavoidably show disadvantages (catalyst-standing time, problems of the selectivity, capability to heterogenization, limitation of use etc.) so that further research work has to be dedicate to the finding of the alternative oxidation catalysts.

Following the work in our lab in epoxidation catalysis using organorhenium complexes, the complexes of the type $MoO_2R_2(L_2)$ (R=Me, Et) where L_2 represents a variety of bidentate ligands, were tested in epoxidation catalysis. [128a, 128b, 145] Screening tests with MoO_2Me_2(*t*-Bubipy)$_2$ using cyclooctene as substrate and TBHP, H_2O_2 and Ph_3COOH as oxidants showed that TBHP was the only oxidant for which product formation is significant. Epoxidation activity was also explored for other olefins, such as 1-octene, 2-octene, cyclododecene, limonene, [128c] cyclohexene and styrene. [128a]

The L ligands strongly influence the catalytic activity according to their rigidity, the steric hindrance and electron attracting capacities. [128a, 128b, 145] Bipyridine and bipyrimidine ligands originate rather slow catalysts of general low activity but substituted 1, 4-diazabutadienes seem to be very promising ligand. [128c] The best results were obtained for MoO_2Me{p-tolyl-CH_3DAB}. [128c] In this case, cyclooctene conversion was quantitative up to 70° C and can be reused in a second catalytic cycle leading to equivalent results. [128a] During the course of the catalytic reaction, the oxidizing agent TBHP is transformed to tert-butanol, which slows down the reaction velocity since it can also coordinate to the molybdenum centre.

The generally comparatively good catalytic activities of several molybdenum(VI)-oxo complexes in oxidation reactions make this type of complexes - in principle - promising candidates for asymmetric catalysis by using chiral ligands. Mimoun et al. reported on the enantioselective epoxidation of prochiral alkyl-substituted olefins in 1979 untilizing a Mo(VI) complex bearing a chiral ligand, [109b, 109d] but the enantioface selectivity was not high. Molybdenum(VI) complexes, which originate from $MoO_2(acac)_2$ and chiral ligands which are from chiral pool have been also used as catalyst for the symmetric epoxidation of olefin with hydroperoxide as oxidant. For example, Yamada applied catalytic amount of mixture of $MoO_2(acac)_2$ and N-alkylephedrin for the epoxidation of allylic alcohols with up to 33% ee. [146]. Using N-methylprolinol the enantiomeric excess increases to 50%.[147] A heterogeneous catalyst with $MoO_2(acac)_2$ and (2S, 4R)-4-hydroxyprolin immobilized on an USY-zeolithe was developed by Corma and up to 45% ee can be reached. [148] Brunner et al obtained 43% ee when $MoO_2(acac)_2$ and diisopropyltartrat were used for the epoxidation of N-allyl-

trichloracetamide. [149] Several other attempts to achieve chiral epoxidation, e.g. with Mo based catalysts have been made, but usually led only to moderate enantiomeric excesses. For example, chiral ligands, 2'-pyridyl alcohols [109b, 109d] and phosphinoalcohols [150] have been reported to induce epoxidation with 20-40% ee for functionalized olefins when coordinated to dioxo or peroxo molybdenum(VI) fragments. The synthesis of a variety of *cis*-MoO_2^{2+} epoxidation catalysts bearing chiral ligands, such as bis-oxazoline, [107, 110b] *cis*-diol and *cis*-8-phenylthiomenthol [151] have been reported with moderate ee values.

1.1.3.2. Mechanistic Considerations for the Epoxidation with Mo(VI) Complexes

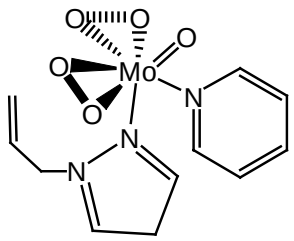
Molybdenum complexes are well-established catalysts for the epoxidation of olefins with alkylhydroperoxide. The nature of the metal species responsible for oxygen transfer has been extensively debated in the literature. In all cases, the active species is believed to be a Mo(VI) compound. [136, 152] Despite its long history and industrial relevance, the mechanism of Mo(VI) catalyzed epoxidation of olefins with alkylhydroperoxides remains a subject of debate. [128b, 153]

The major problem with respect to mechanism determination seems to be the fact that different complexes follow different mechanistic pathways, which does not enable the exclusion of certain pathways for each new Mo(VI) complex tested in epoxidation catalysis.

Although the selectivity of the Mo(VI) complexes in epoxidation reactions seemed to exclude a radical pathway (radical or homolytic pathways of oxidative reactions are believed to yield a mixture of products), [154] the homolytic pathway could not be completely excluded due to the work of Koch and Skibida. [155] For that reason, some studies still perform tests with radical scavengers in order to exclude a radical mechanism. [128b]

Determination of the catalytically active species has also been a subject of many publications. Isolation of cis- dioxomolybdenum (VI) species from epoxidations, regardless of which molybdenum compound is initially added as catalyst, and ubiquity of oxo groups in molybdenum chemistry, led to the belief that the active catalytic species should bear oxometal group. [156] Due to the fact that peroxo species are active in olefin epoxidation and can be

obtained from the reaction of oxometal groups with alkylhydroperoxides, peroxo complexes were considered active intermediates. [142a, 157] Due to early labeling studies, [156, 157] and to the study of the steric effects of the alkyl substituents of the hydroperoxides on the reaction rate, [158] intact alkyl peroxo complexes were also considered as possible active intermediates.



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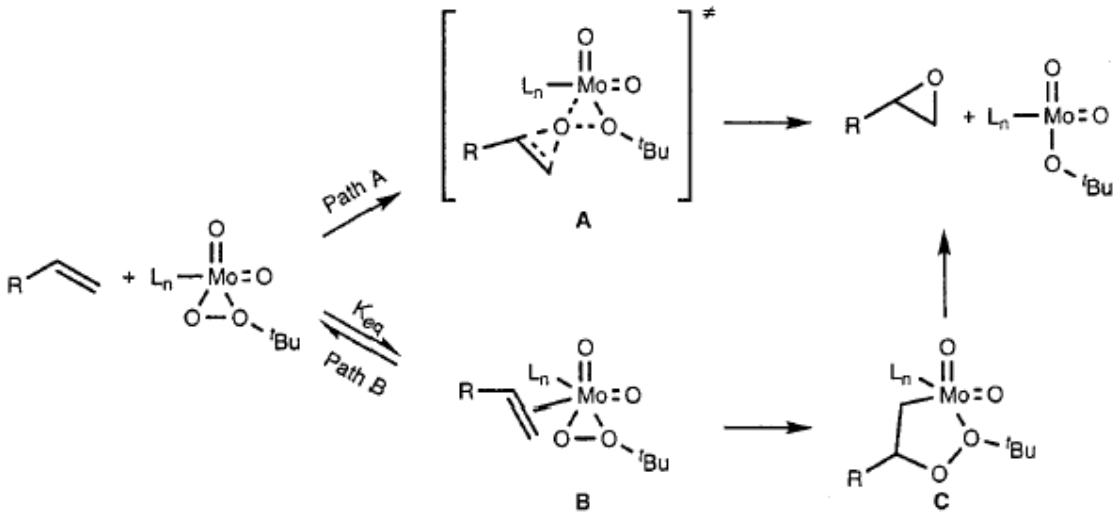
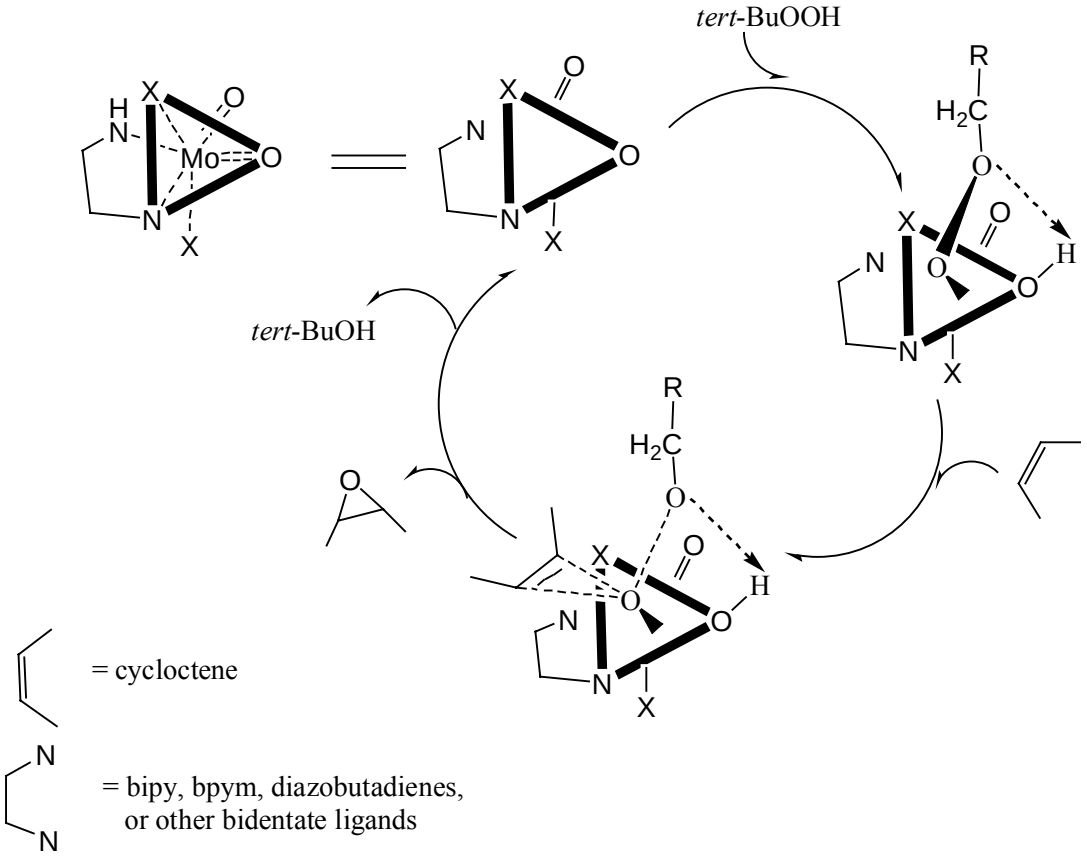
Many years later Thiel et al. proposed again the alkyl peroxo complexes as active intermediates by studying seven-coordinated bisperoxo complexes with non dissociating ligands. [159] In one of these studies, Thiel et al. [159a] showed the unreactivity of the peroxo complex towards olefins by synthesizing a molybdenum peroxo complex with a tethered olefin (**23**), for which epoxidation only occurs in the presence of TBHP.



Scheme 1.8. Mechanism suggested for oxygen transfer to the olefin. Upper pathway originally suggested by Sharpless, lower suggested by Mimoun.

Nowadays, the formation of a Mo(VI) alkyl hydroperoxide complex and the transfer of the distal (α) oxygen of the alkyl rather than the terminal metal oxo ligand, are generally agreed upon. However, despite the fact that several theoretical and mechanistic studies have been presented, [160] it still remains a point of contention whether the reactions proceed by the mechanism originally suggested by Sharpless et al,. which includes direct oxygen transfer, or by the mechanism suggested by Mimoun et al., which includes the formation of a Mo(VI)-olefin complex (Scheme 1.8). [128b, 153]

Based on spectroscopic data, theoretical calculations [128b] and previous studies from other groups, [160a, 160b] our group proposed a new mechanism. Radical species and mono or bisperoxo complexes were considered as unlikely to take part in this catalytic reaction (Scheme 1.9)



Scheme 1.9. Proposed mechanism for TBHP activation and olefin epoxidation taking place at the NOX face of the distorted octahedral complex $MoO_2X_2L_2$ (X = Me, Cl or Br). In the drawings, the metal is hidden behind the face for clarity.

The first step of the catalytic cycle is the reaction of TBHP with the complex. The peroxidic hydrogen of TBHP is transferred to one of the terminal oxygen atoms of the complex and the remaining –OOR coordinates as seventh ligand in a η^1- manner to the molybdenum center. This addition takes place on the NOX face of the octahedron and promotes the activation of the TBHP. The second step of the reaction should proceed by approach of the olefin to the coordination α oxygen. At this stage, there seems to exist a hydrogen bond between beta-oxygen of the oxidant and the coordinated OH group. This favours the formation of the epoxide and the release of the alcohol, leaving the unchanged catalyst precursor for a new cycle.

1.1.3.3. Epoxidation with Cyclopentadienyl - Dioxomolybdenum (VI) Complexes

To the best of my knowledge, catalytic activity of dioxomolybdenum complexes with a cyclopentadienyl ligand was only reported by Trost and Bergman for the complex Cp^*MoO_2Cl. [136] These authors have shown that Cp^*MoO_2Cl can act as catalyst for the epoxidation of several olefins as long as they do not include electron- withdrawing groups. Besides TBHP, other alkyl hydroperoxides, such as cumene hydroperoxide, 3-ethyl-hexyl hydroperoxide and *n*-hexyl hydroperoxide were found to function as oxidants. In contrast, both hydrogen peroxide and Ph_3COOH failed to give any catalytic reactions. In the case of TBHP, the authors found out that Cp^*MoO_2Cl react with the oxidant originationg a peroxo complex of the type $Cp^*Mo(O_2)OCl$. Catalytic tests using this peroxo complex as only available catalytic species have shown that it is completely inactive in olefin epoxidation. The lack of reactivity of the peroxo complex demonstrates that in this system it can not be the intermediate responsible for oxygen transfer, in agreement with the findings of Thiel et al. for related Mo (VI) compounds (see previous part). [159c] The use of a catalyst that forms a non-reactive peroxo complex may lead to a cleaner reaction with fewer by-products but has the disadvantage that peroxo formation poisons the active catalyst. Except for the formation of the peroxo complex, Cp^*MoO_2Cl seems to maintain its integrity during the catalytic reaction, showing no observable oxidation of the Cp* ligand.

Trost and Bergman also studied the effect of the alkyl hydroperoxide on the relative rate of the epoxidation and found out that the obtained rates were consistent with the formation of an intermediate species in which the alkyl group of the hydroperoxide moiety is intact. Sterically demanding alkyl groups of alkyl hydroperoxides retard the relative rates of epoxidation, meaning that at some point in the mechanism there exists a substantial steric interaction between the hydroperoxide alkyl group and the olefin.

1.2. Objectives

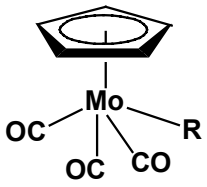
The most important drawbacks of the Mo based oxidation catalysts known at the starting point of this work were the difficulties to modify their reactivity by ligand modification, the lack of easy heterogenizability and the difficulties in introducing chirality in the systems in order to apply them for chiral oxidations, particularly epoxidations (see also previous chapter and the references cited therein). To find solutions to these problems was also attempted in some other research groups, among them that of W. R. Thiel, of J. Sundermeyer and of I. S. Gonçalves. While the former two research groups concentrated mainly on $Mo(O_2)_2O$ and $Mo(O_2)_2OL_{1\text{-}2}$ type catalyst systems, the latter group was working mostly on $MoO_2X_2L_2$ systems, being L a Lewis Base and X usually a halogeno ligand.

In our research group, however, $MoO_2R_2L_2$, MoO_2L_3 and $CpMoO_2X/R$ systems were being examined. The idea behind choosing such compounds was to have both strongly attached ligands (being either tridentate or Cp-derivatives, which are equivalent to a tridentate ligand considering their steric bulk) and an easily tunable ligand system in order to finetune the catalytic activity, to introduce chirality and to heterogenize the catalyst systems on mesoporous materials.

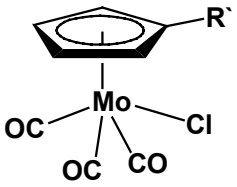
The goal of this work was to examine MoO_2L_3, MoO_2L_3L' and $CpMoO_2Cl/R$ systems with respect to their synthetic availability and their applicability as homogeneous and heterogenized catalysts. Systems of these types are usually applied in olefin epoxidation with *t*-BuOOH (TBHP) as oxidizing agents. Despite the fact that from an environmental point of

view hydrogen peroxide (water as byproduct) or oxygen (no byproduct) seem to be more desirable as TBHP (*t*-BuOH as byproduct), the mild and selective oxidation ability of TBHP and its easy handling make it still to a preferred oxidizing agent, even in the eyes of most industrial chemists, working on related topics. It was therefore not planned to replace TBHP as oxidizing agent by H_2O_2 or (molecular) oxygen.

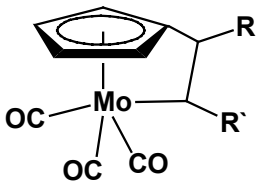
For the synthesis of the $CpMoO_2X/R$-systems $CpMo(CO)_2X/R$-precursors where chosen, since they are comparatively easy to synthesize and the oxidative decarbonylation with TBHP, the same oxidation agent as to be applied in the catalytic reactions, leads directly to $CpMoO_2X/R$ products. This was found in a cooperation project between our research group and that of C. C. Romão briefly before the start of my work at the Technische Universität München. Based on this finding it was decided to synthesize both chiral and heterogenizable derivatives of $CpMo(CO)_3Cl$. For the insertion of a chiral group or a linker to the surface three potential possibilities where considered. They are given as formulae I – III.



I



II



III

A second synthetic pathway, aiming at the application of tri-and tetrdentate ligands, including chiral derivatives was also chosen to be followed, since it was assumed that compounds of formula MoO_2L_3, MoO_2L_3L' and MoO_2L_4 would not easily loose their ligands and could open the possibility of introducing chirality based on nature's chiral pool.

The following chapters describe the details of the work, which was performed to achieve these goals and the outcome of the synthetic and catalytic efforts.

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2. Molybdenum(VI) *cis*-dioxo Complexes Bearing Sugar Derived Chiral Schiff Base Ligands and their Applications in Epoxidation Catalysis

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Dalton Trans., **2003**, 3736–3742

2.1. Abstract

Molybdenum(VI)-*cis*-dioxo complexes bearing sugar derived chiral Schiff base ligands of general formula $MoO_2(L)(Solv)$ have been synthesized (with L = N-salicylidene-D-glucosamine; N-salicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine; N-5-chloro-salicylaldehyde-1,3,4,6-tetraacetyl-α-D-glucosamine; N-salicylaldehyde-1,3,4,6-tetraacetyl-β-D-glucosamine; N-5-chloro-salicylaldehyde-1,3,4,6-tetraacetyl-β-D-glucosamine; N-salicyliene-4,6-O-ethylidene-β-D-glucopyranosylamine, and Solv = methanol or ethanol). Analytical data including IR, 1D- and 2D-NMR, MS and EA are in accord with their descriptions as monometallic compounds with one ligand L and a coordinated solvent molecule. One of the complexes and two of the chiral ligands have been exemplary examined by X-ray crystallography. In the case of the sugar –OH groups being protected as acetyl groups, one of them is selectively deacetylated and coordinates to the metal centre during the reaction process. Furthermore, an inversion takes place at the C1 carbon atom. This uncommon behaviour has been examined in some detail. The high catalytic activity of the title compounds for epoxidation is also described as well as the moderate enantiomeric induction of up to 30% ee for *cis*-ß-methyl styrene.

2.2. Introduction

The recent years have seen an increasing interest in the synthesis of chiral oxometallate complexes and their use as catalysts for asymmetric olefin epoxidation. [1] The generally comparatively good catalytic activities of several molybdenum(VI)-oxo complexes in oxidation reactions make this type of complexes - in principle - promising candidates for asymmetric catalysis by using chiral ligands.[2] 2'-pyridyl alcohols[3] and phosphinoalcohols[4] have been reported to induce epoxidation with 20-40% ee for functionalized olefins when coordinated to dioxo or peroxo molybdenum(VI) fragments. In this context, we and others have reported on the synthesis of a variety of *cis*-MoO_2^{2+} epoxidation catalysts bearing chiral ligands, such as bis-oxazoline,[5] *cis*-diol and *cis*-8-phenylthiomenthol.[6]

Carbohydrates are naturally occurring enantiomeric pure compounds ("chiral pool")[7] that might be of interest in metal-assisted or metal-catalyzed enantioselective synthesis. During the past decade, the nature of their interactions with metal ions has been delineated by the characterization of many complexes.[8] Furthermore, strategies for saccharide ligand modification have also been developed in order to make the isolation and characterization of the products more straightforward. In this respect, one of the most successful ligands are the Schiff base analogues derived from the condensation of a saccharide containing a NH_2 group with a salicylaldehyde or one of its derivatives, in order to obtain a ligand prone to N, O coordination to the metal centre.[9,10]

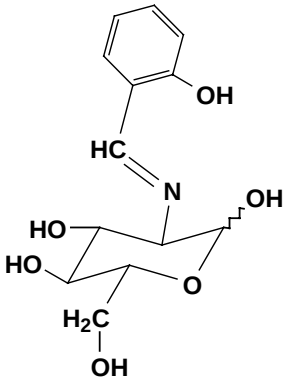
Still, catalytic applications of metal centres with sugar-derived ligands are quite rare. Among the few examples yet known are the hydroformylation of styrene with Rh(I)-diphosphine complexes,[11] catechol oxidation with Cu(II)-aminocarbohydrate ß-ketoenaminic complexes,[12] hydrogenation with iridium-dithioether complexes[13] and allylic alkylation with palladium complexes.[14] However, despite some sugar derived ligands coordinated to *cis*-MoO_2^{2+} moieties have been reported recently,[9] the potential of this class of compounds as catalysts for olefin epoxidation, has not been, to the best of our knowledge, so far explored. In this work a study on the catalytic activity of molybdenum dioxo complexes bearing sugar containing Schiff base ligands is presented and the first example of a molybdenum catalyzed

deacetylation and an unusual ligand transformation during the coordination process with the molybdenum moiety is reported.

2.3. Results and Discussion

2.3.1. Synthesis and spectroscopic examinations

The chiral Schiff base ligands **1**- **6** (see Chart 1) were prepared by the condensation of salicylaldehyde and the corresponding D-glucose amines in water or methanol according to literature procedures.[15]



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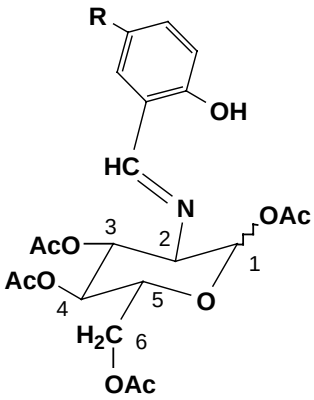
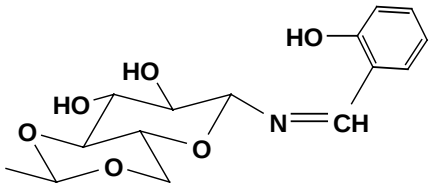
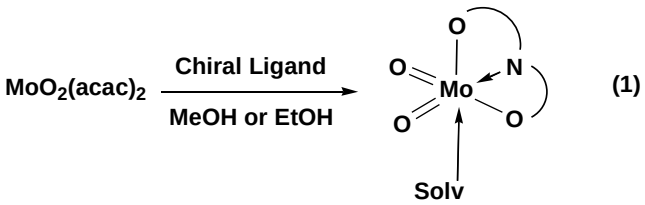


α-configuration at C-1, R = H (**2**)
α-configuration at C-1, R = Cl (**3**)
β-configuration at C-1, R = H (**4**)
β-configuration at C-1, R = Cl (**5**)

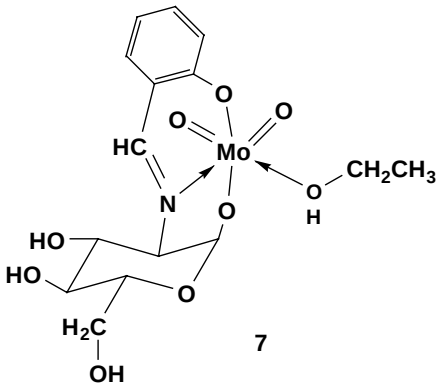


6

The corresponding Mo-complexes **7**-**12** of these ligands were synthesized by the reaction of $MoO_2(acac)_2$ and 1.1 equivalents of the corresponding chiral sugar ligands in methanol or ethanol, respectively, and could be isolated by precipitation on the addition of diethyl ether as shown in Eq. 1.



(1)



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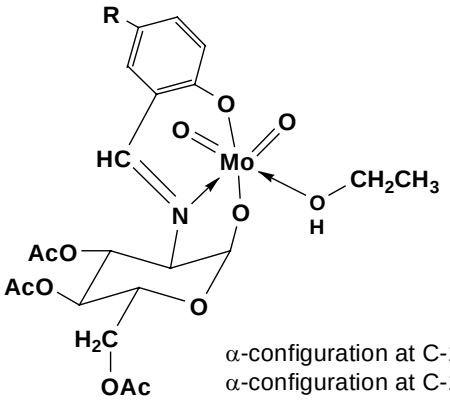
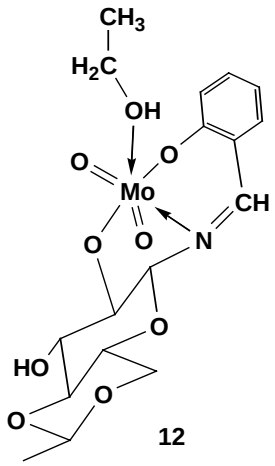


α-configuration at C-1, R = H (**8/10**)
α-configuration at C-1, R = Cl (**9/11**)



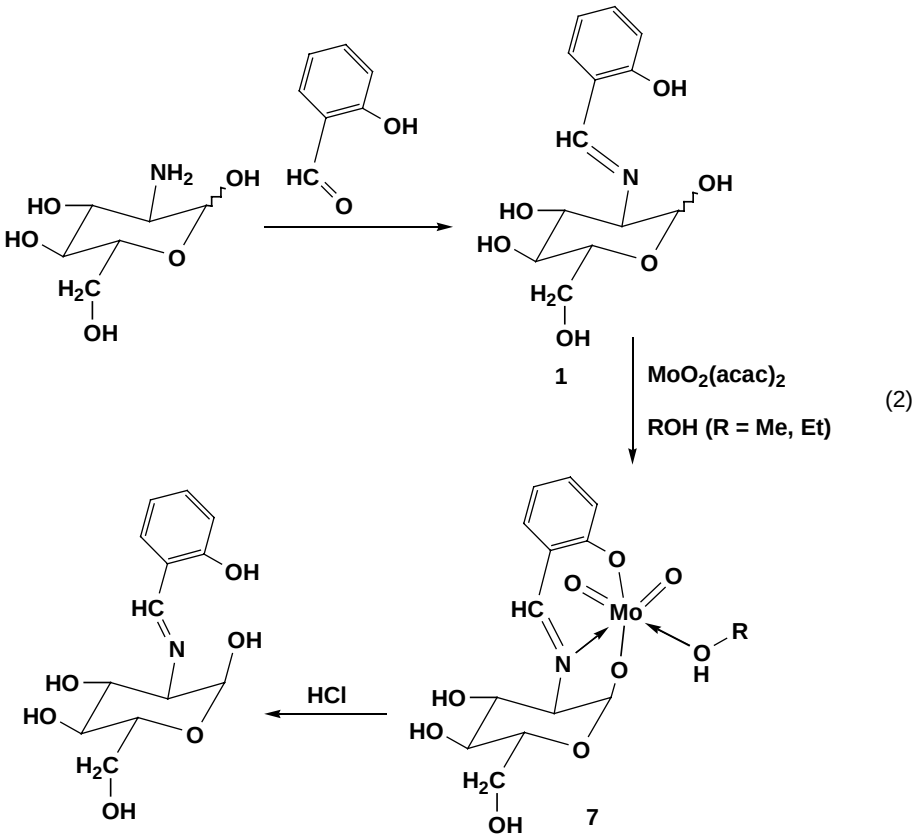
12

All the new complexes are fairly air stable as solids, albeit decomposition occurs slowly in solution and the colour changes from yellow to green in the presence of moisture or moist air. Comparison of the FT-IR spectra of all the complexes with those of their precursor ligands supports the formation of the respective complexes since significant spectral changes are observed. The infrared spectra of the compounds exhibit two strong $\nu_{Mo=O}$ bands in the region of 920-940 and 900-910 cm^{-1}, characteristic of the symmetric and asymmetric stretching vibrations of the *cis*-$[MoO_2]^{2+}$ fragments. Furthermore, the disappearance of the –OH-hydrogen of the phenol group at *ca* 12 ppm in the ^{1}H-NMR spectra also proves the coordination of the central metal with the $–O^-$ group of the phenol moiety.

Compounds **7**-**12** exhibit their ^{95}Mo NMR resonances shifted to higher field (-15 to - 22 ppm) in comparison with the starting material $MoO_2(acac)_2$ (0 ppm). As expected, compound **7** with the ligand bearing free -OH groups exhibits the shift at higher field. These values can be

compared with those reported in the literature for complexes bearing the *cis*- $[MoO_2]^{2+}$ moiety and two bidentate N-O ligands.[1b]

Spectroscopic and elementary analyses are consistent with monomeric complexes with a ligand:Mo ratio of 1:1. The mass spectra give no hint of the presence of dimeric species[16] or indicative fragments. For example, the molecular mass *m*/*z* = 409 and 536 was found in the mass spectra for the complexes **7** and **8,** respectively, and there are no other peaks in the higher mass region. When the synthesis reactions were performed using two equivalents of ligands, the same products were formed as observed with 1.1 equiv. ligand.



Interestingly, complex **7** is found to be a pure α-configurated compound according to the ^{1}H and ^{13}C NMR spectral study and could be obtained with yields of around 80% from ligand **1**. The ^{1}H NMR spectra of ligand **1**, however, shows two sets of signals, which represent α- and ß-configuration with an integration area relationship of 1:2, while the $J_{1,2}$ coupling constants are 3.5 and 7.8 Hz for the *cis*-configuration of the α-sugar ring and the *trans*-configuration of

the ß-sugar ring, respectively.[17] After coordination, the ^{1}H-NMR spectrum of complex **7** consists of only one set of peaks. The chemical shift of H1 changes to 5.58 ppm and the coupling constant $J_{1,2}$ is 3.04 Hz, indicating H1 and H2 to be in a *cis*-configuration. Furthermore, it demonstrates that the inversion of ß-configuration into α-configuration occurs during the coordination of Mo, because the product yield is much higher than the content of α-configuration in the ligand precursor. To the best of our knowledge, such a phenomenon has not yet been reported in molybdenum coordination chemistry. The most possible structure of compound **7** is shown below, and a coordinated ethanol molecule is also found in the ^{1}H NMR. This reaction could therefore be even used as a possible method for the resolution of a diastereomeric sugar derived Schiff base into a enantiomeric pure chiral one as outlined in Eq. 2.

This interesting configuration transformation prompted us to a further examination of the interaction between the Molybdenum dioxo moiety and the protected sugar ligands **2** and **4**, which have differently configurated acetyl groups at their C1 positions. Again, inversion takes place when the ß-configuration ligand is used, while the α–analogue remains in its original configuration, as it can be seen by comparison of the coupling constants between H1 and H2 of the ligands **2** and **4** and their complexes **8** and **10**. Besides, it is interesting to note that the structures of complexes **8** and **10** are identical, since a deacetylation process occurs in both coordinations. The NMR spectra of complexes **8** and **10** demonstrate that in both cases one of the methyl groups and one of the carbonyl groups, which belong to the acetyl group, disappeared. By comparison of the ^{13}C NMR spectra of the complexe **8**/**10** with the ligands **2** and **4**, it is found that the chemical shift of the C1 in the ligand increases about 8 ppm after the coordination to Mo, while the other ^{13}C-signals of the sugar ring remain almost unchanged. This observation indicates that the deacetylation reaction occurs solely at the C1 position during the coordination. Furthermore, the pure complex **8**/**10** can be obtained when ligands **2** and **4** are mixed and used together. When a 1:1 mixture of the ligands **2** and **4** is reacted with $MoO_2(acac)_2$, only the C1-α-configurated ligand is consumed while the C1-ß-configurated ligand remains in solution. Obviously the deacetylation/coordination reaction runs

considerably faster than the inversion at C1 position. The same phenomenon can be also found in the case of ligands **3** and **5** to give the same α-configurated product **9**/**11**. Representative chemical shifts and coupling constants are listed in Table **1**.

Table1: Selected ^{1}H NMR chemical shifts and coupling constants

	1 (α-)	**1** (β-)	**7**	**2** (α-)	**4** (β-)	**8/10**	**3** (α-)	**5** (β-)	**9/11**
δ(ppm)H-1	5.09	4.74	5.58	6.25	5.88	5.87	6.24	5.87	5.84
$J_{1,2}$	3.52	7.80	3.04	3.74	8.05	3.74	3.66	8.32	3.56
δ(ppm)C<u>H</u>=N	8.32	8.31	8.54	8.37	8.30	8.37	8.30	8.24	8.27

An ester-exchange reaction catalyzed by a molybdenum moiety has been mentioned in the literature only once.[18] For the deacetylation of this kind of ligand, Lewis acids such as $ZrCl_2$ and $SnCl_4$ have also been successfully used.[19, 20] Furthermore, by using $Ba(OMe)_2$ as catalyst, a similar process named Zemplén deacetylation[21] occurs, accompanied by a similar inversion at the C1 position.[17] The reaction described here provides another method for a selective deacetylation at the C1 position.[22] When complex **8/10** was decomposed in acids such as hydrogen chloride, the resulting amine salt was shown to display α–configuration by ^{1}H-NMR spectroscopy and chiral GC.

Another important observation is the partial replacement of the ligand when compound **8**/**10** is stirred for prolonged times (24 h) at 40 °C with an excess of ligand **3** or **5** under formation of complex **9**/**11**. A similar observation is made when stirring compound **12** with excess ligand **2**. The ease of the ligand exchange in solution may account at least in part for the quite low *ee*'s obtained in the catalytic reactions (see below).

2.3.2. The crystal structure of complex 8/10 and the ligands 2 and 3

In order to confirm the structure of the complexes described above, derived from spectroscopic results the X-ray crystal structure of compound **8/10** was exemplary determined.

Selected bond distances and bond angles are given in Tab. 2, an ORTEP style presentation is shown in Fig. 1.

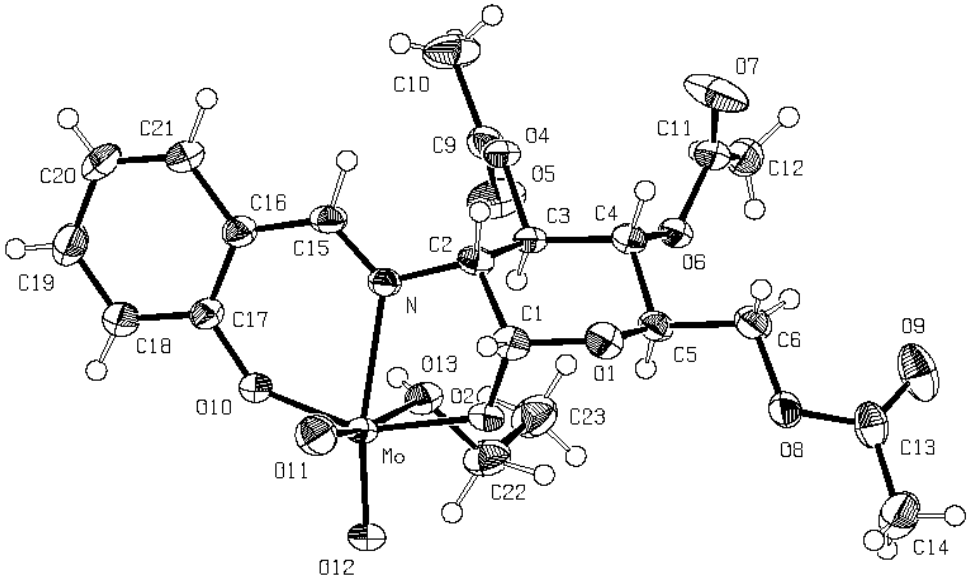


Figure 1: ORTEP style drawing of the structure of compound **8/10**. The thermal ellipsoids are given at a 50 % probability level.

The bond distances between the Mo core and the terminal oxygens are around 170 pm, the bond distances to the sugar derived Schiff base ligand oxygens ca. 195 pm. The ethanol OH-group oxygen-Mo bond is, as expected, significantly longer (234.76(15) pm). While the terminal Mo-O bonds can be regarded as double bonds, the Mo-O ligand bonds are single bonds. The ethanol molecule, however, is only acting as a neutral donor ligand, which should therefore be replaceable quite easily. This ease of replacement might be the reason for both the good catalytic activity (high initial TOF, see below) and the moisture sensitivity of the complexes. The nitrogen donor atom is 228.48(15) pm away from the Mo core. While the terminal oxygens occupy a *cis*-position, the ligand oxygens are located in a trans position to each other with an O-Mo-O angle of ca. 150°. Together with the ligand nitrogen atom they coordinate the Mo centre in a distorted T-fashion. The nitrogen atom and the ethanol-oxygen atom are in *trans*-position to the terminal, double bonded oxygens. The coordination around the metal is a highly distorted octahedron, as it is typical for six-coordinated Molybdenum (VI)

complexes. Compound **12**, first synthesized by Rao *et al.* has also been crystallographically examined by Rao's group.[9] Despite the higher steric rigidity of its ligand, the overall structure as well as the observed bond distances and angles are very similar to that of compound **8/10**.

For sake of completeness the structures of the sugar derived chiral Schiff bases **2** and **3** have also been examined by X-ray crystallography. The structures are depicted in Figures 2 and 3 and selected bond angles and distances are given in the respective figure captions. The bond angles and distances are only marginally influenced by the coordination to the Mo centre (see complex **8**/**10** for comparison), showing that the complex geometry is strongly influenced by the ligand geometry.

Table 2 Selected bond lengths (pm) and bond angles (deg) of complex **8/10**

Mo – O2	194.38(13)	Mo – O10	195.38(14)
Mo – O11	169.21(15)	Mo – O12	171.26(13)
Mo – O13	234.76(15)	Mo – N	228.48(15)
N-C2	146.6(3)	N-C15	128.9(2)
C17-O10	134.4(2)	C1-O2	141.1(2)
O2 – Mo – O10	150.33(6)	O2 – Mo – O11	99.09(6)
O2 – Mo – O12	97.95(6)	O2 – Mo – O13	79.98(5)
O2 – Mo – N4	74.60(6)	O10 – Mo – O11	97.16(7)
O10 – Mo – O12	101.31(6)	O10 – Mo – O13	79.98(6)
O10 – Mo – N	80.12(6)	O11 – Mo – O12	105.74(8)
O11 – Mo – O13	170.65(7)	O11 – Mo – N	92.28(7)
O12 – Mo – O13	83.59(6)	O12 – Mo – N	161.50(7)
O13 – Mo – N	78.48(5)	Mo – O2 – C1	118.51(12)
C2 – N – C15	119.20(16)	C2 – C1 – O2	108.29(15)
C1 – O1 – C5	115.16(13)	C1 – C2 – C3	110.63(15)

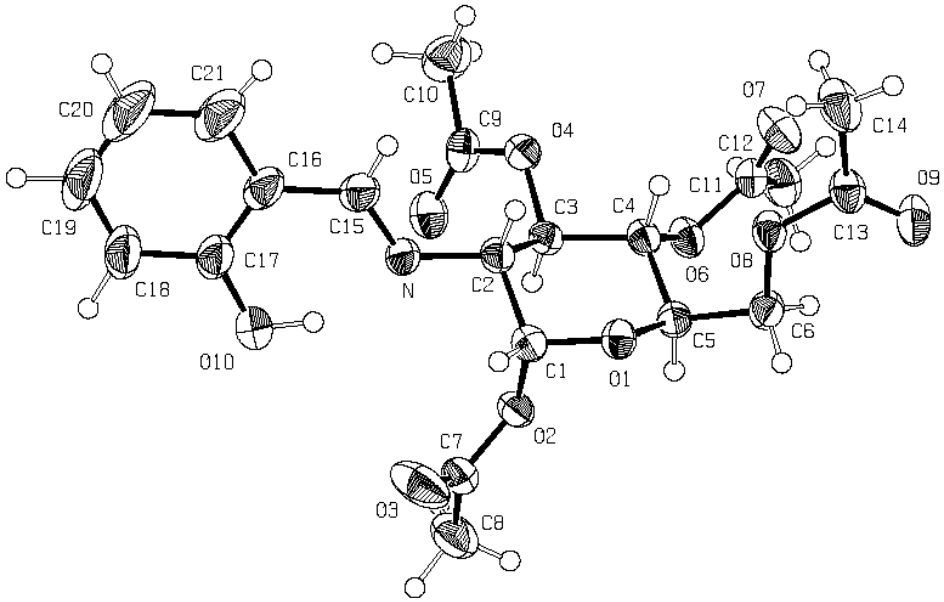


Figure 2: ORTEP style drawing of the structure of compound **2**. The thermal ellipsoids are given at a 50 % probability level. Selected bond distances (pm) and bond angles (deg): N–C2 145.1(2), N–C15 127.1(2), C17–O10 134.1(2), C1–O2 145.0(2), C3–O4 144.4(2); C2–N–C15 117.37(12), C2–C1–O2 108.29(10), C1–O2–C7 119.31(11), C1–C2–C3 107.48(10).

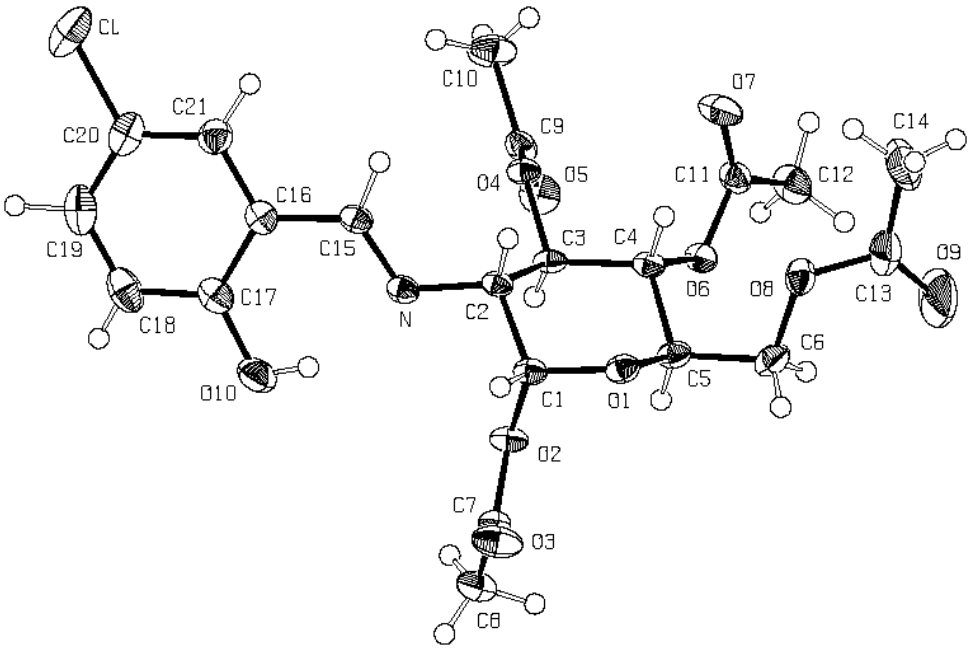


Figure 3: ORTEP style drawing of the structure of compound **3**. The thermal ellipsoids are given at a 50 % probability level. Selected bond distances (pm) and bond angles (deg): N–C2 145.2(2), N–C15 127.6(2), C20–Cl 174.8(2), C17–O10 134.7(2), C1–O2 143.3(2), C3–O4 144.2(2); C2–N–C15 117.70(12), C2–C1–O2 106.57(11), C1–O2–C7 117.41(11), C1–C2–C3 110.03(11).

2.3.3. Complexes 7-12 in oxidation catalysis

The molybdenum-Schiff base complexes **7**-**12** were examined as catalysts in the epoxidation of cyclooctene and both of *cis*- and *trans*-β-methylstyrene, with *t*-butylhydroperoxide (TBHP) as the oxidant. Details about the conditions applied are given in the experimental section. Blank runs were performed and, as expected, without catalyst, no significant epoxide formation was observed under the applied conditions.

In general, complexes **7**-**12** catalyzed the epoxidation of all three examined alkenes with good activity and complete stereo-retention, without significant by-product formation, the selectivity being close to 100%. In the case of epoxidation of cyclooctene, the yield reaches after 4 h a value of 60-70%, and after 22h the reaction is completed in all cases (with the only exception of compound **7**), when the catalyst:substrate:oxidant ratio is 1:100:200. Complex **9**/**11** and **8**/**10** show the best catalytic activities with the highest TOFs of around 13000/h with catalyst:substrate:oxidant ratios of 1:10000:20000. The substituent at the phenyl ring (H or Cl) seems of little effect for the catalysis. The lowest activity is found for catalyst **7**: after 4 h only 20% yield could be obtained, while 70% were reached after 24hrs, when the catalyst:substrate:oxidant ratio is 1:100:200. The main reason for this is probably the bad solubility of compound **7** in the oxidation solution. This explanation is supported by the observation that the general catalyst activity remains fairly unchanged for a much longer time than in the case of the other catalysts described in this work. When the soluble part of the catalyst decomposes, other catalyst molecules are dissolved and maintain the overall catalyst activity for some more time.

For the epoxidation of *cis*- and *trans*-ß-methylstyrene, as expected, the general observation is that the catalytic activity as well as the asymmetric induction for the *cis* substrates is much better than that for the *trans* analogues. The effects of temperature, solvent and the amount of catalyst used have also been studied, and indicate that low temperature is beneficial for the *ee* obtained in this reaction. Within experimental error the results are the same in both CH_2Cl_2 and toluene solvents. Higher amounts of catalyst also improve both *ee* and yield values. Accordingly, the highest observed *ee* of *ca* 30% could be obtained with compound **12** as

catalyst at 0°C (Tab. 3). The low temperature effect is probably due to a slower ligand exchange rate (see also above).

Table 3 Epoxidation of cis- and trans-β-methylstyrene catalyzed by molybdenum-sugar complexes[a]

Catalyst	Temp (°C)	*cis*-β-methylstyrene		*trans*-β-methylstyrene	
		ee(%)	Yield(%)	ee(%)	Yield(%)
7	0	0	15	0	6
	55	0	72	0	11
8/**10**	0	17	29	5	38
	55	5	94	2	72
9/**11**	0	22	31	3	46
12	0	23	35	10	17
	0[b]	30	52	12	25
	55	4	96	3	70

[a] The reactions were carried out by using a catalyst: substrate: oxidant ratio of 1:100:200 unless specified otherwise, the reaction time was 22h and toluene as the solvent. Lower temperature (-23°C) has also been applied in this reaction, but the low reactivity retards the attempts for the improvement of enantioselectivity.
[b] Using a 5 mol% amount of catalyst.

2.4. Experimental Section

2.4.1. Synthesis and Characterization

The preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere using the standard Schlenk techniques. Solvents and substrates were dried by standard procedures, distilled, and kept under argon over molecular sieves. Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching (M. Barth). ^{1}H, ^{13}C, ^{1}H-^{1}H COSY and ^{95}Mo NMR (0.5 M solution of Na_2MoO_4 was used as reference) spectra were obtained with a Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer using KBr pellets as IR matrix. Far-IR measurements were performed in a Bio-Rad FTS 525 system as Nujol mulls or polyethylene

pellets using a 6 µm Mylar beam splitter.Mass spectra were carried out in a Finnigan MAT 311 A and a MAT 90 spectrometers.

The parent sugar, acetyl protected glucosamine derivatives, 1,3,4,6-tetraacetyl-α-D-glucosamine[23] and 1,3,4,6-tetraacetyl-ß-D-glucosamine[24] were prepared as described previously. The sugar salicylaldimines were all prepared readily by the method of Irvine and Earl [15] by mixing vigorously the amino sugar and salicylaldehyde together in water, or in a methanol-water mixture, with one equivalent of sodium bicarbonate added. Compound **6** and **12** can be obtained by the reported method.[9] The chemical shift of the protons of sugar ring is partially assigned here according to ^{1}H-NMR and ^{1}H-^{1}H COSY.

N-salicylidene-D-glucosamine (**1**):

Yield: 80%. Anal. Calcd. For $C_{13}H_{17}NO_6$ (283.28): C 55.12; H 6.05; N 4.94. Found C 55.43; H 6.18; N 4.69 %. IR (KBr, ν cm^{-1}) = 3385 br vs (OH), 1623vs (C=N), 1515s, 1485s, 1400s, 1146s, 1092vs, 1039vs, 1008vs, 892s, 762vs, 592s; ^{1}H NMR (CD_3OD, δ ppm) = 13.91 (1H, s, α-Ar-OH) 13.20 (2H, s, ß-Ar-OH), 8.32 (1H, s, α-CH=N), 8.31 (2H, s, ß-CH=N), 7.28-6.64 (4H, m, α-Ar-H), 7.22-6.75 (8H, m, ß-Ar-H), 5.09 (1H, d, $J_{1,2}$ 3.52 Hz, α-H-1), 4.74 (2H, d, $J_{1,2}$ 7.80 Hz, ß-H-1), 3.82- 2.85 (18H, m, mixture of other α- and ß-sugar ring Hs).

N-salicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine (**2**)

Yield 84%. Anal. Calcd. For $C_{21}H_{25}NO_{10}$ (451.43): C 55.87; H 5.58; N 3.10. Found C 55.35; H 5.54; N 3.05 %. IR (KBr, ν cm^{-1}) = 1751 vs (acetyl), 1629vs (C=N), 1458m, 1368s, 1226vs, 1123m, 1037vs, 760m; ^{1}H NMR ($CDCl_3$, δ (ppm)) = 12.39 (1H, s, OH), 8.37 (1H, s, CH=N), 7.35-6.86 (4H, m, Ar-H), 6.25 (1H, d, $J_{1,2}$ 3.74 Hz, sugar H-1), 5.60 (1H, t, sugar H-3), 5.17(1H, t, sugar H-4), 4.37-4.33 (1H, q, sugar H-6), 4.24-4.213 (1H, q, sugar H-6'), 4.208-4.08 (1H, m, sugar H-5), 3.71-3.68 (1H, q, sugar H-2), 2.21 (3H, s, acetyl-1), 2.09 (3H, s, acetyl-3), 2,04 (3H, s, acetyl-4), 1.91 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) = 170.58, 169.73, 169.70 and 168.94 (four C=O of acetyl), 168.89 (C=N), 161.05, 133.45, 131.92, 118.91, 118.11 and 117.30 (six carbons of aryl), 91.12 (sugar C-1), 71.00(sugar C-5),

70.01(sugar C-3), 69.46(sugar C-4), 67.88(sugar C-6), 61.66 (sugar C-2), 20.74, 20.67, 20.60 and 20.51 (four acetyl CH_3)

N-5-chloro-salicylaldehyde-1,3,4,6-tetraacetyl-α-D-glucosamine (**3**)

Yield 78%. Anal. Calcd. For $C_{21}H_{24}ClNO_{10}$ (485.86): C 51.91; H 4.98; N 2.88. Found C 51.68; H 4.92; N 2.73 %. IR (KBr, ν cm^{-1}) = 1752, 1740vs (acetyl), 1636vs (C=N), 1576m, 1376s, 1222vs, 1139m, 1028s, 822m; ^{1}H NMR ($CDCl_3$, δ (ppm)) = 12.37 (1H, s, OH), 8.30 (1H, s, CH=N), 7.29-6.85 (3H, m, Ar-H), 6.24 (1H, d, $J_{1,2}$ 3.66 Hz, sugar H-1), 5.58 (1H, t, sugar H-3), 5.16(1H, t, sugar H-4), 4.37-4.31 (1H, q, sugar H-6), 4.24-4.17 (1H, q, sugar H-6'), 4.11-4.10 (1H, m, sugar H-5), 3.72-3.67 (1H, q, sugar H-2), 2.19 (3H, s, acetyl-1), 2.08 (3H, s, acetyl-4), 2.03 (3H, s, acetyl-3), 1.91 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) = 170.55, 169.68, 169.65 and 168.86 (four carbonyl groups), 167.70 (C=N), 159.67, 133.32, 130.89, 123.58, 118.99, 118.82 (six carbons of aryl), 91.00 (sugar C-1), 70.91 (sugar C-5), 70.08 (sugar C-3), 69.47 (sugar C-4), 67.81 (sugar C-6), 61.63 (sugar C-2), 20.73, 20.68, 20.59 and 20.53 (four CH_3 of acetyl); M+1=486.4.

N-salicylaldehyde-1,3,4,6-tetraacetyl-ß-D-glucosamine (**4**)

Yield 82%. Anal. Calcd. For $C_{21}H_{25}NO_{10}$ (451.43): C 55.87; H 5.58; N 3.10. Found C 55.55; H 5.52; N 3.07 %. IR (KBr, ν cm^{-1}): 1746 vs (acetyl), 1631vs (C=N), 1580m, 1370s, 1279s, 1215vs, 1155m, 1089s, 1065s, 1035vs, 760s; ^{1}H NMR ($CDCl_3$, δ (ppm)) = 11.97 (1H, s, OH), 8.30 (1H, s, CH=N), 7.32-6.83 (4H, m, Ar-H), 5.88 (1H, d, $J_{1,2}$ 8.05 Hz, sugar H-1), 5.42 (1H, t, sugar H-3), 5.10(1H, t, sugar H-4), 4.35-4.31 (1H, q, sugar H-6), 4.11-4.07 (1H, q, sugar H-6'), 3.96-3.93 (1H, m, sugar H-5), 3.47-3.41 (1H, q, sugar H-2), 2.04 (3H, s, acetyl-1), 1.99 (6H, s, acetyl-3,4), 1.87 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) = 170.45, 169.67, 169.34 and 168.93 (four C=O of acetyl), 168.43 (C=N), 160.80, 133.31, 131.86, 118.84, 118.00, 117.26 (six carbons of aryl), 92.55(sugar C-1), 72.95(sugar C-5), 72.74(sugar C-3), 71.66(sugar C-4), 67.69(sugar C-6), 61.54 (sugar C-2), 20.60, 20.59, 20.50 and 20.33 (four CH_3 of acetyl)

N-5-chloro-salicylaldehyde-1,3,4,6-tetraacetyl-ß-D-glucosamine (**5**)

Yield 78%. Anal. Calcd. For $C_{21}H_{24}ClNO_{10}$ (485.86): C 51.91; H 4.98; N 2.88. Found C 51.36; H 5.09; N 2.80 %. IR (KBr, ν cm^{-1}) = 1751 vs (acetyl), 1636 vs (C=N), 1576 m, 1466 s, 1374s, 1265 s, 1222 vs, 1083 s, 1040 s, 978 m, 756 m; ^{1}H NMR ($CDCl_3$, δ (ppm)) = 11.92 (1H, s, OH), 8.24 (1H, s, CH=N), 7.28-6.88 (3H, m, Ar-H), 5.87 (1H, d, $J_{1,2}$ 8.32 Hz, sugar H-1), 5.43 (1H, t, sugar H-3), 5.13(1H, t, sugar H-4), 4.37-4.33 (1H, q, sugar H-6), 4.13-4.09 (1H, q, sugar H-6'), 3.97-3.93 (1H, m, sugar H-5), 3.50-3.45 (1H, q, sugar H-2), 2.07 (3H, s, acetyl-1), 2.03 (3H, s, acetyl-4), 2.02 (3H, s, acetyl-3), 1.91 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) = 170.53, 169.72, 169.43 and 168.48 (four C=O of acetyl), 167.82 (C=N), 159.42, 133.24, 130.92, 123.58, 119.01, 118.75 (six carbons of aryl), 92.48(sugar C-1), 72.90(sugar C-5), 72.88(sugar C-3), 71.80(sugar C-4), 67.64(sugar C-6), 61.56 (sugar C-2), 20.68, 20.67, 20.57 and 20.42 (four CH_3 of acetyl)

MoO_2(*N*-salicylidene-D-glucosamine) (**7**)

N-salicylaldehyde-D-glucosamine **1** (0.300g, 1.06 mmol) was dissolved in ca. 15 mL of dried methanol. After complete dissolution, $MoO_2(acac)_2$ (0.313 g, 0.954 mmol) was added to the yellow solution. The mixture was allowed to react for 4 hours, then the volume was then reduced to ca. 5 mL and 20 mL of diethyl ether were added to precipitate the compound as a yellow solid. This solid was washed two times with diethyl ether and dried under vacuum. Yield 78%. Anal. Calcd. For $C_{13}H_{15}NO_8Mo{\bullet}CH_3OH$ (441.25): C 38.11; H 4.34; N 3.17. Found C 38.49; H 4.76; N 3.30 %. IR (KBr, ν cm^{-1}) = 3376 br (O-H), 1636 vs (N=C), 1601 s, 1558 s, 1475 s, 1448 s, 1280 vs, 1091 vs, 1018 vs, 919 vs, sh(ν_{sym} (Mo=O)), 905 vs (ν_{asym} (Mo=O)), 821 m, 763 m. ^{1}H NMR (CD_3OD, δ ppm) = 8.54 (1H, s, CH=N), 7.47-6.84 (4H, m, Ar-H), 5.58 (1H, d, $J_{1,2}$ 3.04 Hz, sugar-H-1), 3.76-1.05 (9H, m, CH_3 of methanol and other sugar ring H); MS: M^{+}- methanol = 409.

MoO_2(*N*-salicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine)(**8**/**10**)

N-salicylaldehyde-1,3,4,6-tetraacetyl-α-(or β-)D-glucosamine **2** (or **4**) (0.4736 g, 1.05 mmol) was dissolved in ca. 20 mL of dried methanol or ethanol. After complete dissolution,

$MoO_2(acac)_2$ (0.3279 g, 1 mmol) was added to the yellow solution. The mixture was allowed to react for 12 hours and then the solvent was partially evaporated. During this procedure a small amount of yellow precipitation formed. After the addition of 15 mL of diethyl ether, more compound precipitated as a yellow solid, it was washed with diethyl ether twice and dried under vacuum. Yield 62% for **8** and 70% for **10**. Anal. Calcd. for $C_{19}H_{21}NO_{11}Mo•CH_3OH$. (567.36): C 42.34; H 4.44; N 2.47. Found: C 42.40, H 4.33, N 2.55% or for $C_{19}H_{21}NO_{11}Mo•CH_3CH_2OH$. (581.38): C 43.38; H 4.68; N 2.41. Found: C 43.13, H 4.66, N 2.37 %. IR (KBr, ν cm^{-1}) = 3383s, (ν(OH)), 1757vs, 1742vs (acetyl), 1630vs (C=N), 1600s, 1552s, 1367s, 1291vs, 1229vs, 1150s, 1131s, 1036vs, 931vs(ν_{sym}(Mo=O)), 902vs(ν_{asym} (Mo=O)); ^{1}H NMR ($CDCl_3$, δ (ppm)) = 8.36 (1H, s, CH=N), 7.49-6.87 (4H, m, aryl H), 5.84 (1H, d, $J_{1,2}$ 3.75Hz, sugar H-1), 5.43 (1H, t, sugar H-3), 5.10 (1H, t, sugar H-4), 4.41-4.35 (2H, m, sugar H-6, H-5), 4.12-4.07 (2H, m, sugar H-6', H-2), 3.83 (2H, q, ethanol CH_2), 2.12 (3H, s, acetyl-3), 2,11 (3H, s, acetyl-4), 2.08(3H, s, acetyl-6), 1.24 (3H, t, ethanol CH_3). ^{13}C NMR ($CDCl_3$, δ(ppm)) = 170.67, 170.27, 166.68 (three C=O of acetyl groups), 166.71(C=N), 162.06, 136.81, 134.15, 121.02, 120.37, 119.97 (six carbons of aryl), 99.65 (sugar C-1), 73.66 (sugar C-5), 70.75 (sugar C-3), 69.02 (sugar C-4), 67.66 (sugar C-6), 61.91 (sugar C-2), 59.36 (CH_2, ethanol), 20.70, 20.66, 20.23 (acetyl, CH_3), 17.98 (CH_3, ethanol). ^{95}Mo-NMR (CD_3OD, δ (ppm)) =-15. MS, M^+-ethanol+1=536.

MoO_2(*N*-5-chloro-salicylidene-1,3,4,6-tetraacetyl-α-D-Glucosamine)(**9/11**)

N-5-chloro-salicylaldehyde-1,3,4,6-tetraacetyl-α- (or ß-) D-glucosamine **3** (or **5**) (0.5098 g, 1.05 mmol) was dissolved in ca. 30 mL of dried ethanol. After complete dissolution by heating to 40-50 °C, $MoO_2(acac)_2$ (0.3279 g, 1 mmol) was added to the yellow solution. The mixture was allowed to react for 12 hours at 40-50 °C and then solvent was partially evaporated. During this time a small amount of yellow precipitate formed. After the addition of 15 mL of diethyl ether, more compound precipitated as a yellow solid, it was washed with diethyl ether twice and dried under vacuum. Yield 70%. Anal. Calcd. for $C_{19}H_{20}NO_{11}ClMo•CH_3CH_2OH$. (615.83): C 40.96; H 4.26; N 2.27 %. Found: C 41.13, H 4.66,

N 2.37 %. IR (KBr, ν cm^{-1}) = 3378 br (ν(OH)), 1758 vs, 1738 vs (acetyl), 1637 vs (C=N), 1544 s, 1371 s, 1283 vs, 1230 vs, 1213 vs, 1139 s, 1122 s, 1033 vs, 935 vs(ν_{sym}(Mo=O)), 903 vs(ν_{asym} (Mo=O)); ^{1}H NMR ($CDCl_3$, δ (ppm)) = 8.27 (1H, s, CH=N), 7.43-6.84 (3H, m, aryl H), 5.84 (1H, d, $J_{1,2}$ 3.56 Hz, sugar H-1), 5.38 (1H, t, sugar H-3), 5.12 (1H, t, sugar H-4), 4.375 (2H, d, sugar H-6, H-5), 4.13-4.08 (2H, m, sugar H-6', H-2), 3.82 (2H, q, methanol CH_2), 2.14 (1H, s, acetyl-3), 2.08(6H, s, acetyl-4,6), 1.25 (3H, t, methanol CH_3). ^{13}C NMR ($CDCl_3$, δ(ppm)) = 170.67, 170.00, 165.44 (there C=O of acetyl groups), 165.42(C=N), 160.61, 136.51, 132.61, 125.48, 121.69, 120.92 (six carbons of aryl), 99.71 (sugar C-1), 73.53 (sugar C-5), 70.84 (sugar C-3), 69.04 (sugar C-4), 67.35 (sugar C-6), 61.81 (sugar C-2), 59.38 (CH_2, ethanol), 20.72, 20.69, 20.32 (three CH_3 of acetyl groups), 17.99 (CH_3, ethanol). MS, M^+-ethanol = 570.

2.4.2. X-ray Crystallography

Preliminary examination and data collection were carried out on a KappaCCD device (NONIUS MACH3) with an Oxford Cryosystems cooling device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo–K_α radiation (λ = 71.073 pm). Data collection was performed using the Collect Software.[25] The detector to crystal distance was 40 mm. A correction for absorption effects and/or decay was applied during the scaling procedure.[26] The structures were solved by a combination of direct methods[27] and difference-Fourier syntheses.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2\text{-}F_c^2)^2$ and converged with a maximum shift/error < 0.001. The final difference-Fourier maps show no striking features. The absolute configuration was given by synthesis and proofed by Flack's parameter. Pertinent crystal data are given in Table 4.

Table 4 Crystal data and summary of intensity data collection and structure refinement of *N*-salicylidene-1,3,4,6-tetraacetyl--D-glucosamine [4(**2**)•H_2O]**,** *N*-5-chloro-salicylaldehyde-1,3,4,6-tetraacetyl-D-glucosamine (**3**), and MoO_2 (*N*-salicylidene-1,3,4,6-tetraacetyl-D-glucosamine) (**8/10**)

	4(**2**)•H_2O	**3**	**8/10**
Empirical formula	$C_{84}H_{102}N_4O_{41}$	$C_{21}H_{24}ClNO_{10}$	$C_{21}H_{27}MoNO_{12}$
Formula weight	1823.70	485.86	518.38
Color / shape	Colorless / Fragment	Colorless / Fragment	Yellow / Fragment
Crystal size/mm	0.13 × 0.20 × 0.25	0.66 × 0.89 × 0.89	0.13 × 0.18 × 0.61
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)
a/pm	788.53(1)	1225.73(1)	1605.32(1)
b/pm	1583.27(1)	714.73(1)	802.34(1)
c/pm	1871.71(2)	1449.14(2)	1888.65(1)
β/°	90	113.2552(4)	90
$V/10^6$pm^3	2336.75(4)	1166.40(3)	2432.60(4)
Z	1	2	4
D_c/g cm^{-3}	1.296	1.383	1.587
F(000)	962	508	1192
μ/mm^{-1}	0.104	0.219	0.603
Wavelength/pm	Mo–K_α/71.073	Mo–K_α/71.073	Mo–K_α/71.073
T/K	173	173	173
Index ranges	h: ±9; k: ±19; l: ±22	h: ±14; k: ±8; l: ±17	h: ±19; k: ±9; l: ±22
Reflections collected	56775	25017	54662
Independent reflections	4268 (R_{int} = 0.028)	4229 (R_{int} = 0.040)	4450 (R_{int} = 0.035)
Completeness/%	99.8 (to Θ = 25.33°)	99.6 (to Θ = 25.28°)	100.0 (to Θ = 25.34°)
Observed reflections ($I>2\sigma(I)$)	4058	4183	4386
Data/restraints/parameters	4268/0/398	4229/1/394	4450/0/424
*R*1 (observed/all data)	0.0267/0.0291	0.0267/0.0269	0.0179/0.0183
*wR*2 (observed/all data)	0.0647/0.0665	0.0712/0.0714	0.0455/0.0457
GOF (observed/all data)	1.063/1.063	1.055/1.055	1.081/1.081
Largest diff. peak and hole /e Å^{-3}	0.11 and -0.13	0.21 and -0.23	0.39 and -0.28
Flack's parameter	-0.3(6)	0.03(5)	-0.02(2)

2.4.3. Catalysis reactions with compounds 7-12 as catalysts

The catalytic reactions were performed under an air atmosphere, in a reaction vessel equipped with a magnetic stirrer, immersed into a thermostated bath.

Achiral catalytic epoxidation: *Cis*-cyclooctene (800 mg, 7.2 mmol), mesitylene (1g, internal standard), 1 mol % (72 μmol) of compounds **7-12** as catalyst were added to the reaction vessel. With the addition of TBHP (2 mL, 5.5 M-6.0 M in *n*-decane) the reaction was started. The course of the reactions was monitored by quantitative GC analysis. Samples were taken and diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a chiral GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

Chiral catalytic epoxidation: *cis*-, or *trans*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene (100 mg, 0.83 mmol, internal standard), and 1 mol% (17 μmol), 5 mol% and 10 mol% of the compounds **7-12** as catalysts and 2 mL toluene as solvent were added to the reaction vessel. With the addition of TBHP (450 μl, 7.5 M in toluene) the reaction started. The course of the reactions was monitored by quantitative GC analysis. The samples were processed as described above. The enantiomeric excess was calculated with the ratio of the peaks corresponding to both epoxides formed.

2.5. Conclusions

Complexes of the type $MoO_2(L)(Solv)$ (with L = tridentate, sugar derived chiral Schiff base, Solv = alcohol) are easily prepared by the reaction of the ligands L with $MoO_2(acac)_2$ in alcohols. Depending on the position of the potential coordination sites of the ligand L, the reactions lead to selective inversion at the C1 atom of the sugar ligand in order to reach the optimal coordination geometry. When esterification is used to protect the –OH groups of the sugar ligand, Lewis acid catalyzed deacetylation takes place to allow a tridentate coordination of the ligand. The coordination of two bidentate ligands is not observed, even if the ligand

size would allow it, as in the case of the non-protected ligand **1**. It can be assumed that during the epoxidation catalysis, where the examined complexes can be used as catalysts, the weakly coordinating alcohol ligand is replaced by TBHP. The TOF in the beginning of the reaction is very high in the case of cyclooctene as the substrate. During the course of the reaction, however, the velocity slows down considerably since an increasing amount of *t*-butyl alcohol molecules is competing for the same coordination sites as the TBHP molecules Furthermore, a significant portion of the tiny amounts of catalyst, used to reach the high TOFs, falls victim to decomposition due to traces of water in the catalytic system. The catalytic epoxidation reaction is much slower with styrene as the substrate, but in case of cis-ß-methylstyrene moderate enantiomeric excesses of up to 30 % can be reached. The moderate enantiomeric excess may be – at least in part – due to an ongoing ligand exchange in solution, which can be slowed down at lower temperatures.

2.6. References

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3. Molybdenum(VI) *cis*-Dioxo Complexes with Chiral Schiff Base Ligands and their Applications in Epoxidation Catalysis

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3.1. Abstract

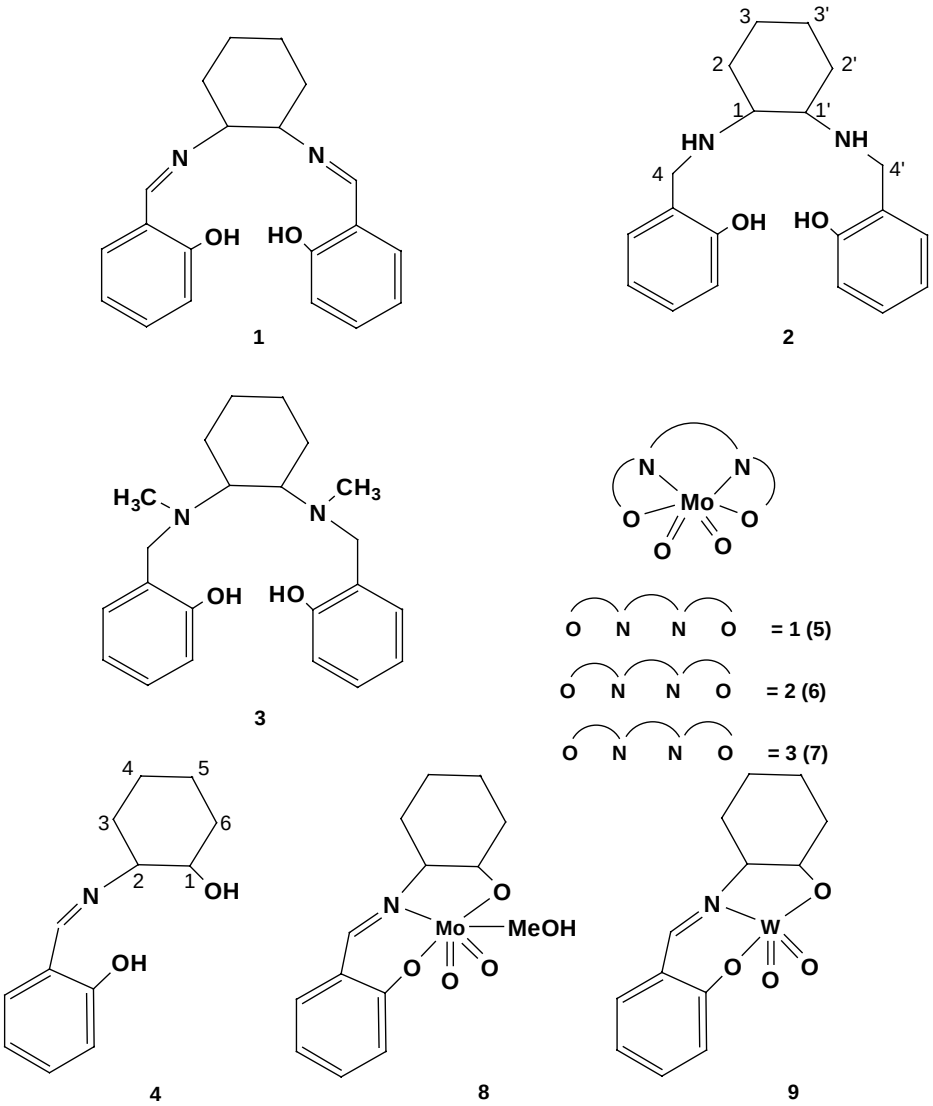
Three optically active Molybdenum (VI) dioxo complexes with tetrahydro salen and substituted tetrahydro salen derivatives as ligands were synthesized and examined as catalysts for asymmetric epoxidation. Complexes of the type $MoO_2(L)(Solv)$ and $WO_2(L)$ (L = tridentate, trans-2-aminocyclohexanol derived chiral Schiff base, Solv = alcohol) were prepared and characterized by elemental analysis, NMR and IR spectroscopy. These complexes are applicable as catalysts for olefin epoxidation reactions with TBHP (*tert*-butyl hydroperoxide) being the oxidizing agent. In case of cis-ß-methylstyrene moderate enantiomeric excesses of up to 26 % can be reached when the reaction is carried out at 0°C.

3.2. Introduction

For the preparation of chiral epoxides, the transition metal-catalyzed enantioselective epoxidation of different organic substrates is of the utmost importance and has been widely studied over the past decades.[1] Recently, we reported the synthesis of some molybdenum(VI)-*cis*-dioxo complexes bearing sugar derived chiral Schiff base ligands of general formula $MoO_2(L)(Solv)$, which showed moderate enantiomeric induction of *ca.* 30% ee for the epoxidation of *cis-ß*-methyl styrene.[2]

The pioneering studies by the groups of Katsuki[3] and Jacobsen[1] have led to a variety of chiral Mn(III) salen-based catalysts which epoxidized non-functionalized alkenes with high

enantioselectivity. Manganese salen complexes are regarded as the most efficient catalysts for enantioselective epoxidation of unfunctionalized olefins.[4] More recently, chromium oxo complexes bearing salen ligands were also examined for the asymmetric epoxidation of *trans*-methylstyrene reaching ee's up to 90%.[5] Although Mo(VI)-dioxo complexes bearing tetradentate salen ligands have been prepared and spectroscopically characterized 20 years ago,[6, 7] to the best of our knowledge, their catalytic application for epoxidation reactions has not been, so far, explored.



Scheme 1

In this work, optically active Molybdenum (VI) dioxo complexes bearing tetrahydro salen and substituted tetrahydro salen derivatives as ligands were synthesized and tested for their catalytic activity. Additionally, some molybdenum and tungsten dioxo complexes with tridentate Schiff base ligands were prepared and their catalytic activity in olefin epoxidation was investigated (see Scheme 1).

3.3. Results and Discussion

3.3.1. Synthesis and spectroscopic examinations

The preparation of ligand **1** was performed according to literature procedures[8] by condensation of salicyl aldehyde and 1,2-diamino cyclohexane in methanol. Ligands **2** and **3** were prepared from ligand **1** by reduction with $NaBH_4$ and $Na[(CN)BH_3]$ in CH_3CN, respectively, according to the literature procedures.[7, 9] The related chiral ligands were prepared using (1R, 2R)-(-)-1,2-diamino cyclohexane as starting material. The corresponding Mo-complexes **5** and **7** were synthesized by reacting $MoO_2(acac)_2$ with 1.1 equivalents of the respective ligands in methanol according to literature procedures.[6, 7] As the new complex, compound **6** was prepared by a similar method. Ligand **4** was prepared by the condensation of salicylaldehyde and (+,-) trans-2-aminocyclohexanol in methanol. Complexes **8** and **9** were synthesized by the reaction of $MoO_2(acac)_2$ and $WO_2(acac)_2$ with ligand **4** in methanol.

All complexes are fairly air stable as solids, albeit decomposition occurs slowly in solution and the colour changes from yellow to green in the presence of moisture.

The proton signals of compounds **2, 3, 6** and **7** were determined by H-H COSY- NMR spectroscopy. Comparing the chemical shifts of ligand **2** and complex **6**, being formed after coordination of **2** to a MoO_2-moiety, the H-5 and H-5' signals are shifted to lower field, since the shielding effect of the neighbouring N atom decreases due to coordination to the Mo centre. The same effect can be observed for the chemical shifts of H-1 and H-1' as well as H-2 and H-2'. Unfortunately, it was not possible to obtain crystals of sufficient quality for determining the X-ray crystal structure of compound **6**. Nevertheless, according to the NMR

and IR data the structure of **6** should be very similar to that of compounds **5** and **7**, which have been published elsewhere.[6, 7]

Elementary analysis of the compounds **8** and **9** suggests that both complexes contain a dioxo metal moiety, thus giving evidence for the monomeric nature of these complexes. IR spectroscopy further shows, that the metal-oxygen bonds are in the typical M=O region for both molecules. Mass spectrometry also gave no hint for the presence of dimeric species [10] or indicative fragments, the molecular mass m/z = 345 and 433 was found for **8** and **9,** respectively, and there are no other peaks originating from fragments of dimeric molecules at higher molecular masses. The same products (**8** and **9**) were formed when two equivalents of ligand **4** were used in the synthesis.

Interestingly, the NMR and element analyses as well as the MS results indicate that in complex **8** molybdenum is hexa-coordinated, bearing a dioxo moiety, the tridentate ligand and a methanol molecule. This is in accordance with the coordination behaviour of other molybdenum dioxo complexes bearing tridentate Schiff base ligands.[2] For the tungsten analogue **9**, however, there is no hint for the presence of a coordinated solvent molecule, and both spectroscopic and elementary analyses indicated a penta-coordinated W core.

It was previously observed that during the reaction of a molybdenum(VI)-*cis*-dioxo species with a *ß*-configurated glucosamine derived chiral Schiff base ligand an inversion of the *ß*-configuration into *α*-configuration occurs.[2] This interesting configuration transformation prompted us to further examine the interaction between the molybdenum dioxo starting material and other ligands with comparable configuration to the above mentioned sugar derived ligands. Ligand **4** shows the OH and imine group in the cyclohexane ring in *trans*-configuration, *i. e. ß*-configuration with $J_{1,2}$ = 16.38 Hz. After coordination to Mo or W, the coupling constants $J_{1,2}$ are 14.18 Hz and 16.64 Hz, respectively. This suggests that in this case no configuration inversion occurs during coordination. This observations seems further to indicate that the inversion of configuration follows a ring opening mechanism of the sugar ring, which in this case is not available, since cyclohexane can not undergo ring opening

reactions as can oxygen containing rings, as applied in our earlier experiments.[2] Representative chemical shifts and coupling constants are listed in Table **1**.

Table 1. Selected ^{1}H NMR chemical shifts and coupling constants

	trans-2-Aminocyclohexanol hydrochloride	**4**	**8**	**9**
δ ring H-1 (ppm)	3.49	3.64	3.67	3.69
$J_{1,2}$ (Hz)	15.88	16.38	14.18	16.64

3.3.2. Complexes 5-9 in oxidation catalysis

Complexes **5-9** were examined as catalysts in the epoxidation of cyclooctene. The chiral complexes **6-7** were used also in the asymmetric epoxidation both of *cis*- and *trans*-β-methylstyrene. *t*-Butylhydroperoxide (TBHP) was used as the oxidant. Details about the conditions applied are given in the experimental section. Blank runs were performed and, as expected, without catalyst, no significant epoxide formation was observed under the applied conditions.

Table 2. Epoxidation of cyclooctene catalyzed by complexes **5-9** at 55 °C

Compound	Conversion or yield	
	4h	22h
5	30	65
6	20	71
7	22	66
8	35	72
9	5	25

In general, complexes **5-8** catalyzed the epoxidation of all three examined alkenes with moderate activity and complete stereo-retention, without significant by-product formation, the

selectivity being close to 100%. When the catalyst: substrate: oxidant ratio is 1:100:200, for cyclooctene, the yield reaches after 4 h a value of 20-35%, and after 22h of 65-70% in all examined cases (Table 2). The substituent at the N atom seems to have little effect on the catalytic behaviour, as it can be seen from the performance of compounds **5-7**. Despite having different coordination behaviour, complexes **5** and **8** show a quite similar catalytic activity. This, however, is probably due to their poor solubility in the oxidation solution. There is a strong decrease in activity on going from molybdenum to tungsten. Accordingly, the lowest activity is found for catalyst **9**, after 4 h only 5% yield can be obtained, while 25% were reached after 24h, when the catalyst:substrate:oxidant ratio is 1:100:200.

Table 3. Epoxidation of *cis*- and *trans*-*β*-methylstyrene catalyzed by compounds **5-7** at 0 °C

Compound	*cis*-Methyl-styrene			*trans*-Methyl-styrene		
	Conversion		*ee*	Conversion		*ee*
	4h	22h		4h	22h	
5	6.5	11.8	25.8	11.8	32.5	14.9
6	5.7	13.7	7.81	14.4	38.3	7.35
7	6.4	13.1	4.72	12.9	34.7	3.76

For the asymmetric epoxidation of *cis*- and *trans*-*β*-methylstyrene, the general observation is that the asymmetric induction for the *cis* substrates is much better than that for the *trans* analogues, whereas higher conversions can be obtained with the trans substrate. Unfortunately, at lower temperatures the conversions are rather low, when the best *ee*'s can be achieved, at higher temperatures the conversions increase considerably but the *ee*'s decrease dramatically probably due to easier ligand displacement during the catalytic cycle. The effects of solvent and the amount of catalyst used have also been studied. Within the experimental error the results are the same in both CH_2Cl_2 and toluene as solvent, although compounds **5-7**

are more soluble in CH_2Cl_2 than in toluene. Higher amounts of catalyst also improve both *ee* and yield. Accordingly, the highest observed *ee* of *ca.* 26% could be obtained with compound **5** as catalyst at 0 °C. Compounds **6** and **7** show a poor chiral induction for *cis*- and *trans-ß*-methylstyrene even at 0 °C. (Table. 3). This indicates that the reduction of imine to amine does not have a positive influence on the *ee* values obtained, regardless, whether a hydrogen or a methyl group is coordinated to the amine nitrogen.

3.4. Experimental Section

3.4.1. Synthesis and Characterization

All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. Solvents and substrates were dried by standard procedures, distilled, and kept under argon over molecular sieves. Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching (M. Barth). ^{1}H, ^{13}C, and H-H COSY NMR spectra were obtained with a Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer using KBr pellets as IR matrix. Mass spectra were carried out in a Finnigan MAT 311 A and a MAT 90 spectrometers.

Ligands **1**, **2** and **3** were prepared according to literature procedures.[7-9] The related chiral ligands were prepared using (1R, 2R)-(-)-1,2-diaminocyclohexane as starting material. The preparation of chiral complexes **5** and **7** was performed according to established procedures.[6,7] The proton signals of compounds **2, 3, 6** and **7** were determined by H-H COSY NMR spectroscopy. $WO_2(acac)_2$ was prepared according to literature method.[11]

2: IR (KBr): ν = 3444br (νOH), 3318w (νNH), 2930, 2850, 1590s (aryl), 1455 vs, 1259vs, 1151m, 1098s, 908m, 757vs cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.15-6.76 (m, 8H, aryl-H), 4.06 (d, 2H, H-5), 3.94 (d, 2H, H-5'), 2.45 (t, 2H, H-1and H-1'), 2.14 (m, 2H, H-2) 1.69 (m, 2H, H-2'), 1.23-1.14 (m, 4H, H-3 and H-3'); MS: M^{+}+1=327.

3: IR (KBr): ν = 3445br (νOH), 2943, 2863, 1580s (aryl), 1486vs, 1456m, 1365m, 1283m, 1240s, 1116w, 1022w, 763s cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ = 7.15-6.76 (m, 8H, aryl-H), 3.84 (d, 2H, N-CH_2 or H-5), 3.62 (d, 2H, N-CH_2' or H-5'), 2.70 (m, 2H, N-CH-ring or H-1and H-1'), 2.21 (s, 6H, N-CH_3), 2.00 (m, 2H, CH_2-ring or H-2), 1.79 (m, CH_2'-ring or H-2'), 1.23-1.12 (m, 4H, CH_2-ring or H-1 and H-1'); MS: M^+=354.

4: 500 mg (3.3 mmol) of trans-2-aminocyclohexanol hydrochloride and 277 mg of $NaHCO_3$ were dissolved in 5 ml of water. To this solution 0.38 ml (3.6 mmol) of salicyl aldehyde were added. After a few minutes, a bright yellow solid precipitated. The mixture was further stirred for 2 hours, the precipitate was collected by filtration and washed with water and then re-crystallised from methanol. Yield: 75%. $C_{13}H_{17}NO_2$ (219): calcd. C 71.23, H 7.76, N 6.39; found: C 71.21, H 7.82 N 6.31; IR (KBr): ν = 3359 br s, 3048w, 2935s, 2860m, 1633vs (ν C=N), 1578m, 1492s, 1461m, 1397m, 1274s, 1041s, 751vs, 734m cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ = 13.30 (s, br, OH), 8.40 (s, 1H, CH=N), 7.28 (m, 2H, aryl-H), 6.93 (m, 1H, aryl-H), 6.86 (m, 1H, aryl-H), 3.64(six, $J_{1,2}$ = 16.38 Hz, 1H, ringH-1), 2.98 (m, 1H, ring H-2), 2.05 (m, 1H, ring-H), 1.78 (m,3H, ring H), 1.62 (m, 1H, ring H), 1.35 (m, 3H, ring H); MS: M^+ = 219.

6: 0.31 mmol of **2** and 0.29 mmol of $MoO_2(acac)_2$ were dissolved in 10 ml of dried MeOH yielding a clear yellow solution. After stirring for half an hour, a yellow solid precipitated. The precipitate was washed with ether twice and dried under vacuum to yield 95 mg of product. Yield: 70%. $C_{20}H_{24}O_4N_2Mo$ (452): calcd. C 53.10, H 5.31, N 6.19; found: C 53.21, H 5.22 N 6.21;.IR (KBr): ν = 3278m, 3179s (νNH), 2928m, 2856w, 1597m, 1572m, 1482s, 1449s, 1256s, 1228s, 1098m, 1013m, 920s(νMo=O), 893sm, 878s, 766m, 751m, 638s, 502m cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ = 6.84-6.80 (m, 8H, aryl-H), 5.30 (d, 2H, H-5), 4.22 (d, 2H, H-5'), 2.65 (t, 2H, H-1 and H-1'), 2.33 (m, 2H, H-2) 1.73 (m, 2H, H-2'), 1.11-1.06 (m, 4H, H-3 and H-3'); MS: M^++1= 453.

7: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21-6.82 (8H, m, aryl-H), 5.07 (d, 2H, H-5), 3.68 (d, 2H, H-5'), 2.65 (t, 2H, H-1 and H-1'), 2.60 (s, 6H, H-4 and H-4'), 1.82 (d, 2H, H-2), 1.64 (t, 2H, H-3), 1.15 (d, 2H, H-2'), 0.86 (t, 2H, H-3'); ^{13}C NMR (100.28MHz, $CDCl_3$): δ = 159.26, 129.54, 129.40, 122.28, 120.68, 118.40 (aryl), 61.45 (N-CH_3), 58.14 (N-CH_2), 42.53 (CH-ring), 24.22 (CH_2-ring), 21.95 (CH_2-ring).

8: A solution of 220 mg (0.68 mmol) of $MoO_2(acac)_2$ in 10 ml dried methanol was treated with 150 mg (0.69 mmol) of **4**. After a few minutes a bright yellow precipitate formed. The mixture was stirred for further 2 hours and the precipitate filtered, washed with diethyl ether and dried under vacuum. Yield: 80%. $C_{14}H_{19}O_5NMo$ (377): calcd. C 44.56, H 5.04, N 3.71; found: C 43.91, H 4.97 N 3.61; IR: ν = 3429 br, m, 2936m, 2862w, 1637vs (ν C=N), 1600m, 1556m, 1450m, 1287s, 1040m, 928vs (ν_{sym}Mo=O), 907vs (ν_{asym}Mo=O), 842s, 756m cm^{-1}; ^{1}H NMR (400MHz, CD_3OD): δ = 8.44 (d, *J*= 2.44 Hz, 1H, CH=N), 7.51 (m, 1H, aryl-H), 7.38 (m, 1H, aryl-H), 6.88 (m, 2H, aryl-H), 3.67(six, $J_{1,2}$ = 14.18 Hz, 1H, ring H-1), 3.23 (s, 3H, CH_3 of methanol), 3.09 (m, 1H, ring H-2), 2.47 (d, 1H, ring H-3), 2.07 (d, 1H, ring H-3'), 1.86 (d, 1H, ring H-6), 1.80 (t, 1H, ring H-6'), 1.36 (m, 4H, ring H-4 and H-5); ^{13}C NMR (100.28Hz, d^6-DMSO): δ = 161.26 (C=N), 159.90, 134.49, 134.31, 121.29, 119.26 and 119.16 (aryl), 85.43 (ring C-1), 70.34 (ring C-2), 48.63 (CH_3 of methanol), 33.82 (ring C-3), 27.68 (ring C-6), 23.89 (ring C-4), 23.62 (ring C-5); MS: M^+-CH_3OH = 345, M^+-CH_3OH +2 = 347.

9: A solution of 197 mg (0.48 mmol) of $WO_2(acac)_2$ in 25 ml dried methanol was treated with 109 mg (0.5 mmol) of **4**. After 2-3 minutes the clear yellow solution turned unclear and the light yellow precipitate formed more and more. The mixture was stirred for 2 hours and the precipitate was filtrated and washed with dried ether, then dried under vacuum. Yield: 77%. $C_{13}H_{15}O_4NW$ (433): calcd. C 36.04, H 3.47, N 3.23; found: C 35.75, H 3.81, N 3.14; IR (KBr): ν = 3435 br m, 2936m, 2864w, 1643vs (ν C=N), 1600m, 1560m, 1479m, 1451s, 1285s, 1042m, 938vs (ν_{sym} W=O), 915vs (ν_{asym} W=O), 830s, 784vs, 757vs, 686s cm^{-1}; ^{1}H NMR (400MHz, d^6-DMSO): δ = 8.49 (d, *J*= 2.04Hz, 1H, CH=N), 7.68 (dd, 1H, aryl-H), 7.52 (m, 1H, aryl-H), 6.96 (m, 2H, aryl-H), 3.69 (six, $J_{1,2}$ = 16.64Hz, 1H, ringH-1), 3.25 (m, 1H,

ring H-2), 2.47 (d, 1H, ring H-3 was covered by DMSO), 2.01 (d, 1H, ring H-3'), 1.80 (s, 2H, ring H-6), 1.34 (m, 4H, ring H-4 and H-5); ^{13}C NMR (100.28Hz, d^6- DMSO): δ = 160.69 (C=N), 160.24, 135.04, 134.42, 121.98, 119.85 and 119.71 (aryl), 83.82 (ring C-1), 70.54 (ring C-2), 34.36 (ring C-3), 27.56 (ring C-6), 24.02 (ring C-4), 23.60 (ring C-5); MS: M^+ = 43.

3.4.2. Catalytic reactions with compounds 5-9 as the catalysts

Cyclooctene epoxidation: *cis*-cyclooctene (800 mg, 7.2 mmol), mesitylene (1g, internal standard), 1 mol % (72 μmol) of compounds **5-9** as catalyst were added to the reaction vessel. With the addition of TBHP (2 ml, 5.5 M-6.0 M in *n*-decane) the reaction was started. The course of the reactions was monitored by quantitative GC analysis. Samples were taken and diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a chiral GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

Chiral epoxidation: *cis*-, or *trans*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene (100 mg, 0.83 mmol, internal standard), and 1 mol% (17 μmol), 5 mol% and 10 mol% of the compounds **5-7** as catalysts and 2 ml toluene as solvent were added to the reaction vessel. With the addition of TBHP (450 μl, 7.5 M in toluene) the reaction started. The course of the reactions was monitored by quantitative GC analysis. The samples were processed as described above. The enantiomeric excess was calculated from the area ratio of the peaks corresponding to both epoxides formed.

3.5. Conclusions

Three optically active molybdenum (VI) dioxo complexes bearing tetrahydro salen and substituted tetrahydrosalen derivatives ligands were synthesized and tested as catalysts for asymmetric epoxidation. With cis-ß-methylstyrene moderate enantiomeric excesses of up to

26% can be reached with compound **5** at 0°C. Using a chiral amine instead of an imine improves neither the catalytic activity nor the chiral induction. Complexes of the types $MoO_2(L)(Solv)$ and $WO_2(L)$ (L = tridentate, trans-2-aminocyclohexanol derived chiral Schiff base) are easily prepared by the reaction of the ligand L with $MoO_2(acac)_2$ or $WO_2(acac)_2$ in alcohols as the solvent. All examined Mo compounds show good to moderate activity for olefin epoxidation, while the W analogue displays quite low epoxidation activity. A comparison of the coupling constant of $J_{1,2}$ before and after coordination to the metal, indicates that there is no inversion of configuration from β to α, as it has been observed earlier for sugar derived Schiff base ligands.

3.6. References

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4. Heterogenization of Chiral Schiff Base Ligated Molybdenum(VI) Complexes on Mesoporous Materials and Their Application in Catalysis

This chapter originated the following publication:
A. Sakthivel, J. Zhao, G. Raudaschl-Sieber, M. Hanzlik, A. S. T. Chiang, F. E. Kühn
Appl. Catal. A Gen., **2005**, *281,* 267-273

4.1. Abstract

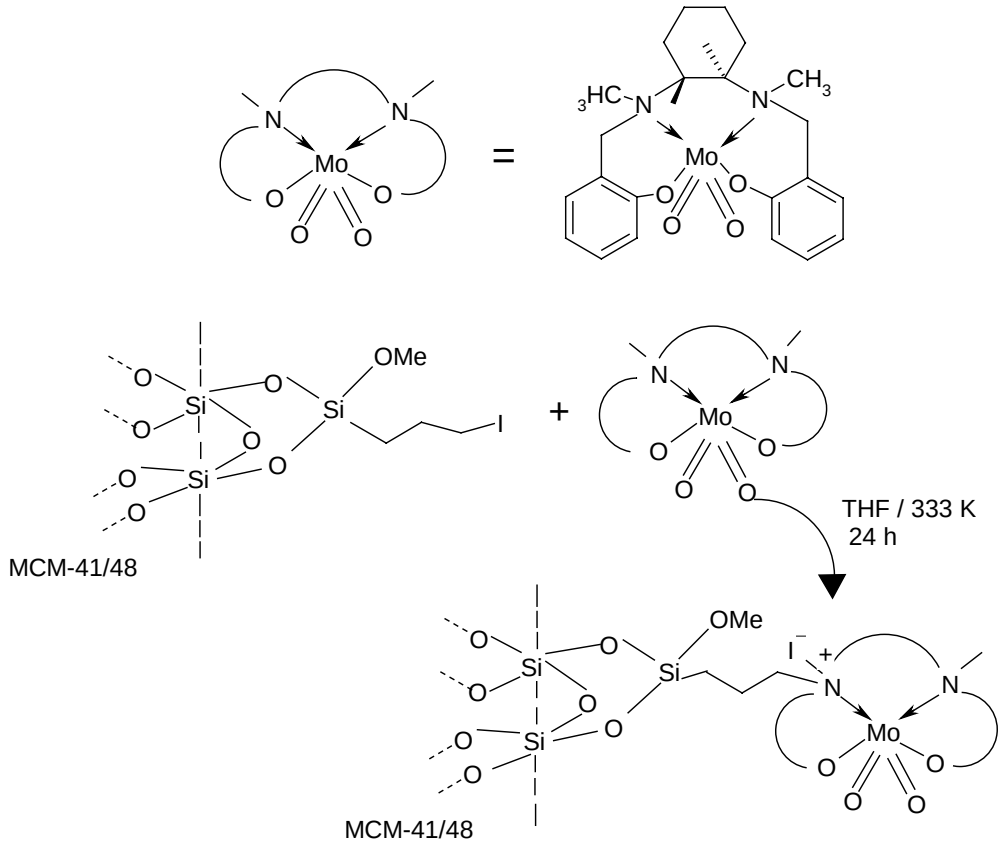
Optically active molybdenum (VI) dioxo complexes bearing hydrosalen derivatives as ligands were synthesized, grafted on the surface of MCM-41 and MCM-48 and examined as catalysts for asymmetric epoxidation. In case of cis-ß-methylstyrene and trans-ß-methylstyrene moderate enantiomeric excesses of up to 31 % can be reached when the reaction is carried out at room temperature. The catalysts can also be applied for non chiral oxidation reactions.

4.2. Introduction

During the last years significant efforts were dedicated to the heterogenization of homogeneous catalysts in order to combine the advantages of heterogeneous catalysts such as easier product/catalyst separation with the advantages of homogeneous catalysts, e.g. higher selectivity.[1] Among the various supporting materials studied, the mesoporous silicates, designated as MCM-41 and MCM-48 by Mobil scientists[2] with regular pore size, large surface areas, large number of surface silanol groups, and high chemical and thermal stability are potential and promising candidates as both catalysts and catalyst supports.[3] In this regard, very recently modified MCM-41 and MCM-48 materials were synthesized by grafting MoO_2X_2 (X = Cl, Br),[1a- f] the latter being quite efficient homogeneous epoxidation catalysts. [4] Additionally, surface-fixed bidentate Lewis bases have been used to bind

catalytically active Mo(VI) complexes as described by *Gonçalves et al*.[1a-f, 5] and *Thiel et al*.[6] Silylation using halosilane to remove residual Si-OH groups, which were considered to be favourable for the catalytic reaction on the surface of the mesoporous material, reduced the catalyst leaching significantly.[6]

The above mentioned homogeneous chiral molybdenum (IV) dioxo complexes bearing hydrosalen derivatives as ligands with one or more N-methyl groups were found to be - among other applications - interesting candidates as catalysts.[7] One of the N-methyl groups on the chiral homogenous complex can be reacted with halosilane modified MCM-41 and MCM-48 surfaces, yielding chiral heterogeneous catalysts, as depicted in Scheme 1.



Scheme 1.

Similar reactions are known and have been reported previously.[8, 9] In the present work the MCM-41 and MCM-48 surface are thus modified with trimethoxy iodo propyl silane and

then the chiral catalysts are grafted by reaction of the iodo-groups on the silylated surface materials with the N-methyl groups present on the homogeneous chiral catalysts.

4.3. Results and Discussion

4.3.1. Synthesis and Textural Characterization

The homogeneous molybdenum (VI) dioxo complexes bearing hydrosalen derivatives as ligands were prepared as described previously.[7b] The observed IR, ^{1}H-NMR and ^{13}C-NMR data confirm that the compounds are pure and are identical (within the measurement errors) to the previously reported results.[7b] The heterogenization of the compounds was carried out as depicted in Chart 1 and described above (for details see Experimental part). The grafted samples are of pale yellow colour. The powder XRD pattern of the complexes grafted on MCM-41 (Fig. 1a and 1A) show a single peak, around 2θ angles of 2°–3°, corresponding to the (100) plane of the hexagonal unit cell. The absence of higher angle peaks (corresponding to (110), (200) and (210) planes) - which are present in the parent samples[1c] - indicates that considerable distortion occurs on the channels of the mesopores materials. Fig. 1b and 1B show the XRD pattern of the grafted MCM-48 samples, which exhibit a main reflection corresponding to the (211) plane along with a shoulder peak derived from the (220) plane, typical for cubic cells. These peaks together with the sextet patterns observed between 2θ angles of 3°–6°, are characteristic for a cubic mesoporous MCM-48 structure. Once again compared to parent MCM-48, the grafted samples show a decrease in the relative intensities of the XRD reflections and there is a clear shift to higher 2θ values. These changes originate from a contraction of the unit cells of the grafted samples, because of the immobilization of the bulky chiral molecules on the channels of MCM-41 and MCM-48.[5] However, the XRD pattern clearly indicates that the structure of the mesoporous materials remains intact throughout the grafting procedure. The modified MCM-materials contain about one weight percent Mo complex after the heterogenization process according to elementary analyses.

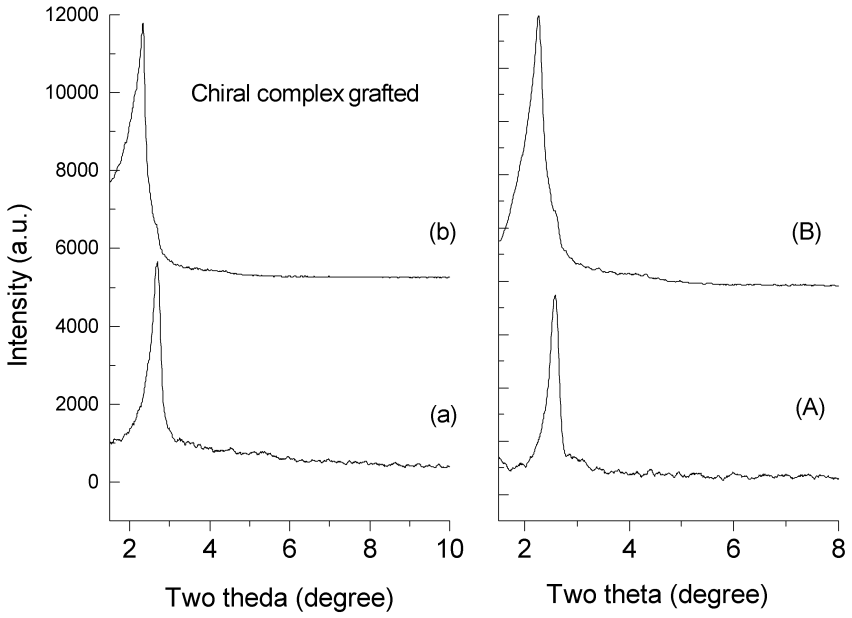


Fig. 1. XRD pattern of (a) SM-41ccg, (b) SM-48ccg, (A) SM-41accg and (B) SM-48accg.

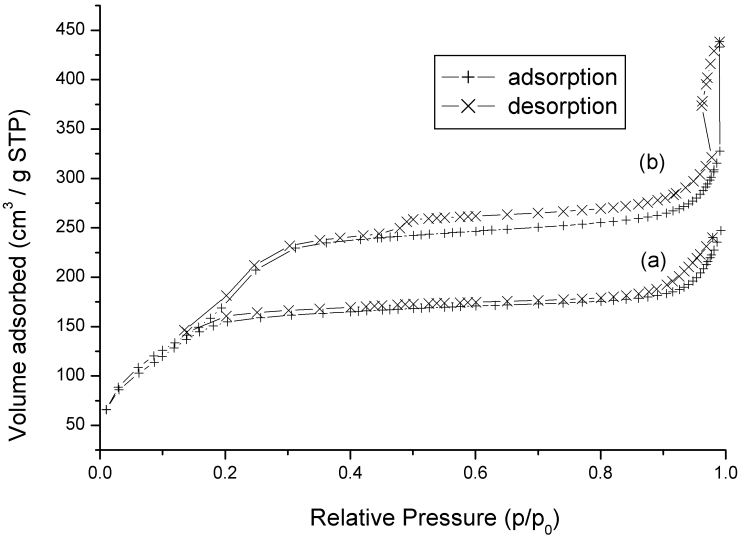


Fig. 2. N_2 adsorption/desorption isotherms of (a) SM-41ccg and (b) SM-48ccg.

The low temperature N_2 adsorption/desorption isotherm of parent MCM-41 and MCM-48 are of type (IV) according to the IUPAC[10] and characteristic for mesoporous solids.[1c] A well-defined sharp inflection is observed between the relative pressure (p/p_0) of 0.3-0.4 due to capillary condensation of nitrogen inside the primary mesoporous. Compared to parent mesoporous samples, the samples bearing grafted chiral molecules (Fig. 2) exhibit a drastic

decrease in N_2 uptake due to the presence of the comparatively bulky organometallic compounds on the surface of the mesoporous channels. Further, the parent MCM-41 and MCM-48 samples exhibit narrow pore size distributions with average pore diameters of 2.7 and 2.4 nm respectively. The grafted materials exhibit a broader pore size distribution and display also a decrease in surface area and unit cell volume. The decrease of the unit cell value and the broad distribution of pore size evidences that the chiral complexes in the grafted mesoporous samples are mainly located on internal surfaces of the mesoporous materials.[1c,5]

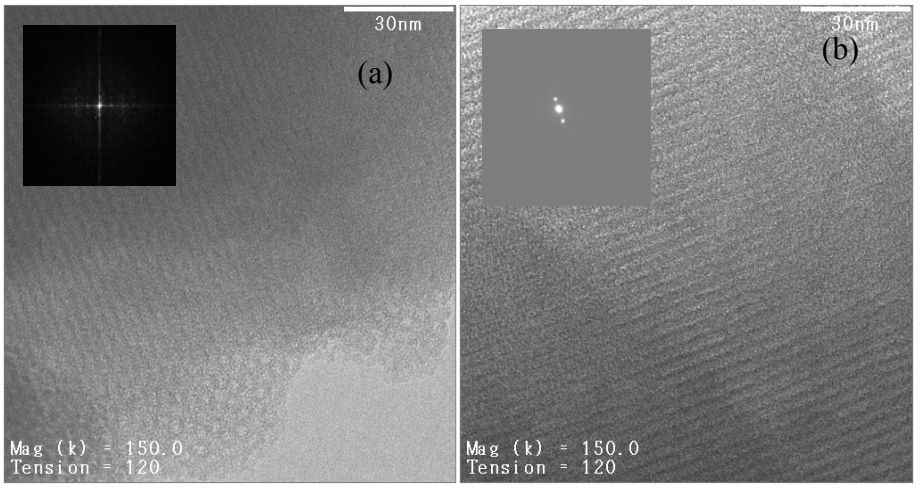


Fig. 3. TEM images of (a) SM-41ccg and (b) SM48ccg.

The TEM images (Fig 3) of the grafted samples show highly uniform distributions of pore size, providing strong evidence that the mesoporous structure of the support retains long range ordering[1-3] throughout the grafting process and that the channels remain accessible. The ED pattern of the grafted samples shows the reflection of the (100) and the (110) plane, which further supports the presence of long rang ordering in the samples.

Fig. 4 depicts the FT-IR spectra of parent calcined mesoporous MCM-41, MCM-48 and grafted samples. The bands at 1206, 1060, and 794 cm^{-1} are attributed to stretching vibrations of the mesoporous framework (Si-O-Si). The band around 960 cm^{-1} is assigned to a vibration mode of the silanol (*Si-O*H) groups in the mesoporous channels.[1-3] The grafted samples show

(Fig. 4b,4c,4e,4f) a decrease in the relative intensity of the silanol (*Si-O*H) band, indicating that the surface hydroxyl groups are efficiently used for the grafting. New bands around 1580s (aryl) and two bands around 2949 and 2853 cm^{-1} arise due to C-H stretching vibrations, originating from CH_2 groups. The presence of these bands after the heterogenization process further confirms the presence of the chiral complexes on the MCM samples.

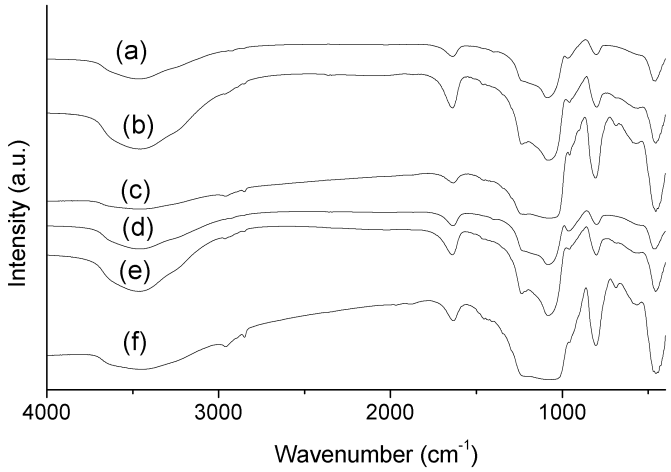


Fig. 4. FT-IR spectra of (a) MCM-41, (b) SM-41ccg, (c) SM-41accg, (d) MCM-48, (e) SM-48ccg and (f) SM-48accg

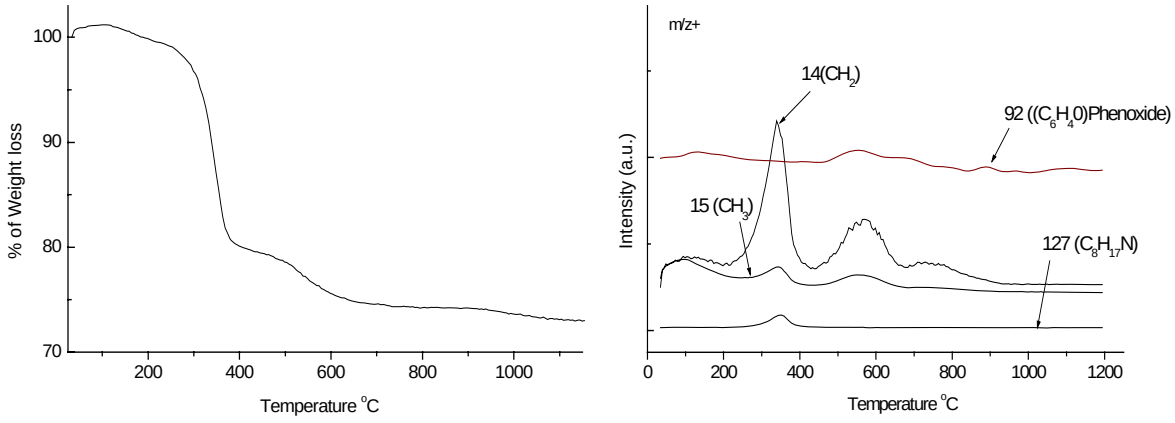


Fig. 5. Thermogravimetry and Mass (TG-MS) spectra of SM-48ccg (no. indicates m/z^+ value of mass spectrum)

The TG-MS spectrum of SM-48ccg (Fig. 5) shows about 26 % weight loss up to 1000 °C, due to decomposition of the chiral Mo-complex and silane molecules present in the channels of the mesoporous molecular sieves. The observed mass value m/z^+ = 92 corresponding to a phenoxide group confirms once again the presence of the Mo-complex on the mesoporous channel.

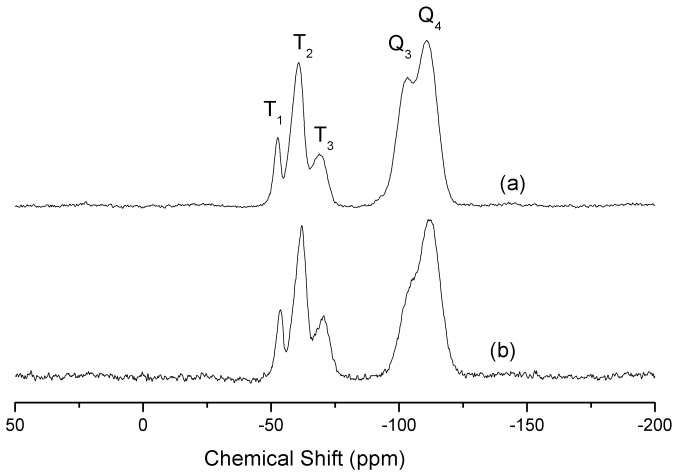


Fig. 6. ^{29}Si CP MAS NMR spectrum of (a) SM-41ccg and (b) SM-41accg.

The ^{13}C CP MAS NMR spectrum of the chiral complex grafted on MCM-41 (SM-41ccg) shows broad peaks at 59.44 (N-CH_2),), 29.88 (CH_2-ring) and 21.95 (CH_2-ring) ppm, thus also supporting the presence of the Mo-compounds on the samples. Furthermore, the parent MCM-41 and the grafted samples were examined by solid-state ^{29}Si CP MAS NMR spectroscopy. The parent MCM-41 exhibits two broad elaborate resonances in the ^{29}Si CP MAS NMR spectrum at δ = -113.0 and -103.8 ppm, assigned to Q_4 and Q_3 species of the silica framework, respectively, [$Q_n = Si(OSi)_n(OH)_{4-n}$].[14] A weak shoulder is also observed at □ = -94.5 ppm for the Q_2 species. As expected, the silyated and grafted samples show (nearly) identical ^{29}Si CP MAS NMR signals (Fig. 6), since the chemical environment of the Si atoms is not changed during the grafting process. The ^{29}Si CP MAS NMR spectra also exhibit three signals at δ = -49.8, -57.9 and -66.2 ppm assigned to T_1, T_2 and T_3 organosilica species, respectively, [$T_m = RSi(OSi)_m(OR)_{3-m}$].

4.3.2. Catalytic Applications

The grafted samples are tested as heterogeneous catalysts in olefin epoxidation, with cyclooctene as substrate and TBHP as oxidizing agent. The results are summarized in Table 1.

Table 1 Oxidation of cyclooctene chiral and achiral complexes grafted mesoporous molecular sieves.

Catalysts	Conversion (%)	Selectivity (%)
SM-41accg†	28	89
2nd run†	26	98
3rd run†	25	93
SM-48accg†	34	88
2nd run†	32	88
3rd run†	31	85
SM-41ccg†	30	100
2nd run†	21	100
3rd run†	22	80
SM-48ccg†	34	100
2nd run†	34	100
3rd run†	34	65

† Reaction Temperature = 55 °C

The SM-41accg and SM-41ccg materials show about 28 % cyclooctene conversion with 89-100 % epoxide selectivity after 24 h reaction time. In the cases of SM-48accg, and SM-48ccg conversions between 35 and 38 % and selectivities of 85-100 % of are obtained. The observed higher activity in case of the later materials is due to easier diffusion of reactant molecules in the three dimensional pore openings of the mesoporous structure of MCM-48 in comparison to the one dimensional pore openings of MCM-41 being accessible only from one direction. After the first catalytic run the catalyst is washed several times with dichloromethane to remove physisorbed molecules and the reaction is repeated several times. The catalysts are found to display the same activity even after several catalytic runs, with considerable decrease

in selectivity, which may due to presence of some chemisorbed coke on the recycled catalysts.[1d] Further, filtration experiments were carried out to filter off (remaining homogeneous) catalyst at the reaction temperature after 50% conversion had been reached for SM-41ccg and SM-48ccg. The conversions obtained by the filtrate alone were monitored for an additional 24 h reaction time. The activity of the filtrate, however, is negligible, thus demonstrating that catalyst leaching does not play a significant role (homogeneous catalyst seems not to be present in significant amounts). The chiral catalysts, SM-41ccg and SM-48ccg are examined for the asymmetric epoxidation of *cis*- and *trans*-ß-methylstyrene. The results are summarized in Table 2.

Table 2 Oxidation of cis and trans-ß-methyl styrene over chiral complex grafted mesoporous molecular sieves.

Catalysts (Reactant)	Conversion (%)	ee (%)
SM-41ccg (trans-methyl styrene) ‡	36	21
SM-41ccg (cis-methyl styrene) ‡	27	30
SM-48ccg (trans-methyl styrene) ‡	46	21
SM-48ccg (trans-methyl styrene)†	89	19
SM-48ccg (cis-methyl styrene) ‡	55	31

‡ Reaction Temperature = 25 °C

† Reaction Temperature = 55 °C

The conversion and asymmetric induction for the *cis* substrates is in all examined cases notably better than that for the *trans* analogues. About 21 % ee could be obtained for *trans*-ß-methylstyrene epoxidation reaction on both SM-41ccg and SM-48ccg associated with 36 and 46 % of conversion, whereas in case of *cis*-ß-methylstyrene, about 31 % ee with 27 and 55 %

conversion was observed. The catalytic reaction was additionally carried out at a reaction temperature of 55 °C with the more active SM-48ccg catalyst. The results show that the catalytic conversion increases to 89 % *trans*-ß-methylstyrene at this temperature, however the chiral induction of the *trans* compound changed very slightly from 21 % ee to 19 % ee.

4.4. Experimental Section

4.4.1. Synthetic Procedures

Mesoporous molecular sieves were synthesized following the procedures described earlier[1d,3] with molar gel compositions of SiO_2 : 0.2 NaOH : 0.27 TMAOH : 0.27 CTABr : 60 H_2O for MCM-41, and 5.0 SiO_2 : 2.5 NaOH : 0.87 CTABr : 0.13 Brij30 : 400 H_2O for MCM-48 respectively. Solvents were dried by standard procedures (THF with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under argon and kept over 4 Å molecular sieves. All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. The chiral homogeneous Schiff base ligated catalysts were synthesized by a procedure described earlier.[7]

4.4.2. Grafting and Characterization Methods

First the mesoporous molecular sieves (MCM-41 and MCM-48) were silylated with iodo-propyl trimethoxy silane using dry toluene (30 ml) as solvent under an argon atmosphere at 383 K (reaction time: 24 h). The excess silane was then removed by filtration followed by repeated washing with dichloromethane. The resulting solid was dried under vacuum at room temperature. Grafting experiments were carried out using standard Schlenk techniques under argon atmosphere applying the following procedure: first the silylated mesoporous molecular sieves MCM-41/48 were pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove physisorbed water. The activated sample was treated with 0.2 mmol of a chiral complex in 30 ml dry THF under argon atmosphere. The mixture was stirred at 339 K for 24 h. The resulting solution was filtered off and the pale yellow solid was then washed repeatedly with

CH_2Cl_2 until all physisorbed complex was removed from the surface. The washed samples were dried under vacuum at RT. For sake of comparison achiral complexes were also grafted in an analogous manner. The resulting material prepared from chiral and achiral complexes on MCM-41 and MCM-48 are designated as SM-41ccg, SM-48ccg, SM-41accg and SM-48accg, respectively.

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). IR spectra were measured with a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Powder XRD data were collected with a Phillips X'pert diffractometer using Cu-Kα radiation filtered by Ni. Nitrogen adsorption-desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41/48 was degassed at 723 K overnight to a residual pressure of about 10-24 mbar. A lower degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas *(*SBET) were determined by the BET method. The total pore volume *(*VP) was estimated from the N_2 uptake at $p/p_0 = 0.95$, using the liquid nitrogen density of 0.8081 $g \bullet cm^{-3}$. The pore size distribution curves (PSD, the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron microscopy (TEM) was recorded on a JEOL JEM2010 operated at 120 kV. Thermogravimetric mass spectra analysis (TG-MS) measurements were conducted with a Netzsch TG209 system; typically about 10 mg of sample was heated from 300 to 1473 K at 10 K min^{-1} under argon. ^{29}Si CP MAS NMR spectra were recorded at 59.627 MHz, with a (7.05 T) Bruker Avance 300 spectrometer, with 5.5 μs ^{1}H 90º pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays. ^{13}C CP MAS NMR spectra were recorded at 75.468 MHz with a 2.8 μs^{1} H 90º pulses, 8 ms contact time, a spinning rate of 8 kHz and 5 s recycle delays.

4.4.3. Catalytic reactions

Chiral epoxidation: *cis*-, or *trans*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene (100 mg, 0.83 mmol, internal standard), and SM-41ccg / SM-48ccg (200 mg, 1 mol% based on complex loading) as catalysts and 2 mL toluene as solvent were added to the reaction vessel. With the addition of TBHP (615 µl, 5.5 M in decane) the reaction started. The samples were analyzed every 30 min for 4 h and the reaction was terminated after 24 h. The analyses were carried out using a gas chromatograph (HP 5890) equipped with a capillary column (Chiraldex G-BP) and using FID detector. The enantiomeric excess was calculated from the area ratio of the peaks corresponding to both epoxides formed. The oxidation of cyclooctene (0.8020g; 8 mmol) was also tested on the grafted samples (175 mg) at 328 K in a liquid phase batch reactor with TBHP (5.5 M in decane; 16 mmol) as the oxidizing agent.

4.5. Conclusion

Optically active molybdenum (VI) dioxo complexes bearing substituted hydrosalen ligands were successfully grafted on the surface of mesoporous MCM-41 and MCM-48 molecular sieves. The obtained heterogenized compounds are found to be applicable for asymmetric epoxidation of *trans*-ß-methylstyrene and *cis*-ß-methylstyrene, with moderate optical induction (enantiomeric excesses of up to 31%). The catalysts are also found to be active for the epoxidation of cyclooctene. The catalytic activity remains virtually unchanged throughout several recycling experiments.

4.6. References

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5. Molybdenum and Tungsten Complexes of Composition (η^5-C_5R_5)MR'$(CO)_3$ and Their Use as Olefin Epoxidation Catalyst Precursors

This chapter originated the following publication:
J. Zhao, A. M. Santos, E. Herdtweck, F. E. Kühn
J. Mol. Catal. A, **2004**, *222*, 265–271

5.1. Abstract

Carbonyl complexes of formula Cp'M$(CO)_3$R (M = Mo, W; R = alkyl) can be applied as very active (TOFs up to ca. 6000 1/h; TON > 500) and selective olefin epoxidation catalysts. The X-ray crystal structure of one of those complexes is reported. The carbonyl compounds are *in situ* oxidized by *tert*-butyl hydroperoxide (TBHP) and transformed to the catalytic active species without loss of the Cp'- and R-ligands. Mo complexes are far more active than W compounds, increasing alkylation of the Cp ligand lowers the catalytic activity. Ansa-bridged derivatives, being more difficult to synthesize than unbridged congeners, show no significant advantage when applied in catalysis. The catalysts lose activity after several runs, mainly due to competitive coordination of the increasing presence of the by-product *t*-BuOH.

5.2. Introduction

Carbonyl complexes of transition metals have been applied as oxidation catalysts since more than 30 years.[1] The characterization and successful catalytic application of high oxidation state congeners such as oxides and peroxides during the last two decades, however, shifted the attention in oxidation catalysis to these latter complexes.[2] Nevertheless, it also turned out that carbonyl complexes bearing other ligands, such as Cp derivatives are in several cases – with

or without catalysts – oxidizable to oxide and peroxide complexes without loosing their Cp ligands.[3]

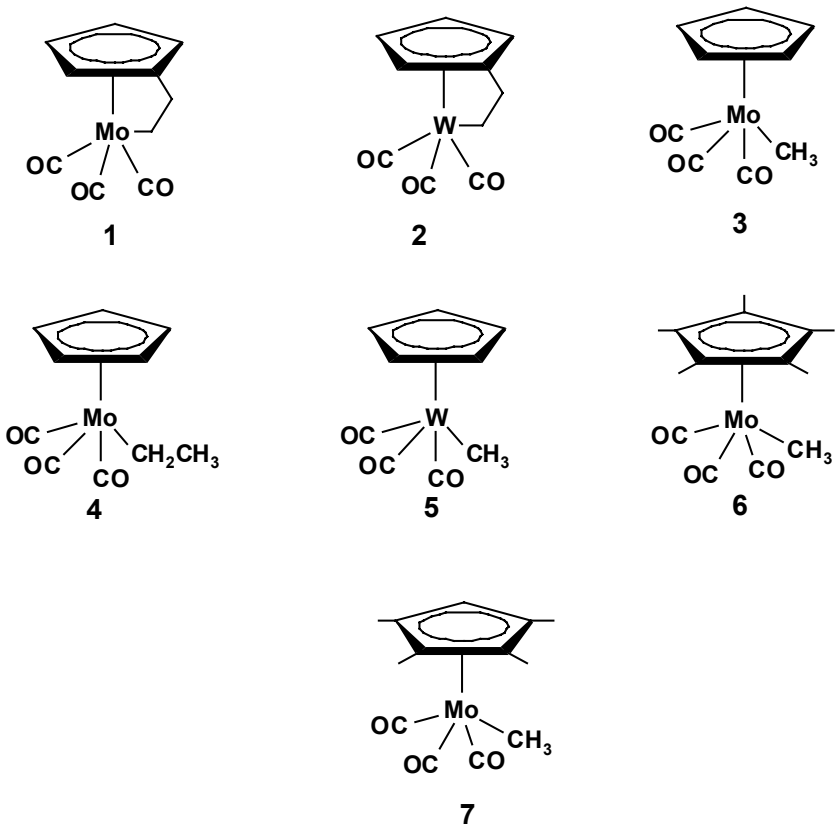
Based on the successful catalytic application of organorhenium oxides of formula $RReO_3$, such as methyltrioxorhenium(VII) (MTO) in oxidation catalysis[4] we started to examine molybdenum and tungsten compounds of the composition $MX_2O_2L_2$ (X = Cl, Br, Me; L = Lewis base)[5] and $Cp'MO_2Cl$ (Cp' = Cp (C_5H_5), Cp* (C_5Me_5), BzCp ($C_5(CH_2C_6H_5)_5$))[6] as oxidation catalysts. Some compounds of formula $Cp'MO_2X$ surpass the $MX_2O_2L_2$ derivatives in catalytic activity in the olefin epoxidation and rival the most active $RReO_3$ complex, MTO, in its epoxidation activity. There are, however, some important differences between the Mo, W and Re complexes mentioned above. In the presence of the $RReO_3$ catalysts H_2O_2 can be used as oxidizing agent while the Mo and W compounds of formulae $MX_2O_2L_2$ and $Cp'MO_2Cl$ need TBHP as oxidant. Furthermore, while $Cp'MO_2X$ compounds are quite active catalysts, $Cp'ReO_3$ derivatives do not catalyze the olefin epoxidation at all.[4,7]

Recently we have shown that $Cp'MoO_2Cl$ complexes can be easily obtained from carbonyl precursors by oxidation with TBHP in yields up to 75 %. Applying $Cp'Mo(CO)_3Cl$ as oxidation catalyst in the presence of TBHP, however, leads to similar results as the application of $Cp'MoO_2Cl$. The carbonyl precursor is oxidized to the oxide and catalyzes the olefin epoxidation with the same oxidizing agent, which was previously applied for its own oxidation. During this oxidation process the ligands Cp' and Cl remain attached to the metal. The carbonyl complexes are even more stable than the oxides and therefore ideal storage forms of the catalyst, which can be generated *in situ* from the carbonyl precursor.[6] In this work we use this concept for the catalytic application of several compounds of formula $Cp'M(CO)_3R$ (M = Mo, W; R = alkyl) as oxidation catalysts and compare their catalytic activity with respect to variations in the ligands R and Cp'.

5.3. Results and Discussion

5.3.1. Synthesis and spectroscopic examinations

Compounds **1**-**7** (see Scheme 1) were synthesised according to literature procedures or to modified literature procedures as described in the experimental part. The compounds are stable at room temperature and can be handled in laboratory atmosphere for several hours. Spectroscopic data, particularly IR vibrations, ^{1}H- and ^{13}C-NMR shifts have already been presented in the literature and will not be further discussed here. The X-ray crystal structure of compound **7** has been determined (see Figure 1). The bond distances and bond angles are, as expected, similar to their congeners described elsewhere.[11]



Scheme 1

The ^{95}Mo chemical shift is not an appropriate tool to distinguish between complexes in different oxidation states, however, it is highly sensitive to structural and electronic variations within a series of closely related mononuclear compounds,[12] allowing insight into the electronic situation of the molybdenum centre. The present series of compounds exhibits

highly shielded chemical shifts, which can be in general associated with low formal oxidation states. ^{95}Mo-NMR data was only available for compound **3**[13] (δ = -1736 ppm in C_6D_6 and –1729 ppm in $CDCl_3$), compounds **1**, **4**, **6** and **7** display their ^{95}Mo-NMR signal in $CDCl_3$ at -1708, -1685, -1596 and –1628 ppm respectively. It is observed that increasing the ring methyl substitution, which is expected to increase the electron density in the Cp ring and presumably also around the metal, leads in fact to a shift to *low* field. This, at a first glance strange observation had already been made for the series of compounds (*mes*)$Mo(CO)_3$, (*p*-xyl)$Mo(CO)_3$ and (tol)$Mo(CO)_3$.[14] The authors explain these results based on thermodynamic data showing that there is an increase of the molybdenum-arene bond strength with increasing ring methyl substitution, however, no quantitative interpretation was possible due to incomplete understanding of the complexity and relative importance of the several terms in the Ramsey equation.

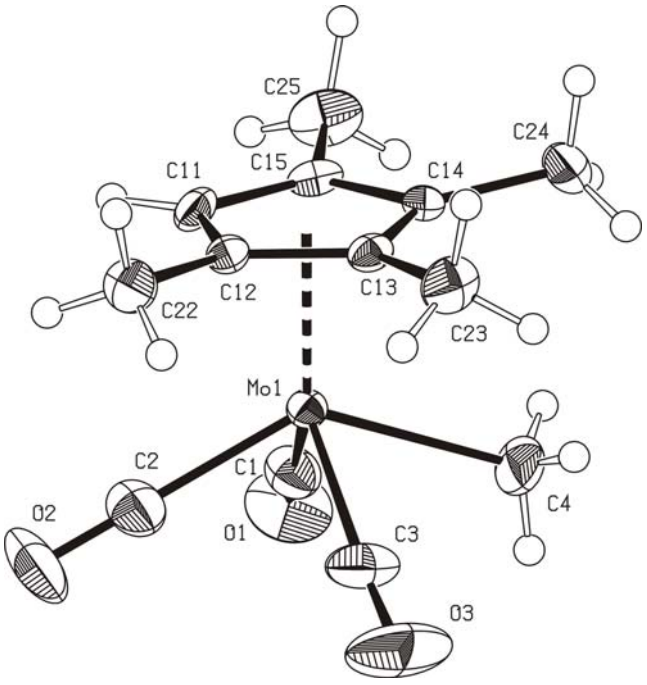


Figure 1 ORTEP style plot of molecule **A** in the solid state of compound **7**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Mo1-C1 1.983(3), Mo1-C2 1.979(3) Mo1-C3 1.981(3) Mo1-C4 2.311(4) Mo1-Cg 2.006; C1-Mo1-C2 79.8(1), C1-Mo1-C3 106.1(1), C1-Mo1-C4 72.3(1), C1-Mo1-Cg 128.2, C2-Mo1-C3 79.5(1), C2-Mo1-C4 133.2(1), C2-Mo1-Cg 117.0, C3-Mo1-C4 73.4(1), C3-Mo1-Cg 124.5, C4-Mo1-Cg 109.8. Cg denotes the center of gravity in the Cp*-ring

5.3.2. Complexes 1-7 in oxidation catalysis

Compounds **1-7** were tested as catalysts for the epoxidation of cyclooctene, styrene and 1-octene with TBHP in order to compare the effect of the central atom, the presence of an *ansa*-bridge and the influence of the cyclopentadienyl ligand used in the catalytic performance.

Table 1: Cyclooctene epoxide yields reached with Cp'Mo$(CO)_3$R-derived catalysts at a given time when applied at 55 °C with a catalyst:cyclooctene:TBHP-ratio of 1:100:200.

Complex	Yield 4h (%)	Yield 24h (%)	TOF (h^{-1})
1	92	100	250
2	10	35	25
2[a]	41	90	110
3	95	100	820
3[b]	100	100	960
4	94	100	230
5	15	30	60
5[a]	62	100	240
6	68	100	270
7	75	100	150

a) at 90°C. b) at 75°C.

The details concerning the catalytic reaction are given in the experimental part. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst. The catalysts were first stirred with TBHP until a colour change from orange to yellow occurred, indicating the oxidation of the carbonyl complexes to the corresponding dioxo Mo(VI) compounds. For cyclooctene and 1-octene no significant formation of by-products (e.g. diol) was observed. For styrene, being the epoxide more prone to ring opening reactions detectable amounts of diol as well as benzaldehyde and benzoic acid as by-products were

found. The time dependent curves for compounds **1**-**7** are shown for cyclooctene in Figure 2 and the TOF´s in Table 1.

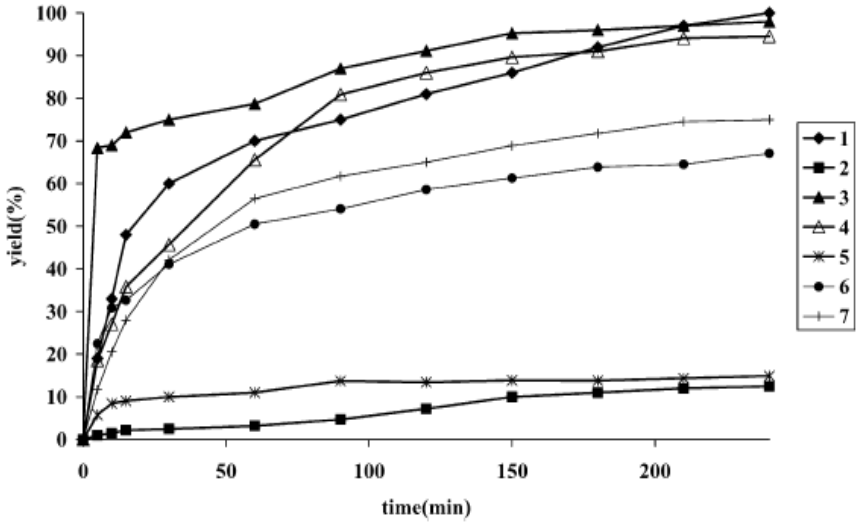


Figure 2: Catalytic activity of compounds **1**-**7** in the presence of TBHP in the catalytic epoxidation of cyclooctene.

The curves show a similar evolution, having a quick increase of the yield during the first reaction hour and then slowing down (first order kinetics). From these curves it can be observed that there is a strong increase in activity on going from tungsten to molybdenum. This had already been observed before[5m,15] but in this case the difference is particularly pronounced. Increasing the reaction temperature increases the activity of the tungsten complexes, for instance for complexes **2** and **5** the yield rises from 10 to 41% and 15 to 61% after 4h when the reaction is performed at 90°C, instead of 55°C, furthermore, at 90°C the yields obtained after 24h are almost quantitative (90%, 100%). Compounds **1** and **3** show a similar behaviour indicating that the replacement of a $(CH_2)_2$ *ansa*-bridge by a methyl group does not influence much the electronic situation on the metal centre and therefore also not the catalytic performance, on the other hand, the replacement of the methyl by a more electron-withdrawing group such as Cl leads to better catalytic results if applied in a 0.01:1:2

(cat.:substrate:oxidant) ratio.[6] The replacement of Cp by a more electron donating ligand like Cp* causes a decrease on the catalytic activity, on rendering the molybdenum centre more electron-rich, this phenomena has also been observed in the related compounds Cp'Mo$(CO)_3$Cl, which have been previously studied.[6] The application of compound **7** allows a clearer insight into this phenomena, in fact, the absence of one methyl group in the methylated cyclopentadienyl ring already increases the activity on going from **6** to **7** (68% to 75% after 4h). These results additionally support the conclusion drawn from spectroscopic results (see also ref. [6] with respect to Cp'Mo$(CO)_3$Cl complexes) that the precursor compounds Cp'M$(CO)_3$L are not transformed to an uniform catalyst species, e. g. a simple Mo$(O_2)_2O_2$-type complex, after losing their organic ligands. On the contrary, the different organic ligands have significant influence on the catalyst performance, as it was observed in the case of $RReO_3$ compounds, which also do not lose their organic ligand R under catalytic conditions[2,4] and this influence is maintained in repeated catalytic runs. No indications for a loss of the Cp' and the R/L-ligand are found in the case of the complexes examined in this work.

A lower catalyst loading than 1 mol% was examined for compound **3** (0.1mol%), increasing the TOF to ca. 6000 h^{-1}. Under the same conditions Cp'Mo$(O)_2$Cl-catalysed oxidations reach maximum TOF's of ca. 4000 h^{-1}.[6] The latter catalyst is easily obtained from Cp'Mo$(CO)_3$Cl in isolated yields up to 75 %. We have already shown that Cp'Mo$(CO)_3$Cl can also successfully applied as catalyst (precursor) *in situ*[6] The direct application of the carbonyl complexes leads to equal activities as the application of the isolated oxides but the latter procedure requires an additional synthesis step, causing a loss of at least 25 % of the desired complex. These facts suggested the direct application of the carbonyl complexes also in the case of the compounds described in this work.

Some of the expected oxide and peroxide products of general formulae Cp'MoO_2R and Cp'Mo(O_2)OR, in this work generated *in situ* from the carbonyl precursors **1**-**7** have been obtained previously by other routes and were isolated and thoroughly characterized.[11c,16] We exemplary isolated the reaction products of excess TBHP with compound **3** and compared the

received ^{1}H-, ^{13}C-NMR and IR data with the available literature data.[16c] The obtained data are identical (within the error range of the experimental methods applied) with the published data of $CpMoO(O_2)(CH_3)$. In situ recorded vibrational spectra suggest intermediary formation of $CpMoO_2(CH_3)$, but this compound could not be obtained without the concomitant formation of $CpMoO(O_2)(CH_3)$, even when stoichiometric amounts of TBHP are applied. $CpMoO(O_2)(CH_3)$, isolated from the oxidation of $CpMo(CO)_3(CH_3)$ (**3**) with excess TBHP as sole product in nearly quantitative yields, was additionally applied in the oxidation of cyclooctene with TBHP. Freshly prepared, it catalyzes the reaction as does the *in situ* generated species under the same reaction conditions. Based on these results it seems justified to assume that $Cp'MoO(O_2)R$ type complexes act as catalytically active species in the cases examined in this work.

The observation that the $Cp'Mo(CO)_3Cl$ derived catalysts are of higher activity at higher catalyst concentration (1 mol %), but of lower activity at lower catalyst concentration (0.1 mol %) than the $Cp'Mo(CO)_3R$ derived catalysts may be due to the more pronounced moisture sensitivity of the chlorine derived systems. At lower catalyst concentration the relative amount of water in the system is higher and catalyst decomposition by reaction with water is more likely and faster. Much stronger effects of the same type, supporting this explanation, have been reported with respect to Re(VII) catalysts of composition $XReO_3$ and $MeReO_3$.[4b] While the latter system is very stable in the presence of water, the highly reactive $ClReO_3$ decomposes immediately in the presence of moisture under the formation of HCl and perrhenic acid ("$HOReO_3$"),[4b] the latter being catalytically inactive under the applied conditions. The overall (absolute) yield however, is generally lower with $Cp'Mo(CO)_3L$ (L = Cl, alkyl) derived catalysts at lower catalyst concentrations than that obtained with a higher catalyst concentration at a given time. At all concentrations catalyst decomposition due to the presence of water takes place to a certain, but minor degree according to *in situ* obtained spectroscopic data (NMR, IR-evidence). At lower catalyst concentrations the relative amount of residual water is higher, thus having a more pronounced effect. Nevertheless, with a catalytic load of 1mol% compounds **1** and **3** could be recycled 5 times without significant loss

of activity, for instance for **3** 100% yield was obtained with 5 new substrate charges each time after ca. 4h, in the 6th charge 60% was obtained after 4 h and on the 7th there was a major activity decrease to 10% yield after 24h. This decrease in activity, however, is not mainly due to catalyst decomposition. The increasing amount of *t*-BuOH, also able to coordinate to the catalyst competes, due to its excessive amount increasingly successful with the substrate, thus slowing down the velocity of the catalysed reaction. Addition of excess *t*-BuOH to a catalytic reaction has exactly the same effect. Theoretical examinations as well as older examinations on other Mo-based catalysts support this explanation.[1,5l] These observations also shed additional light on the earlier catalyst deactivation at lower catalyst concentrations described above. Due to the originally higher substrate concentration relative to the catalyst more *t*-BuOH forms in a given time. This also contributes to the reduction of the catalyst activity during the course of one (or more) catalytic runs depending on the catalyst:*t*-BuOH relationship.

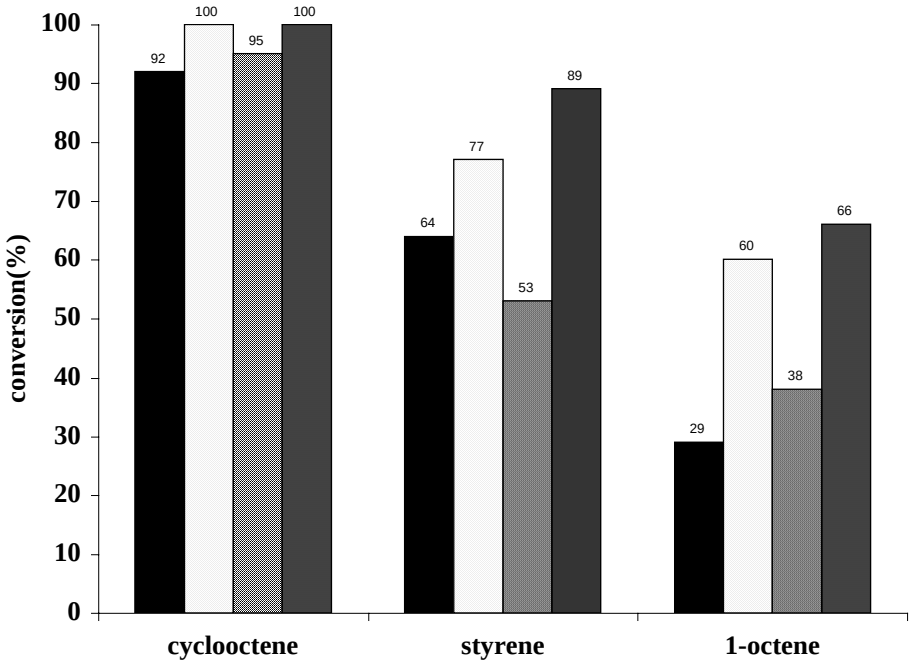


Figure 3: Catalytic activity of compounds **1** and **3** in the presence of TBHP in the catalytic epoxidation of cyclooctene, styrene and 1-octene.

Compounds **1** and **3**, being the most active derivatives, were also tested with styrene and 1-octene as substrates (See Fig. 3). The behaviour of the compounds is similar and with styrene after 24h epoxide yields of about 50 % could be obtained, with 1-octene, a linear non-activated olefin, the results can also be considered as quite good, since after 24h conversion of ca. 60% and epoxide yields of ca. 45 % can be reached. It should be noted that with the closely related and very active complex (η^5-C_5Bz_5)$Mo(CO)_3Cl$ after 24h and under the same catalytic conditions a yield of only ca. 20% was reached, the results found in the literature for other active catalysts are also not higher than this value.[17]

5.4. Experimental Section

5.4.1. Synthesis and Characterization

All preparations and manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 and NCMe over CaH_2), distilled under nitrogen and used immediately (THF) or kept over 4 Å molecular sieves (3Å for NCMe). TBHP was purchased from Aldrich as 5.0-6.0 mol % solution in decanes and used after drying over molecular sieves to remove the water (< 4 % when received).

Compounds **1**, **2**,[8] **3** – **6** [9] were synthesised according to literature procedures and compound **7** was prepared by an adaptations of these procedures, since it can not be properly purified by sublimation. Therefore, after removal of the original solvent in oil pump vacuum at room temperature, the residue is extracted with *n*-hexane and the obtained solution is chromatographed on Florisil (60 – 100 mesh) with *n*-hexane as solvent and eluant. The yellow fraction is collected and crystallized after concentration at – 30 °C. Compound 7 is obtained as pale yellow crystals.

Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra of isolated compounds were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets, *in-situ* spectra were recorded in KBr cells in methylene chloride as the solvent (cat:oxidant 1:5 - 1:10). Far-IR measurements were

performed on a Bio-Rad FTS 525 system as Nujol mulls or polyethylene pellets using a 6μm Mylar beam splitter. ^{1}H-NMR, ^{95}Mo- and ^{13}C-NMR spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer; Catalytic runs were monitored by chiral GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit HP 3396 Series II.

$C_5Me_4HMo(CO)_3CH_3$ (**7**). Yield (80%). Anal. Calcd for $C_{13}H_{16}O_3Mo$ (316.21): C, 49.38; H, 5.10. Found: C, 49.56; H, 5.27. IR (KBr ν cm^{-1}): 3063 w, (CH of Cp), 2005 vs, 1923 vs, (CO). ^{1}H-NMR ($CDCl_3$, 400 MHz, rt., δ ppm): 0.08 (s, 3H, $C_5(CH_3)_4HMoCH_3$), 1.82 and 1.86 (12H, $C_5(CH_3)_4HMoCH_3$), 4.96 (s, 1H, $C_5(CH_3)_4HMoCH_3$). ^{13}C-NMR ($CDCl_3$, 100.28 MHz, rt. δ ppm): -13.0 ($C_5(CH_3)_4HMoCH_3$), 10.1, 12.2 ($C_5(CH_3)_4HMoCH_3$), 88.9, 103.9, 106.8 ($C_5(CH_3)_4HMoCH_3$), 163.9 (CO). ^{95}Mo-NMR ($CDCl_3$, 26.07 MHz, rt. δ ppm): –1685. EI-MS (70 eV), m/z (%); M^+ = 316 (17).

5.4.2. Crystallography

Crystal structure analysis of compound **7**[10]: $C_{13}H_{16}MoO_3$, M_r = 316.20, pale yellow fragment (0.10 × 0.20 × 0.30 mm^3), monoclinic, $P2_1/n$ (No.: 14), a = 13.5372(2), b = 14.3485(2), c = 14.0502(2) Å, V = 2720.23(7) Å^3, Z = 8, d_{calc} = 1.544 gcm^{-3}, F_{000} = 1280, μ = 0.958 mm^{-1}. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection were performed at 123 K within the Θ range of 2.01° < Θ < 25.36°. A total of 63252 reflections were integrated, corrected for Lorentz, polarization, and, arising from the scaling procedure, corrected for latent decay and absorption effects. After merging (R_{int} = 0.051), 4990 [3742: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 435 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement

parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ and converged with $R1$ = 0.0249 [$I_o>2\sigma(I_o)$], $wR2$ = 0.0559 [all data], GOF = 1.039, and shift/error < 0.002. The final difference-Fourier map shows no striking features ($\Delta e_{min/max}$ = +0.31/-0.34 eÅ^{-3}). The unit cell contains two crystallographical independent molecules **A** and **B**. They differ in the orientation of the methyl group bound to molybdenum with respect to the Cp-ring. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-249731 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

5.4.3. Catalytic reactions with compounds 1-7 as catalysts

Method A: Cis-cyclooctene (800 mg, 7.3 mmol), 1.00 g mesitylene (internal standard), 1 mol % (73 μmol) of compounds **1-7** as catalyst.

Method B: Styrene (250 mg, 2.39 mmol), 100 mg mesitylene (internal standard), 1 mol% (24 μmol) of compounds **1** and **3** as catalyst.

Method C: 1-octene (800 mg, 7.12 mmol), 1.00 g mesitylene (internal standard), 1 mol % (71 μmol) of compounds **1** and **3** as catalyst.

For all methods A, B, and C TBHP (5.5 M in *n*-decane) 2.64 mL, 0.869 mL and 2.58 mL were added to a thermostated reaction vessel and stirred for 24 h at 55ºC. The catalyst precursor compounds **1-7** were first reacted with the TBHP until the reaction mixture changed its color to a pale yellow. After this the substrate and the internal standard were added. The reason for this order is that the tricarbonyl carbonyl compounds are first to be oxidized to the catalytically active compounds, before oxidation of the substrate can be achieved. The formation of the catalyst species can be monitored by *in situ* vibrational spectroscopy.

The course of the reaction was monitored by quantitative GC-analysis. Samples were taken after five and ten minutes and then every thirty minutes diluted with chloroform and chilled in

an ice bath. For the destruction of hydroperoxide and removal of water a catalytic amount of manganese dioxide and magnesium sulphate was added. The resulting slurry was filtered over a filter equipped Pasteur pipette and the filtrate injected in the GC column.

The conversion of cyclooctene, styrene, and 1-octene as well as the formation of cyclooctene and styrene oxide was calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

5.5. Conclusions

The carbonyl compounds of composition Cp'Mo$(CO)_3$R (R = alkyl) have proven to be efficient catalyst precursors. The isolation of the more sensitive oxo and peroxo compounds prior to application in catalysis is not necessary, avoiding also material losses: the carbonyl complexes can be oxidized *in situ* and directly be used as catalysts. This oxidation, however, does not include the loss of the Cp' and the R ligand, comparable to the situation observed for Cp'Mo$(CO)_3$Cl complexes. The activity and selectivity of the catalysts is high and they can be reused several times without significant decomposition. The by-product of the oxidation, *t*-BuOH hampers the catalytic reaction with increasing concentration, as it is known for other Mo(VI) oxidation catalysts. Heterogenization of the catalyst or two phase homogeneous catalysis might be promising ways to avoid high amounts of *t*-BuOH in the same phase as the catalyst after several catalytic runs and are accordingly under examination in our laboratories.

Furthermore, the synthetic pathway used for the preparation of compounds **4** and **5** should allow the easy introduction of a chiral ligand instead of methyl group. The presence of a chiral group in the immediate surrounding of the metal centre might lead to much higher enantiomeric excesses as have been reached in the past with related complexes, where the chirality centre was usually quite far away from the metal.

5.6. References

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6. Cyclopentadienyl-Molybdenum Complexes as Epoxidation Catalysts in Room Temperature Ionic Liquids

This chapter originated the following publication:
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I. S. Gonçalves, M. Pillinger, C. C. Romão
Tetrahedron Lett. **2005**, *46*, 47-52

6.1. Abstract

Complexes of the type $(\eta^5\text{-}C_5R_5)Mo(CO)_3X$ (X = Me, Cl; R = H, Me), being efficient homogeneous catalysts for the epoxidation of olefins, have been examined for their catalytic performance at 55°C in systems containing room temperature ionic liquids (RTILs) of composition $[BMIM]NTf_2$, $[BMIM]PF_6$, $[C_8MIM]PF_6$, and $[BMIM]BF_4$. The catalytic performance for cyclooctene epoxidation depends strongly on the water content of the system, the catalyst solubility in the RTIL, and the reaction behaviour of the RTIL under the applied reaction conditions. The catalysts can be recycled without significant loss of activity when a reaction system containing $[BMIM]NTf_2$ and $[BMIM]PF_6$ in a 4:1 relationship is used. High proportions of $[BMIM]PF_6$ lead to a ring opening reaction (diol formation), due to HF formation and the presence of residual water.

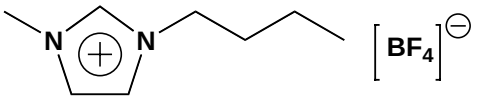
6.2. Introduction

It has been shown that $Cp'Mo(CO)_3Cl$ can be used as olefin epoxidation catalyst precursors – being *in situ* oxidized to the Mo(VI) catalyst - and present advantages over the direct application of the more sensitive Mo(VI) species $Cp'MoO_2Cl$. In fact, the carbonyl compounds display a higher stability and can be stored easily for long periods of time.[1a] Furthermore, $Cp'Mo(CO)_3R$ (R = alkyl, or *ansa*-alkyl) complexes have also been described as

homogeneous epoxidation catalyst precursors, showing a comparable catalytic activity to their chloro-analogues [1b]. This type of complexes surpass most other Mo(VI)-dioxo complexes (e. g. of the composition $MoX_2O_2L_2$ (X = Cl, Br, Me; L = Lewis base)) significantly in their catalytic activity and rival even the highly active and well examined Re(VII) epoxidation catalyst methyltrioxorhenium (MTO).[2] The by-product of the oxidation of olefins with TBHP (*tert*-butyl hydro peroxide) in the presence of Mo(VI) dioxo complexes, *t*-BuOH, however, hampers the catalytic reaction with increasing concentration. Heterogenization of the catalyst, or two-phase homogeneous catalysis are promising ways to avoid high amounts of *t*-BuOH in the same phase as the catalyst after several catalytic runs. [1c] Another important advantage of the application of heterogeneous catalysts is the easy catalyst/product separation, which still causes considerable catalyst losses in purely homogeneous systems.

In the last decade room temperature ionic liquids (RTILs) have been attracting considerably attention as possible replacement for conventional molecular solvents for catalytic and organic reactions due to their unique physical properties such as non-volatility, non-flammability, thermal stability and high polarity. Additionally they enable solubilization of inorganic complexes (catalysts), while being immiscible with most hydrocarbons. As such, they provide a non-aqueous alternative for two-phase catalysis, in which the catalyst is immobilized in the ionic liquid and can be easily separated from the products and recycled.[3] RTILs have been used in several types of reactions such as hydrogenation, hydroformylation, oxidation, oligomerization of alkenes and aldehyde definition. [3] With regard to epoxidation catalysis, however, the application of RTIL is just emerging. Song and Roh first reported a Mn(III) (salen) complex (Jacobsen's complex) catalyzing asymmetric epoxidation in an ionic liquid a few years ago. [4] Since then, RTILs have been successfully applied in the olefin epoxidation with Fe (III) porphyrin, Mn (III) porphyrin, or MTO as catalyst. [5] It was found that some ionic liquids show enhancement in reaction rates and selectivity. An investigation on the catalytic activity of $MoX_2O_2L_2$ (X = Cl, Me; L = Lewis base) complexes in RTIL was reported only recently by Valente, Romão et al., [6] in which a series of RTILs were tested as solvents in the catalytic epoxidation of cis-cyclooctene, using TBHP as oxidant. It shows that

the use of RTILs for recycling of dioxomolybdenum (VI) complexes seems to be promising if the right RTIL is chosen for a certain catalyst. Additionally, catalyst recycling may become much easier.



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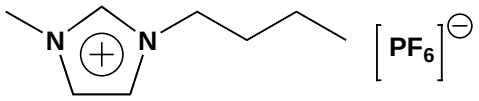

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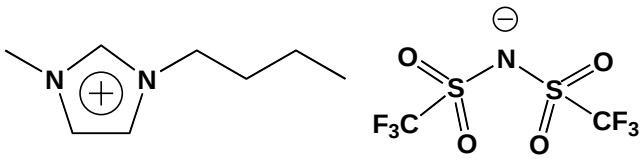

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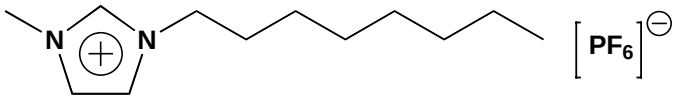

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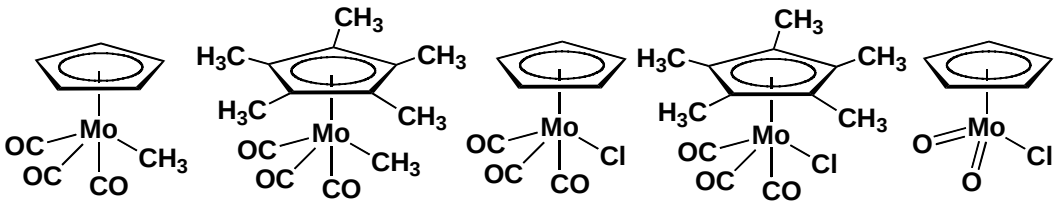

1 **2** **3** **4** **5**

Scheme 1

Among the large variety of RTILs available in the literature, in this study we chose RTILs of the imidazodium salt type with different anions as solvents or immobilizing agents, respectively (Scheme 1), due to their high oxidation and water stability as well as their easy accessibility in terms of synthesis.[2b] The performance of cyclopentadienyl molybdenum carbonyl complexes of the formula Cp'Mo(CO)$_3$X (X = Cl, Me, Cp = C_5H_5, C_5Me_5) in the presence of RTILs is examined in this work. The synthesis of these complexes has been reported elsewhere. [1, 8]

6.3. Results and Discussion

Compounds of the type Cp'Mo(CO)$_3$Me (Cp = C_5H_5 (**1**), C_5Me_5 (**2**)) and CpMo(CO)$_3$Cl (**3**) were tested in epoxidation catalysis at 55 °C, using *cis*-cyclooctene as substrate, TBHP as oxidant and a RTIL as co-solvent. The catalytic reactions were initially performed in air (laboratory atmosphere) in order to test the performance of the system under the easiest possible reaction conditions. The ionic liquids were equilibrated in air prior to use in these reactions.

Compounds **1**-**3** (Scheme 1) dissolve easily in the RTILs [BMIM]NTf$_2$, [BMIM]PF$_6$ and [BMIM]BF$_4$ originating clear solutions. After the addition of TBHP and stirring for 10 min, in the case of [BMIM]NTf$_2$, the reaction mixture changes from being a yellow (for compounds **1** and **2**) or red (for compound **3**) solution to a pale yellow suspension. In the case of [BMIM]PF$_6$, a clear yellow solution forms, while in the case of [BMIM]BF$_4$, a colourless solution with a small amount of bluish-white suspended solid is obtained. After the addition of the substrate and the internal standard, all the systems are biphasic because the RTIL and the substrate are not miscible. At the end of the 1st run all the systems maintain their initial appearance. The turnover frequencies (TOFs) obtained in these reactions are all considerably lower than the TOFs of the reactions performed without solvent (Table 1).

Table 1. Catalytic results for compounds **1-3** with different solvents under laboratory atmosphere with water equilibrated RTILs.

Solvent	TOF[a](mol/mol*h)[a]			Epoxide yield (%) After 4 h			Epoxide yield (%) After 24 h		
	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)
No solvent	820	960	270	100	100	68	100	100	100
[BMIM]PF_6	316	528	144	20	5.6	27	0	0	0
[BMIM]NTf_2	33	46	24	43	58	28	100	100	83
[BMIM]BF_4	14	15	10	8	7	6	38	31	27

[a] Determined after 5 minutes of reaction

This slower catalytic reaction may be due to dilution effects, phase transfer problems between the viscous RTIL and the other components of the reaction system (e. g. the olefin) or may - at least in part - result from a certain amount of decomposition of the catalysts in the RTIL, due to the water content of the RTILs. Notably, all examined catalysts perform worse in the presence of the RTIL with the highest water content ([BMIM]BF_4 is miscible with water)[8a], both in terms of TOFs and conversions after 4 and 24 h. This is as expected considering the water sensitivity of the Mo(VI) species[1] which act as active catalysts. As can be concluded directly from the initial colour changes, the catalysts decompose directly after their formation due to the high water content of [BMIM]BF_4 (bluish colour originates from molybdenum oxide hydrates, EA-evidence). The lowest equilibrated water content is present in [BMIM]NTf_2. Accordingly, the epoxide yields after 4 and 24 h are the best of all RTIL-containing systems. However, the TOFs observed in the [BMIM]NTf_2-containing system are considerably lower than in the [BMIM]PF_6-containing system. This - at first glance - strange outcome, is, however, also explainable. As suggested by the formation of a suspension, the Mo(VI) species are not so easily soluble in this RTIL, therefore leading to a much lower

efficient catalyst concentration. Examination of the solubility of compound **5** in the RTILs confirms this statement.

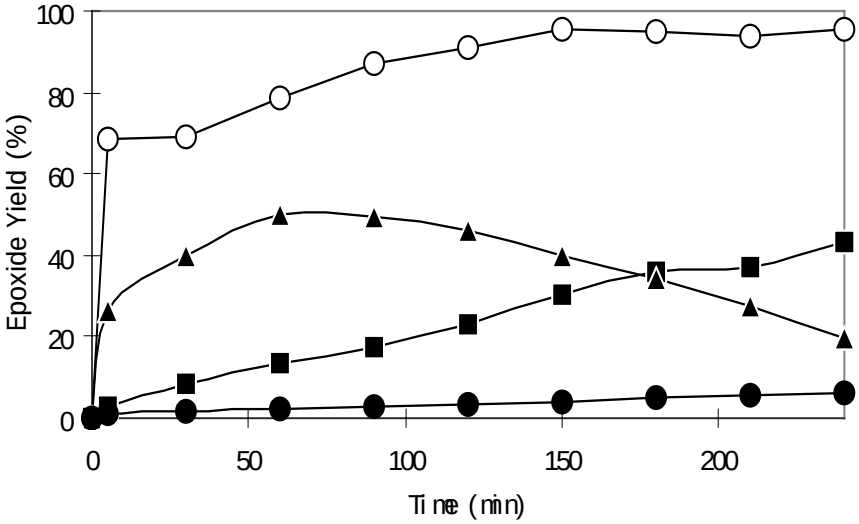

Figure 1. Kinetics of cyclooctene epoxidation in the presence of the complex $CpMo(CO)_3Me$ (**1**) without solvent (open circles), or using $[BMIM]NTf_2$ (closed squares), $[BMIM]PF_6$ (closed triangles) or $[BMIM]BF_4$ (closed circles) as solvent (laboratory atmosphere, water equilibrated RTILs).

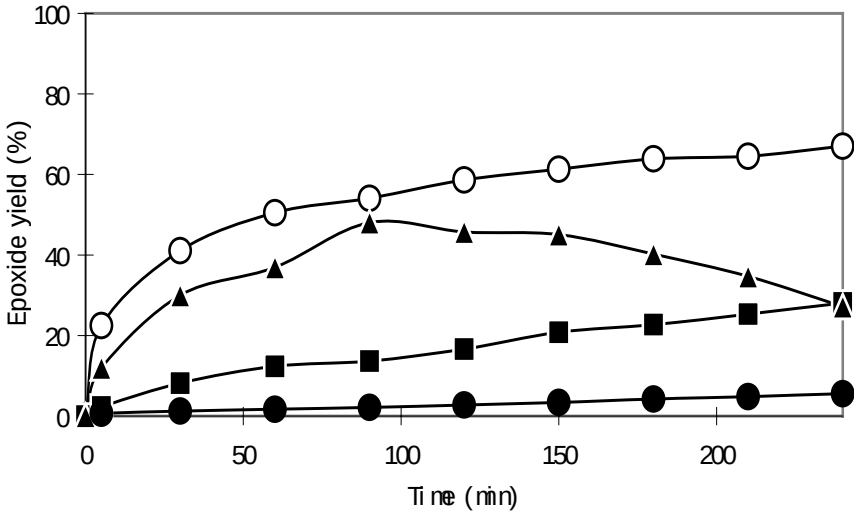

Figure 2 Kinetics of cyclooctene epoxidation in the presence of the complex $Cp^*Mo(CO)_3Me$ (**2**) without solvent (open circles), or using $[BMIM]NTf_2$ (closed squares), $[BMIM]PF_6$ (triangles) or $[BMIM]BF_4$ (circles) as solvent

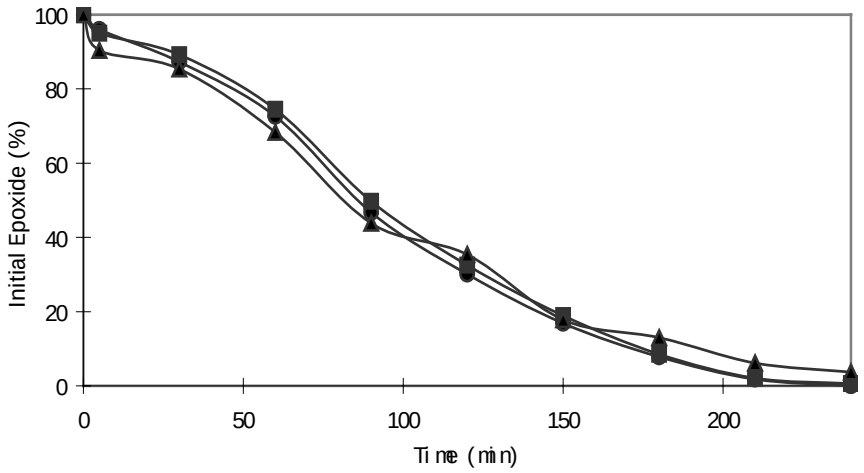

Figure 3 Kinetics of cyclooctene epoxide consumption in the presence of $CpMo(CO)_3Me$ (**1**) (circles), $CpMo(CO)_3Cl$ (**3**) (squares) or $CpMoO_2Cl$ (**4**) (triangles) and using $[BMIM]PF_6$ as solvent

In the $[BMIM]PF_6$ system, despite its high initial activity towards cyclooctene transformation and epoxide formation (GC-evidence, Figure 1, 2), no epoxide is present after 24 h reaction time with all examined catalysts (Table 1). Even in the $[BMIM]BF_4$ system the epoxide yield after 24h is between 27 and 38 % for catalysts **1**-**3**. Therefore, there must be an additional factor, other than solubility and water content, contributing to the final epoxide content of the reaction mixture.

This additional factor is spotted when considering the RTILs not as necessarily "innocent" solvents.[9] While the epoxide content increases in the $[BMIM]PF_6$-containing systems during the early stages of the reaction, its eventual disappearance becomes obvious as the reaction progresses. Analysis of the reaction mixture shows the concomitant formation of diol. This diol formation cannot, however, be only or mainly due to the presence of water. With a large excess of water the catalyst would decompose to a significant degree. An experiment performed with the catalysts **1**, **3** and **5** and the RTIL $[BMIM]PF_6$, in which the reaction vessel was initially charged with cyclooctene epoxide instead of cyclooctene, showed that after the first hour of reaction the amount of epoxide started to decrease and 3 hours is completely absent (Figur 3). 1,2-cyclooctanediol is the only product formed. Furthermore, in the $[BMIM]BF_4$-containing system no significant diol formation is observed. Additionally,

the Cp'Mo(CO)$_3$X-derived catalyst systems are known to display generally a high selectivity towards epoxide formation, due to their comparatively low Lewis acidity. Both MoO_2X_2 and MTO containing epoxidation catalyst systems require the presence of Lewis bases to avoid epoxide ring opening reactions.[2,10] In the [BMIM]PF_6-containing systems, however, the formation of HF can be observed (^{19}F-NMR evidence) due to slow degradation of the RTIL under the applied conditions. HF, being a Lewis acid, promotes the epoxide ring opening in the presence of water. In order to confirm the influence of HF, formed from the PF_6^- counter ion, another RTIL containing this anion was applied, namely [C_8MIM]PF_6. The formation of diols from the epoxide was again observed during the course of the reaction. Due to the (generally) lower water content of this solvent,[7a] the initial catalytic activity is somewhat higher than that observed in the [BMIM]PF_6-containing system.

Table 2. Catalytic results for compounds **3** and **4** with [BMIM]NTf_2-containing systems under nitrogen with dry [BMIM]NTf_2. The black columns stand for the yield after 4h, the white columns for the yield after 24 h.

Solvent	TOF[a](mol/mol*h)[a]			Epoxide yield (%) After 4 h			Epoxide yield (%) After 24 h		
	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)
No solvent	820	960	270	100	100	68	100	100	100
[BMIM]PF_6	316	528	144	20	5.6	27	0	0	0
[BMIM]NTf_2	33	46	24	43	58	28	100	100	83
[BMIM]BF_4	14	15	10	8	7	6	38	31	27

[a] Determined after 5 minutes of reaction

In order to reduce the influence of water, compound **3**, being overall the most active of the examined catalysts, and its Cp* derivative **4** were examined in dried [BMIM]NTf_2. This RTIL does not display the HF-formation problem.[9] Interestingly, the dried [BMIM]NTf_2 seems to enhance the catalyst solubility, since a clear yellow solution is obtained. The initial TOF is

considerably higher than in the system with a higher water content and a lower catalyst solubility (Table 2). Even the generally considerably less active catalyst[1a] derived from compound **4** shows a good catalytic performance in a dryer RTIL (Table 2). The reactions performed with compound **3** were repeated with its isolated reaction product with TBHP, $CpMoO_2Cl$ (**5**), leading to the same results within the measurement errors.

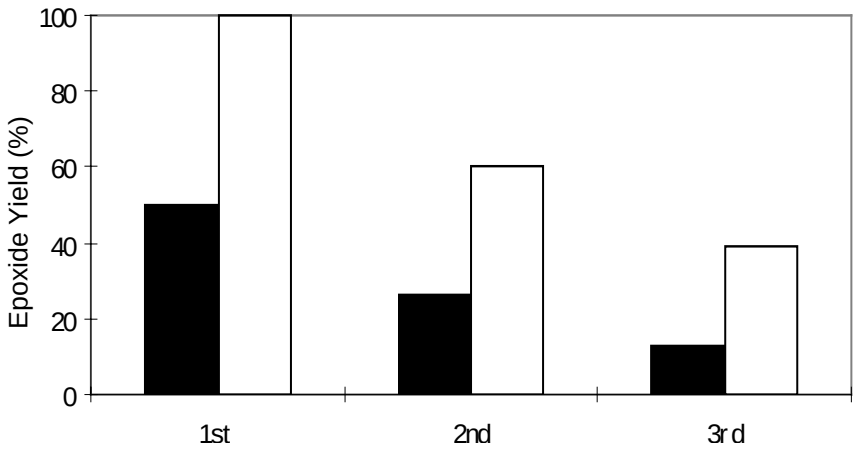

Figure 4 Epoxide yield for the first, second and third run after 4h (black) and 24h (white) reaction time in the presence of $CpMo(CO)_3Me$ (**1**) and using $[BMIM]NTf_2$ as solvent

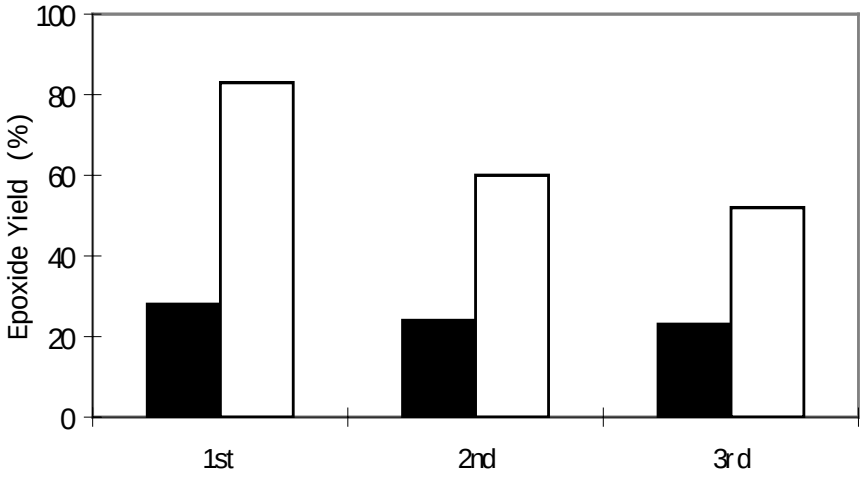

Figure 5 Epoxide yield for the first, second and third run after 4h (black) and 24h (white) reaction time in the presence of $Cp^*Mo(CO)_3Me$ (**2**) and using $[BMIM]NTf_2$ as solvent

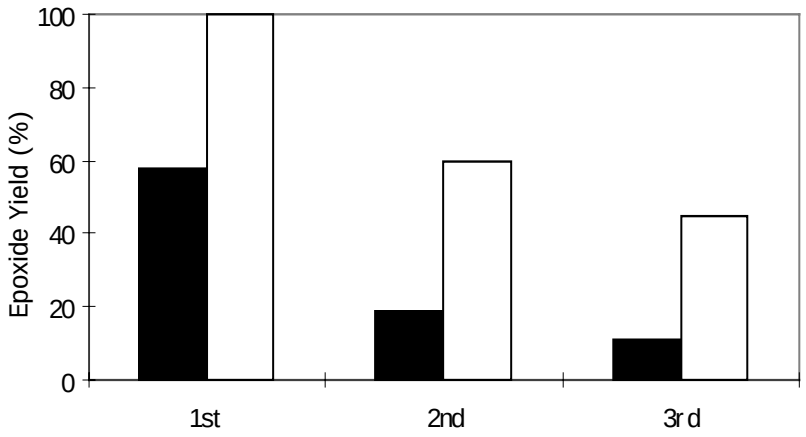

Figure 6 Epoxide yield for the first, second and third run after 4h (black) and 24h (white) reaction time in the presence of $CpMo(CO)_3Cl$ (**3**) and using $[BMIM]NTf_2$ as solvent

In summary, for all the examined catalysts in this study, the best results for olefin epoxidation were achieved using the RTIL $[BMIM]NTf_2$ as co-solvent, which is in accordance with the previous results obtained by Valente *et al*. using the isoelectronic complexes $MoX_2O_2L_2$ (X = Cl, Me; L = Lewis base) in RTILs for olefin epoxidation.[6] These results prompted us to perform some recycling experiments. The systems containing $[BMIM]NTf_2$ can be reused in further catalytic cycles. However, some catalytic activity is lost between the 1st and 2nd runs, probably due to loss of catalyst during the recycling process (see Exp. Part and Figure 4-6). This is common for both the water equilibrated and the dried systems.

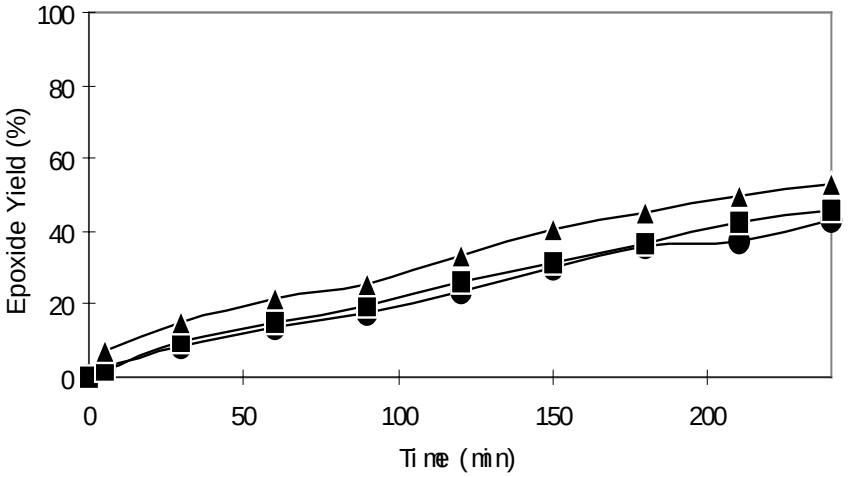

Figure 7 Kinetics of cyclooctene epoxidation in the presence of the complex $CpMo(CO)_3Me$ (**1**) using $[BMIM]NTf_2$ (circles) or the mixture of $[BMIM]NTf_2$ and $[BMIM]PF_6$ with volume ratio (4:1) (squares) or (3:2) (triangles) as co-solvent

In order to optimize our systems under the easiest possible conditions (not dried RTIL, laboratory atmosphere), we tried to combine the advantages of the [BMIM]PF_6 and [BMIM]NTf_2 systems. Although [BMIM]PF_6 promotes ring opening, it was hoped that its presence in small amounts would improve the solubility of the catalysts. Using complex **1** in a 4:1 volume ratio of [BMIM]NTf_2 and [BMIM]PF_6, the reaction proceeds with comparable epoxide yields after 4 and 24 h to that obtained in pure [BMIM]NTf_2 during the first run, thus maintaining the selectivity to the epoxide. The catalyst in the ionic liquid phase can be recovered without significant mass loss and can be reused three times *without any loss of activity*. This result additionally rules out the possibility that the lower catalytic activity of the catalysts in not dried [BMIM]NTf_2-containing systems results from catalyst decomposition. When a mixture of [BMIM]NTf_2 and [BMIM]PF_6 with a volume ratio of 3 : 2 is used as co-solvent, the epoxide yield reaches 53 % with 100 % selectivity after 4 hours reaction. However, after 24 hours, the epoxide yield decreases to 28 % (see Figur 7). In mixtures containing higher amounts of [BMIM]PF_6, the epoxide ring-opening reaction is again preferred, probably due to the higher HF concentration. It should be pointed out in this context, that desirable properties of RTILs can be obtained by simple mixing of different ionic liquids. This opens an additional huge variety of possibilities to modify their behaviour and applications.

6.4. Experimental Section

6.4.1. Synthesis and characterization

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately (THF) or kept over 4 Å molecular sieves. Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets. ^{1}H-, ^{13}C- NMR spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Mass spectra were

obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit HP 3396 Series II. GC-MS spectra were obtained on a Hewlett-Packard 6890 Series GC System and Hewlett-Packard 5973 Series Mass Selective Detector.

The RTILs [BMIM]PF_6, [C_8MIM]PF_6, [BMIM]NTf_2 and [BMIM]BF_4 were prepared and purified as described in the literature.[7] $CpMo(CO)_3Me$ (**1**), $Cp^*Mo(CO)_3Me$ (**2**), $CpMo(CO)_3Cl$ (**3**), $Cp^*Mo(CO)_3Cl$ (**4**), and $CpMoO_2Cl$ (**5**) were prepared according to literature procedures.[1, 8] Their spectroscopic data are in accordance with the data reported previously.

6.4.2. Catalytic reactions with compounds 1-4 as catalysts

All catalytic reactions were performed either under air (if not indicated otherwise) or under dry nitrogen (to exclude moisture) in reaction vessels equipped with a thermostated water bath at 55 ° C. The course of the reactions was monitored by quantitative GC analysis. Samples were taken every 30 min during the first 4 h reaction time, diluted with diethyl ether, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove residual water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of cyclooctene and the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

Cyclooctene epoxidation: In a typical procedure (first run), after stabilization of the temperature of the water bath, the reaction vessel was charged with the catalyst (73 μmol, 1 mol %) and RTIL (0.5 ml) and a clear yellow or orange red solution (in the case of compound **3**) formed. After that, TBHP (2.65 ml, 5.5 M in *n*-decane) was added and the mixture was stirred for 10 min until a colour change occurred, indicating the oxidation of the Mo(II) carbonyl complexes to the corresponding Mo(VI) compounds. With the addition of the substrate, *cis*-cyclooctene (800 mg, 7.3 mmol) and internal standard, mesitylene (1 g), the catalytic reaction was started.

After reacting for 24 h, magnetic stirring was stopped. If the two phases could be easily visually detected, the upper phase was removed from the reaction vessel. If not, 2 ml *n*-hexane were added and the mixture was stirred until two layers could be clearly seen (after allowing the mixture to settle). The upper phase was then removed from the reaction vessel. In both cases, the remaining phase was washed twice with 1 ml aliquots of *n*-hexane and dried at 55 °C. *t*-BuOH is more soluble in the organic phase and can therefore be removed. Additionally, oil pump vacuum allows alternatively the removal of *t*-BuOH from the RTIL phase.

For the second or third runs a new charge of *cis*-cyclooctene (800 mg, 7.3 mmol), mesitylene (1 g, internal standard) and TBHP (2.65 mL, 5.5 M in *n*-decane) were added.

Ring opening reaction of cyclooctene epoxide: compounds **1-5** as catalysts (73 μmol, 1 mol %) and 0.5 ml [BMIM]PF_6 or [BMIM]BF_4 were added to the reaction vessel at 55° C and TBHP (2.65 ml, 5.5 M in *n*-decane) was added. The mixture was stirred until a colour change was observed, then cyclooctene epoxide (920 mg, 7.3 mmol) as substrate and mesitylene (1 g) as internal standard were added.

6.5. Conclusions

For all examined catalysts, the best epoxide yields are obtained for [BMIM]NTf_2-containing systems. Higher amounts of water in the RTIL generally lead to negative effects. Catalyst decomposition, reduced solubility and diol formation may occur depending on the ionic liquid used. These negative effects, however, are counterbalanced by the possibility of complete catalyst recycling, if a mixture of [BMIM]NTf_2 and [BMIM]PF_6 in a volume ratio of 4 : 1 (even with not dried RTILs) is used. Increasing the applied amount of [BMIM]PF_6, however, pushes the reaction towards diol formation, which is the only reaction product in systems containing only [BMIM]PF_6 as the RTIL. Further work to optimize the promising RTIL-containing systems for catalytic epoxidation of other olefins and to reveal more details of the different factors influencing the activities is currently under way in our laboratories.

6.6. References

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7.Heterogenisation of $CpMo(CO)_3Cl$ on mesoporous materials and its application as olefin epoxidation catalyst

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A. Sakthivel, J. Zhao, M. Hanzlik , F. E. Kühn
Dalton Trans., **2004**, 3338-3341

7.1. Abstract

$CpMo(CO)_3Cl$ reacts with the hydroxyl (Si-OH or Si-OH-Al) functionalities of mesoporous molecular sieves such as MCM-41, MCM-48 and its aluminium analogues during grafting. XRD, N_2 adsorption-desorption, BET surface area analysis and TEM show the resulting samples being well ordered and maintaining a uniform pore size. FT-IR spectra, element analysis, and ^{29}Si CP MAS NMR confirm the successful grafting. In the presence of excess TBHP the materials show high activity in cyclooctene epoxidation and good stability.

7.2. Introduction

Molybdenum(VI) complexes are versatile catalysts for the oxidation of organic substrates.[1] Molybdenum based heterogeneous catalysts are applied for the industrial epoxidation of propylene with *t*-butyl hydroperoxide (TBHP) since the late 1960ies.[2] Since then a lot of work has been dedicated to the understanding of the involved catalytic reactions in order to reach better yields and higher selectivities.[3]

Different approaches have been used in order to obtain heterogeneous molybdenum catalysts for olefin epoxidation. A general problem is, that Mo(VI) can not easily be incorporated into the tetrahedral positions of the silicate framework of molecular sieves.[4] Polymer supported Mo(VI) complexes have been reported to be active and recyclable catalysts for olefin epoxidation with TBHP[5]. However, in the latter case problems during the catalytic reactions

such as swelling or leaching of the active species in the organic solution phase are common. Another strategy for the confinement of metal centres in mesoporous silicates is the covalent attachment of organometallic or coordination compounds to form a hybrid material.[6] Recently modified MCM-41 and MCM-48 was synthesized by grafting MoO_2X_2 (X = Cl, Br), which are efficient epoxidation catalysts in homogeneous phase[7] to its surface. Additionally, surface-fixed bidentate Lewis bases have been used to bind Mo(VI) complexes, which are active catalysts in homogeneous phase as described by Gonçalves et al.[8] and Thiel et al.[9] Further silylation using Me_3SiCl to remove residual Si-OH groups was favourable for the catalytic reaction due to the increased hydrophobicity of the surface.[9]

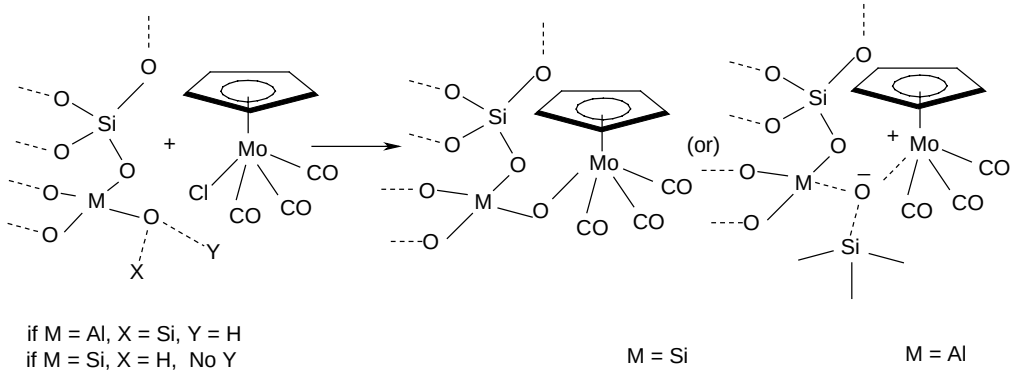
In our previous work, it was found that cyclopentadienyl molybdenum complexes of formula $Cp'MoO_2Cl$ are very efficient homogeneous catalysts for epoxidation of alkenes with TBHP being the oxidizing agent.[10] Furthermore, it became cleair that the utilization of their carbonyl precursor complexes of formula $CpMo(CO)_3Cl$ is equally efficient, since they are oxidized by TBHP to their dioxo congeners and can be stored for long time without any problems (the oxides are somewhat more sensitive).[10] In this work we describe the $CpMo(CO)_3Cl$ complexes being turned into "surface organometallic catalysts" by fixing them to MCM-41, MCM-48 and their aluminium substituted samples.

7.3. Results and Discussion

7.3.1. Synthesis and Textural Characterization

The compound $CpMo(CO)_3Cl$ (**1**) was prepared as described before and its spectroscopic data are in full agreement with the literature data.[10] Complex **1** was grafted through the reaction of the chloro ligand with the hydroxyl group of mesoporous molecular sieves (see Scheme 1). The powder XRD pattern of the parent calcined MCM-41 and MCM-48 are in full agreement with reported pattern, indicating the samples to be well ordered (Fig. 1).[11, 12] Several distinct Bragg peaks are observed in the $2\theta = 2\text{-}8^{\circ}$, which can be indexed to different hkl reflections for a hexagonal unit cell (using the strongest reflection, d_{100}) and a cubic unit cell (using the

strongest reflection, d_{211}) respectively. Upon grafting complex **1** (Fig. 1) the higher 2θ peaks are still observed, indicating the retention of long-range hexagonal and cubic symmetry.



Scheme 1

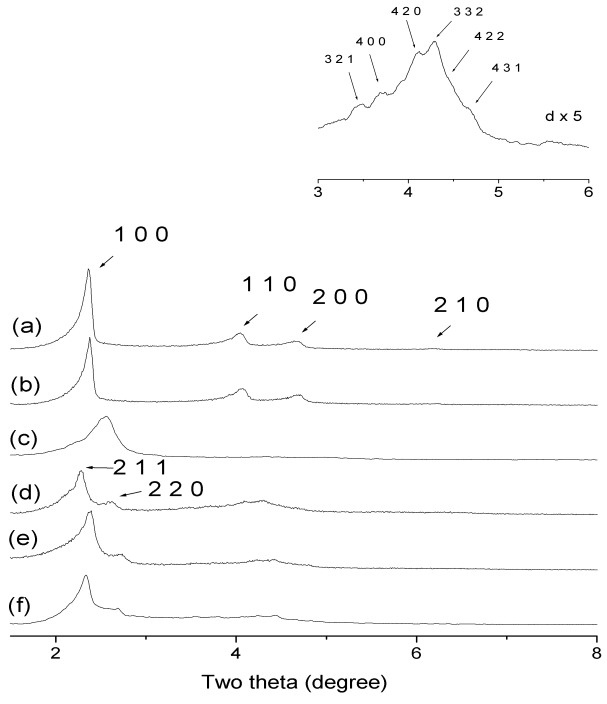


Fig. 1. Powder X-ray diffraction pattern of (a) MCM-41, (b) SM-41-G, (c) AM-41-G, (d) MCM-48, (e) SM-48-G and (f) AM-48-G (insert: enlarged diffraction pattern of (d)).

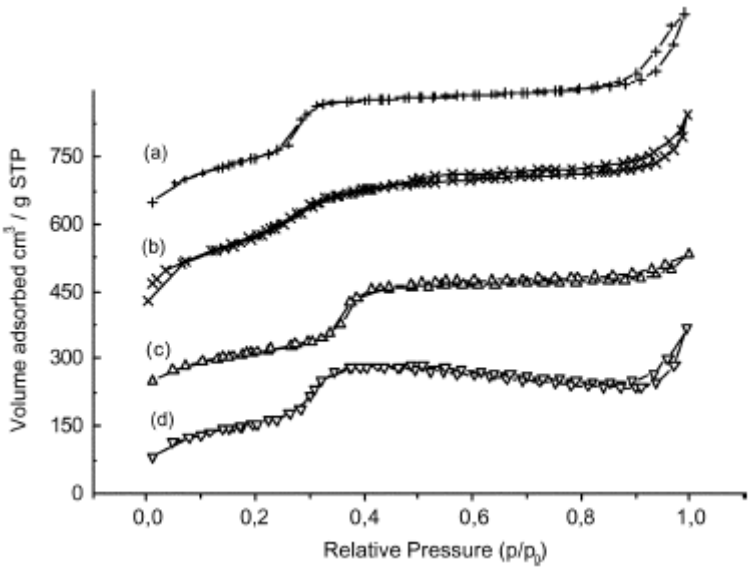


Fig. 2. N_2 adsorption/desorption isotherms of (a) SM-41G (b) AM-48G (c) SM-48G (d) AM-48G.

Table 1. Textural properties of the MCM-41/MCM-48 and the grafted samples.

Sample	Mo wt. %	Interplane distance (nm)[a]	Unit cell parameter ā (nm)[b]	BET surface area (m^2g^{-1})	Pore diameter (nm)
MCM-41	__	3.80	4.39	839	2.74
SM-41G	0.8	3.74	4.31	769	2.57
AM-41G	1.29	3.74	4.02	708.8	2.55
MCM-48	__	3.97	9.72	1043	2.41
SM-48G	0.9	3.48	9.16	993.5	2.31
AM-48G	1.62	3.78	9.25	565.3	2.41

a: d_{100} for MCM-41 and d_{211} for MCM-48.
b: $\bar{a} = 2d_{100}/\sqrt{3}$ for MCM-41; $\bar{a} = d_{hkl}(h^2+k^2+l^2)^{1/2}$ for MCM-48.

The low temperature N_2 adsorption/desorption isotherms of parent MCM-41 and MCM-48 (Fig. 2) are of type IV according to the IUPAC[13] and characteristic for mesoporous solids. A well-defined, sharp inflection is observed between the relative pressure (p/p_o) of 0.3-0.4, due to capillary condensation of nitrogen inside the primary mesopores. Reversible type (IV) isotherms similar to the parent MCM-41/MCM-48 were obtained for the samples grafted with complex **1**. The calculated textural parameters using XRD and adorption/desorption isotherms are summarized in Table 1.

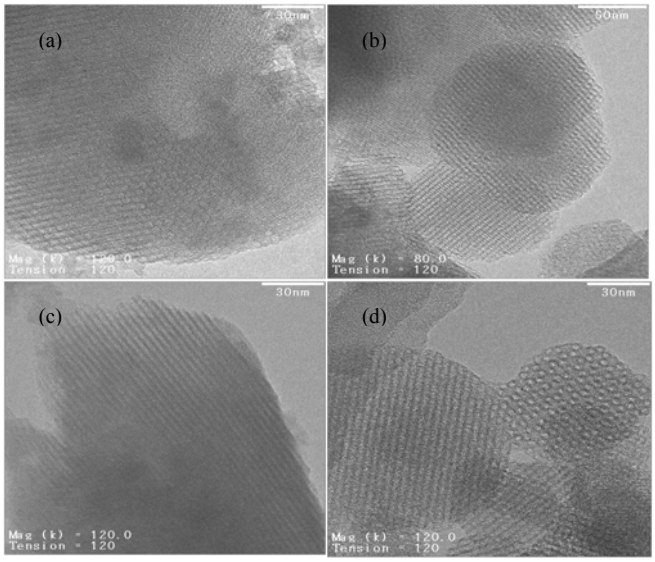


Fig. 3. TEM images of (a) MCM-41, (b) MCM-48, (c) AM-41G and (d) AM-48G.

The grafted materials show a decrease in the unit cell value (ā), surface area and pore size. The decrease in surface area and pore size can be attributed to grafting of bulky complexes on the internal surface of the mesoporous materials.[8] The TEM image analysis of the parent MCM-41, MCM-48 and the grafted samples (Fig. 3) are providing strong evidence that the mesoporous structure of the support retains long range ordering[11] throughout the grafting process and that the channels remain accessible. Elemental analyses (EA) indicate (Table 1) that aluminium containing MCM-41/48 show a higher Mo content (1.3-1.6 wt.%) than siliceous MCM-41/48 (0.8-0.9 wt. %). The presence of more Mo in the aluminium containing

mesoporous samples compared to siliceous samples is attributed to a stronger interaction of the grafted molecules with the Al containing surface as shown in Scheme 1. EA further confirm no detectable amounts of Cl, supporting the anchoring mode suggested in Scheme 1 and the absence of free $CpMo(CO)_3Cl$.

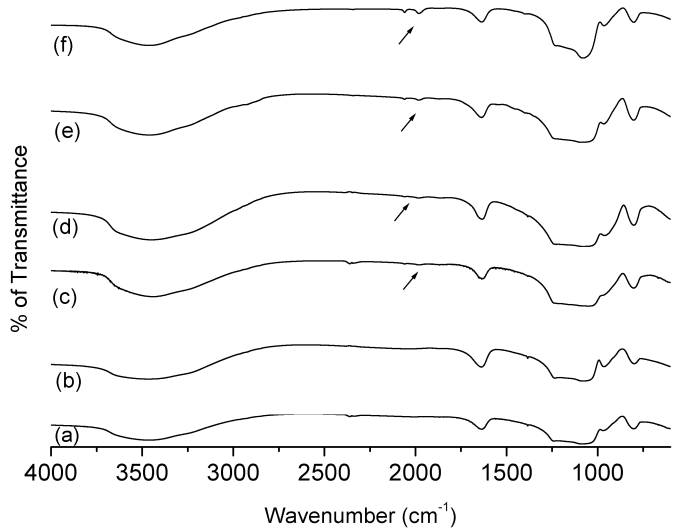


Fig. 4. FT-IR spectra of (a) MCM-41, (b) MCM-48, (c) SM-41-G, (d) SM-48-G, (e) AM-41-G and (f) AM-48-G.

Fig. 4 depicts the FT-IR spectra of parent calcined mesoporous MCM-41/48 and grafted samples. The bands at 1206, 1060, 794 cm^{-1} are attributed to stretching vibrations of the mesoporous framework (Si-O-Si). The band around 960 cm^{-1} is assigned to a vibration mode of the silanol (Si-OH) groups present in the mesoporous channels.[11, 12] The grafted samples show (Fig. 4c-4f) a slight decrease in the relative intensity of the silanol (Si-OH) band. New bands around 2016 and 1956 cm^{-1} can be assigned to terminal carbonyl (CO) group vibrations of the grafted compound **1**. This is clearly shown in the subtracted spectrum of grafted sample from the parent samples (Fig. 5). Further additional bonds appeared in the range of 2949 and 2853 cm^{-1} due to C-H stretching vibrations of Cp ligand. The intensities of these new bands are stronger in the case of aluminium containing samples in comparison to the siliceous MCM-41 and MCM-48 molecular samples. These observations are in agreement with the EA-

results, showing that the amount of surface fixed complex **1** is significantly higher in the case of H-AlMCM-41/48 as carrier material. In addition another absorbtion band around 460 cm^{-1} which is characteristic of bending vibration of Si-O-T bond (where T = Mo). [12]

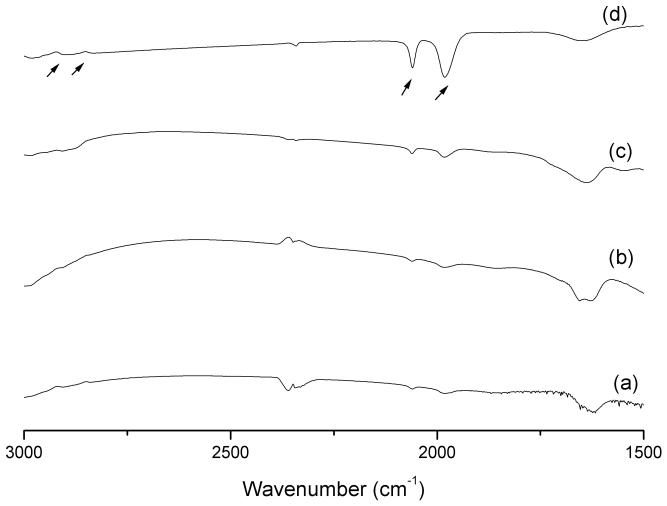


Fig. 5. Subtracted FT-IR spectra of (a) SM-41-G, (b) SM-48-G, (c) AM-41-G and (d) AM-48-G.

Solid-state ^{29}Si CP MAS NMR on grafted samples show reduction of the Q_2 and Q_3 resonances, and a concomitant increase of the Q_4 resonance compared to the parent mesoporous samples, supporting the successful grafting of complex **1**. The ^{13}C CP MAS NMR spectrum of grafted samples show a peak at δ = 113.7 ppm attributed to cyclopentadienyl group, which further support the successful grafting of compound **1** on mesoporous materials.

7.3.2. Catalytic Applications

The oxidation of cyclooctene in the presence of grafted samples, yields cyclooctene epoxide as the only product. Without Mo catalyst being present the reaction does not take place. Upon treatment with TBHP the carbonyl vibrations disappear. In the subtracted spectrum the appearance of Mo=O and Mo-O-O vibrations is detect around 910 and 841 cm^{-1}.

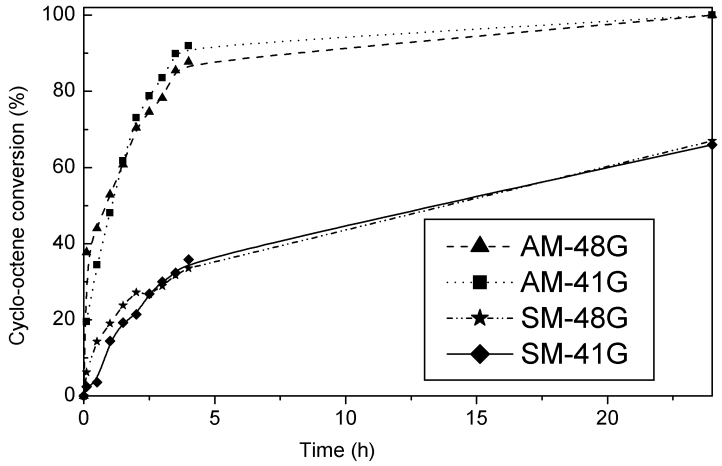


Fig. 6. Kinetic profile for the epoxidation of cyclooctene with $CpMo(CO)_3Cl$ grafted on various mesoporous molecular sieves.

The kinetic profile of the epoxidation reaction with all four examined samples shows a high initial reaction velocity (Fig. 6) Turnover frequencies of > 4000 1/h are reached. These values are in the same order of magnitude than those found previously for the homogeneous catalyst of formula **1**.[10] The reaction velocity slows down during the course of the reaction. This behaviour has been assigned to the interaction of the catalyst with the by-product *tert*-butyl alcohol,[7, 8] which is formed during the course of the reaction from the spent oxidant TBHP.The SM-41G and SM-48G samples lead to about 65-68 % cyclooctene conversion with about 100 % epoxide selectivity after a reaction time of 24 h. The catalysts AM-41G and AM-48G show both 100 % conversion and selectivity. The observed higher yield and activity in case of aluminium containing mesoporous molecular sieves may be due to the higher Lewis activity of the Mo in this system or to the activation of TBHP by the Al sites.[9] After one reaction run (24 h), the catalyst is washed several times with dichloromethane to remove the physisorbed molecules and reused. In order to avoid destruction of Mo complex, all the (chemisorbed organic) cokes are not removed by additional calcination at 823 K. The catalysts are found to be quite active even after four catalytic runs. However, the catalytic activities decrease in all examined cases to about two thirds of the original activities after four runs. The observed activity decrease may be - at least partially - due to an increasing amount

of chemisorbed organic molecules on the surface of the materials. Leaching seems to be less severe than in some of the previously examined cases [8]. In-order to confirm the above the filtrate experiments were carried out on all four fresh and first run catalysts under the reaction temperature. The results are summarized in Table 2. The filtrate of fresh catalysts showed about 10-13 % conversion confirms the leaching of active Mo species is less severe [8]. Further, the filtrate solution of recycle catalysts showed no appreciable conversion (less than 3 %). The above results indicates, that there is small amount of leaching was observed initially due to weakly bonded Mo on the surface. However, after one cycles the remaining Mo retain on surface even after several recycle experiments.

Table 2. Filtrate experiments on grafted samples .

Samples	Conversion (%)	
	Filtrate solution of on fresh catalysts	Filtrate solution of on 1st run catalysts
SM-41G[a]	11.8	2.3
AM-41G[b]	10.4	3.4
SM-48G[a]	13.1	3.9
AM-48G[b]	8.7	3.1

a: Filtrate experiments carried out after 3 h.
b: Filtrate experiments carried out after 2 h.

7.4. Experimental Section

7.4.1. Synthetic Procedures

Mesoporous molecular sieves and its aluminium analogues are synthesized following the procedures described earlier[12] with a molar gel compositions of SiO_2 : 0.2NaOH : 0.27 TMAOH : 0.27CTABr : 60 H_2O : x Al_2O_3 (x = 0 and 0.05) for MCM-41, 5.0SiO_2 : 2.5NaOH : 0.87CTABr : 0.13Brij30 : 400 H_2O : x Al_2O_3 (x = 0 and 0.025) for MCM-48 respectively. Solvents were dried by standard procedures (THF, with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under argon and kept over 4 A ° molecular sieves. $CpMo(CO)_3Cl$ was synthesized by a literature procedure.[10]

7.4.2. Grafting and Characterization Methods

Grafting experiments were carried out using standard Schlenk techniques under argon atmosphere with the following procedure: First the mesoporous molecular sieves MCM-41/48 and its aluminum analogues are pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove physisorbed water. The activated sample is treated with 0.9 mmol of $CpMo(CO)_3Cl$ in 30 ml dry dichloromethane under argon atmosphere. The mixture is stirred at 313 K for 24 h. The resulting solution is filtered off and the resulting pale orange solid is washed repeatedly with CH_2Cl_2 until all physisorbed $CpMo(CO)_3Cl$ is removed from the surface. The washed samples are dried under vacuum at RT. The samples prepared from SiMCM-41, HAlMCM-41, SiMCM-48 and HAlMCM-48 are designated as SM-41G, AM-41G, SM-48G and AM-48G, respectively.

The parent MCM-41, MCM-48, and grafted samples were systematically characterized by various analytical and spectroscopic techniques.Microanalyses were performed at the Mikroanalytisches Laboratorium of the Technische Universität München (M. Barth and co-workers). IR spectra were measured with a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Powder XRD data were collected with a Phillips X'pert diffractometer using Cu-Kα radiation filtered by Ni. Nitrogen adsorption-desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Prior to analysis, calcined MCM-41/48 was degassed at 723 K overnight at a residual pressure of ca. 10-24 mbar. A lower degassing temperature of 413 K was used for the modified materials (to minimize destruction of the Grafted complex). The specific surface areas *(*SBET) were determined by the BET method. The total pore volume *(*VP) was estimated from the N_2 uptake at p/p_0 = 0.95, using the liquid nitrogen density of 0.8081 gcm^{-3}. The pore size distribution curves (PSD, the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron micrograph (TEM) was recorded on a Philips CM 200 microscope operated at 160 kV. ^{29}Si

CP MAS NMR spectra were recorded at 79.49 MHz, with a (9.4 T) Bruker MSL 400P spectrometer, with 5.5 μs ^{1}H 90º pulses, 8 ms contact time, a spinning rate of 4.5 kHz and 4 s recycle delays. ^{13}C CP MAS NMR spectra were recorded with a 4.5 μs^{1} H 90º pulses, 2 ms contact time, a spinning rate of 8 kHz and 4 s recycle delays.

7.4.3. Catalytic reactions

The catalytic behaviour of the grafted samples (175 mg) was tested by examining the oxidation of cyclooctene (0.8020g; 8 mmol) at 328 K in a liquid phase batch reactor with TBHP (5.5 M in decane; 16 mmol) as the oxidizing agent. A catalyst : oxidant : substrate ratio of 0.0063 : 2 : 1 was used. The samples were analyzed every 30 min. for 4 h and the reaction was terminated after 24 h. The analyses were carried out using a gas chromatograph (HP 5890) equipped with a capillary column (Chiraldex G-BP) and using FID detector.

7.5. Conclusions

In summary, successful grafting of $CpMo(CO)_3Cl$ on mesoporous molecular sieves is achieved without significant loss of ordering. The grafted samples are active and highly selective epoxidation catalysts. The aluminium analogues of the mesoporous materials display both higher complex loadings and higher catalytic activity. Catalyst leaching seems not to be a pronounced problem and the catalysts can be reused several times before significant activity losses occurs.

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8. Cyclopentadienyl-Molybdenum Complexes with a Siloxane Functional Group as Models for Efficient Heterogeneous Epoxidation Catalysts

This chapter originated the following publication:

J. Zhao, A. Sakthivel, A. M. Santos, F. E. Kühn

Inorg. Chim. Acta, Accepted

8.1. Abstract

A series of compounds of the type $CpMoR(CO)_3$ and $RCpMo(CO)_3CH_3$ (R = $(CH_2)_3Si(OMe)_3$ or $CH_2Si(OEt)_3$), containing a $(CH_2)_n$ $Si(OR)_3$ functionality as a side chain, either fixed to the metal itself or to the cyclopentadienyl ligand are prepared and spectroscopically characterized. These molecules are applicable as precursors for both homogeneous and heterogeneous phase catalysts. Their homogeneous catalytic activity in the olefin epoxidation is in the same order of magnitude as that of their methyl and chloro analogues of the types $CpMo(CO)_3R$ and $CpMo(CO)_3Cl$.

8.2. Introduction

Several Molybdenum complexes are versatile catalysts for the oxidation of organic substrates and therefore of significant current interest.[1-7] Molybdenum based catalysts are applied for the industrial epoxidation of propylene with *t*-butyl hydroperoxide (TBHP) since the late 1960ies.[8,9] Considerable efforts were dedicated in the following decades to the understanding of the involved catalytic reactions in order to reach even better yields and selectivities. [10-13]

As mentioned in the chapter 5, $Cp'Mo(CO)_3Cl$ (Cp' = Cp or ring substituted Cp derivatives) can be used as olefin epoxidation catalyst precursors – being *in situ* oxidized to the Mo(VI) compounds of formulae $Cp'MoO_2Cl$ and $Cp'MoO(O_2)Cl$ - and present advantages over the

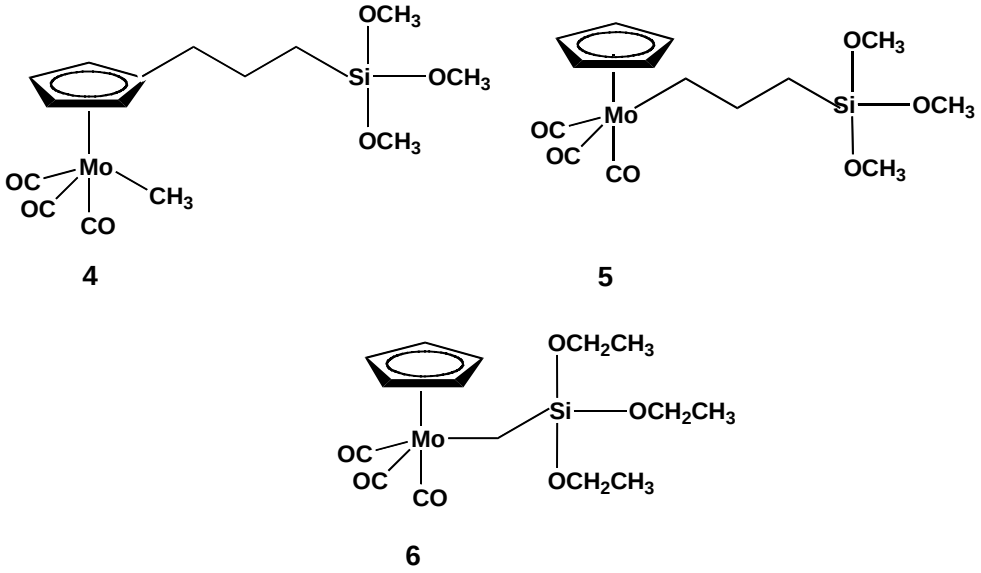
direct application of the Mo(VI) species Cp'MoO_2Cl.[14] Furthermore, Cp'$Mo(CO)_3R$ (R = alkyl, or *ansa*-alkyl) complexes have also been described as homogeneous epoxidation catalyst precursors, showing a comparable catalytic activity to their chloro-analogues.[15,16] This type of complexes surpass in their catalytic activity most other Mo(VI)-dioxo complexes (e. g. of the composition $MoX_2O_2L_2$ (X = Cl, Br, Me; L = Lewis base [17-21])) significantly and rival even the very active and well examined Re(VII) epoxidation catalyst methyltrioxorhenium (MTO) [22-24]. The by-product of the oxidation of olefins with TBHP in the presence of Mo(VI) dioxo complexes, *t*-BuOH, however, hampers the catalytic reaction with increasing concentration.[14,15,17-21] Heterogenization of the catalyst, or two-phase homogeneous catalysis are promising ways to avoid high amounts of *t*-BuOH in the same phase as the catalyst after several catalytic runs.

The "heterogenisation" of homogeneous epoxidation transition metal catalysts has received considerable attention in recent years since such heterogenized homogeneous catalysts ("surface organometallic catalysts") may combine the most advantageous properties of both homogeneous and heterogeneous systems.[25-27] One possibility to link homogeneous catalysts to surfaces is to synthesize organometallic complexes with a siloxane functional group either directly attached to the metal centre or to a ligand e. g. the cyclopentadienyl moiety. Such a functionalisation often results in considerable kinetic stabilization of the modified complexes.[28-31]

Among the approaches to heterogenize MoO_2-units containing catalysts or their precursors (containing a $Mo(CO)_3$ moiety) is the use of surface fixed N-donor ligands (Lewis base ligands) coordinating to the MoO_2-moieties as described by Thiel *et al.*[32-35] and, independently, by Gonçalves *et al.*[36-40] Other possibilities are the direct grafting of a $CpMo(CO)_3Cl$ unit to the surface as $CpMo(CO)_3$-SiO_3 with successive oxidation to the Mo(VI) congener,[41] and the application of a C(O)OH ligand, attached to the Cp moiety to act as a connecting unit with a surface fixed H_2N-$(CH_2)_n$-$OSiO_3$ chain, forming a Cp-C(O)-NH-$(CH_2)_n$-SiO_3 moiety.[42] However, the latter - in principle very elegant - approach leads to heterogeneous catalysts, which seem to be considerably less active than the

heterogeneous catalysts derived from simple grafting of $CpMo(CO)_3Cl$ on MCM materials.[41] The "heterogenization" of $CpMo(CO)_3X$ (X = X, CH_3) and $Mo_2X_2O_2$ was also successfully attempted in room temperature ionic liquids.[43,44]

In this work we describe complexes of the type $CpMoR(CO)_3$ and $RCpMo(CO)_3CH_3$ (R = $(CH_2)_3Si(OMe)_3$ or $CH_2Si(OEt)_3$) (Scheme 1). These compounds will be compared to the closely related and well examined complexes of the type $Cp'Mo(CO)_3Cl$ and $Cp'Mo(CO)_3R$ and their oxidation products in order to exploit the application of the newly described compounds as homogeneous catalysts and to draw conclusions on the possibility of using them in a further step as "surface organometallic catalysts" after heterogenization. It is regarded as important to find out whether $Cp'Mo(CO)_3R$ compounds, containing siloxane functional groups are in general considerably less active than compounds of the type $CpMo(CO)_3Me$ or $CpMo(CO)_3Cl$.



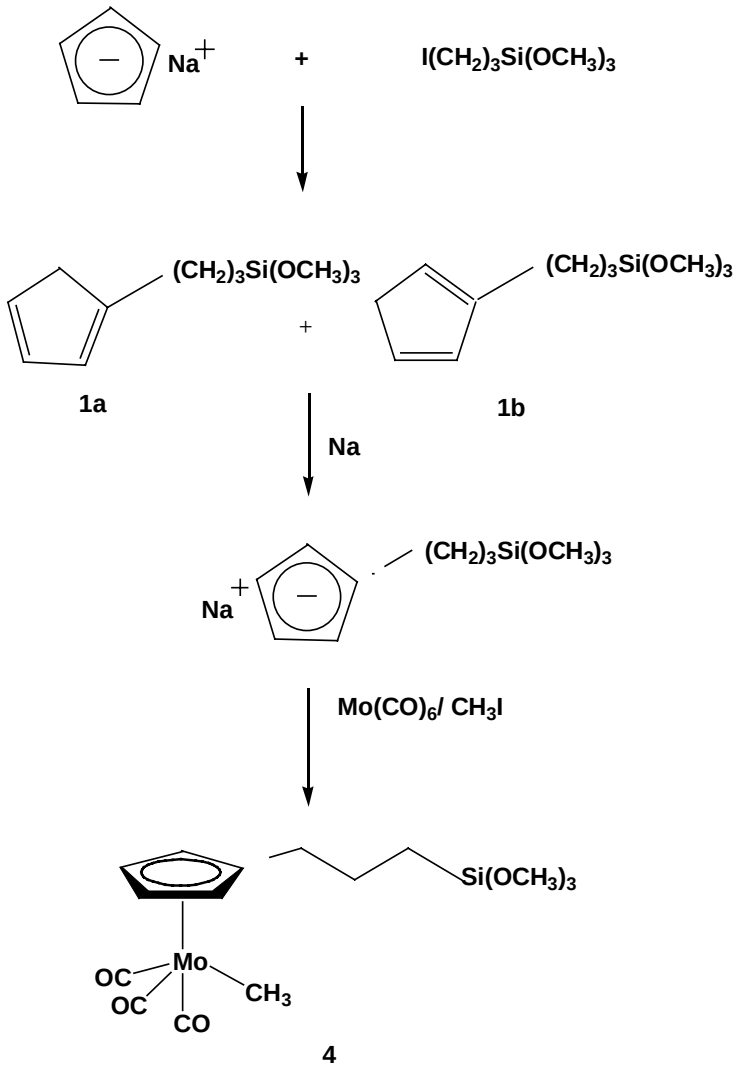
Scheme 1

8.3. Results and Discussion

8.3.1. Syntheses and Characterization.

Complexes **4**-**6** (Scheme 1) are stable at room temperature, can be handled in laboratory

atmosphere and kept under air for some hours without detectable reaction or change.



Scheme 2

Compound **4** was obtained through the procedure shown in scheme 1 in ca. 80 % yield (based on $Mo(CO)_6$). Compounds **5** and **6** were obtained as brownish yellow oils by stirring the salt of the anions $[\eta^5\text{-}C_5H_5Mo(CO)_3]^-$ with **2** or **3** in THF at room temperature, respectively. In contrast to their iron analogues,[30,31] when (3-chloropropyl)trimethoxysilane or (chloromethyl)triethoxysilane was used as starting material, the alkoxy silane group could not be attached as a ligand to the Mo centre. Compound **5** is obtained in higher yield (more than 80%) than compound **6**, where a significant amount of red by-product formed, presumably a dimer. After long time storage (months) under argon atmosphere, the colour of the complexes

changes slowly to deep brownish, and dark, insoluble, difficult to characterize solids precipitate. These can be removed from the desired complexes by filtration with Florisil.

The composition and spectroscopic data of compounds **4**-**6** were determined by EA, IR-, and NMR-spectroscopy (^{1}H, ^{13}C, ^{95}Mo, ^{29}Si) as well as mass spectroscopy (MS).

Table 1: ^{1}H-NMR data of compounds **1**-**6** (δ (ppm), $CDCl_3$)

Compound	Cp	CH_2	$-CH_2-$	CH_2-Si	OCH_3
$Cp(CH_2)_3Si(OMe)_3$ (**1a** and **b**)	2.85,2.92, 5.99, 6.14, 6.23, 6.39	2.39	1.64	0.67	3.54
$C_5(CH_2)_3Si(OCH_3)_3H_4Mo(CO)_3CH_3$(**4**)	5.12, 5.13	2.21	1.54	0.65	3.53
$I(CH_2)_3Si(OMe)_3$ (**2**)	-	3.18	1.89	0.71	3.53
$C_5H_5Mo(CO)_3(CH_2)_3Si(OCH_3)_3$ (**5**)	5.26	1.63	1.63	0.77	3.55
	Cp	CH_2-Si	OCH_2	CH_3	
$ICH_2Si(OEt)_3$ (**3**)	-	1.94	3.86	1.23	
$C_5H_5Mo(CO)_3CH_2Si(OCH_2CH_3)_3$ (**6**)	5.41	-0.41	3.80	1.21	

The ^{1}H-NMR spectrum indicates that the precursor compound **1** exists in solution in two isomeric forms (**1a** and **1b**, Scheme 2). After deprotonation by sodium and coordination to the Mo atom, the presence of the substituent in the Cp ring leads to the appearance of two signals corresponding to two different groups of equivalent protons in compound **4**. The chemical shifts of the two CH_2 closest to the Cp ring are weakly shifted to high field by 0,18 ppm and 0,10 ppm, respectively, in comparison to **1**. As usual, in the case of Cp'$Mo(CO)_3R$ (R = alkyl) complexes, in both ^{1}H- and ^{13}C-NMR spectra of **4**, the chemical shift of the methyl group, which coordinates to the Mo center is observed at the most strongly high field shifted position, in this case at 0.29 ppm. Comparing the ^{1}H-NMR chemical shifts of compounds **2** and **5**, the

latter being formed after coordination of ligand **2** to molybdenum, the α-proton signal of the $(CH_2)_n$ chain is significantly shifted to high field from 3.18 ppm in compound **2** to 1.63 ppm in compound **5**. The proton signal of the ß-CH_2 group is shifted by 0.26 ppm due to the strong shielding effect of the Mo atom on the neighboring protons. The same effect can be also observed for the chemical shifts of the α- and ß-protons in compound **6**, where the chemical shift changes from 1.94 ppm in compound **3**, to -0.41 ppm in **6**. Selected ^{1}H-NMR data of compounds **1**-**6** are shown in table 1.

The ^{95}Mo chemical shift is highly sensitive to structural and electronic variations within a series of closely related mononuclear compounds.[45] The series of compounds examined in this work exhibit highly shielded chemical shifts, which can be in general associated with low formal oxidation states. Compounds **4**-**6** display their ^{95}Mo-NMR signal in $CDCl_3$ at -1715, -1693 and –1644 ppm respectively. Comparing the ^{95}Mo-NMR chemical shifts of compounds $CpMo(CO)_3(CH_3)$, $CpMo(CO)_3(C_2H_5)$ [15] and **5** shows that the latter two compounds display a very similar chemical shift (-1685 and –1693 ppm). The influence of the remote $Si(OR)_3$ group is obviously of no significant importance. Both the ethyl and the $(CH_2)_3Si(OR)_3$ ligand, however, give slightly more electron density to the Mo core than the CH_3 ligand in $CpMo(CO)_3(CH_3)$ δ(^{95}Mo = -1729 ppm). In compond **6** the $Si(OR)_3$ group is closer to the Mo center and, as seen from its chemical shift, able to shift more electron density towards the Mo atom. The ^{95}Mo shift of compound **6** (-1644 ppm) is, accordingly, closer to $C_5(CH_3)_4HMo(CO)_3(CH_3)$ (δ(^{95}Mo) = -1628 ppm) than to that of $CpMo(CO)_3(CH_3)$. The ^{95}Mo chemical shift of compound **4**, however, is found in a region to be expected for a $C_5H_4RMo(CO)_3Me$ compound. It has been already described how changing electron density at the Cp' ligand influences the ^{95}Mo shift of such compounds.

Compounds **4**-**6** display their ^{29}Si-NMR signal in $CDCl_3$ at -42.95, -42.02 and -38.71ppm respectively, which are typical shifts for organosilanes of the type $RSi(OR)_3$. For compounds **4** and **5**, having the same substituent, although in one case directly bound to the molybdenum centre and in the other to the Cp ring the chemical shift is almost identical. Comparing the shifts of **5** and **6** it can be seen that the shielding effect of molybdenum has only a

comparatively small effect on the shift of the ^{29}Si signal. The ^{1}H- and ^{13}C- NMR show no significant changes on the chemical shift of the methoxy and ethoxy groups before and after coordination to Mo centre. These ligands are obviously too far away from the Mo core to be significantly influenced.

Compounds **4-6** show their stretching vibration of the CO group as two very strong peaks at ca. 2015 cm^{-1} and ca. 1920 cm^{-1}. The bands corresponding to the other functional groups present can be found in the expected ranges, such as the C-H stretch in the Cp ring at ca. 3010 cm^{-1} and the Si-O stretching at ca. 1080 and 810 cm^{-1}.

8.3.2. Complexes 4-6 in oxidation catalysis

Compounds **4-6** were tested as catalysts for the epoxidation of cyclooctene with TBHP in order to study the effect of the introduction of organosilica functional groups in comparison with other Cp'$Mo(CO)_3R$ (R = alkyl) complexes.

The details concerning the catalytic reaction are given in the experimental part. Blank runs showed that no significant amount of epoxide was formed in the absence of catalyst. A catalyst:oxidant:substrate ratio of 1:200:100 was used in all experiments unless stated otherwise. The compounds **4-6** are first oxidized with TBHP without losing their organic ligands (NMR, IR-evidence). This oxidation can be easily followed *in situ* by UV/Vis spectroscopy. In the visible part of the spectrum a colour change from yellow to pale yellow occurs during the process. The mechanism of this reaction – an oxidative decarbonylation[14,15,46,47] - will be discussed elsewhere in detail.

During the olefin oxidation epoxide is selectively formed, no significant formation of by-products (e.g. diol) is observed. All catalytic reactions show – as expected - similar time-dependent curves, in which the yield increases quickly at the beginning of the reaction (huge substrate excess) and then slows down considerably (substrate much less abundant, diffusion limitations are becoming increasingly important), the curves for $CpMo(CO)_3Cl$ and $CpMo(CO)_3CH_3$ are also shown for comparison (Figure 1). After 24 h all complexes lead to quantitative epoxide yields (Figure 2). Addition of excess *t*-BuOH at the onset or during the

epoxidation reaction reduces the activity of the catalysts considerably. Similar observations have been made for several other Mo catalyzed epoxidation reaction and have been interpreted by the possible coordination of *t*-BuOH to the Mo catalyst.[14,15,17-21]

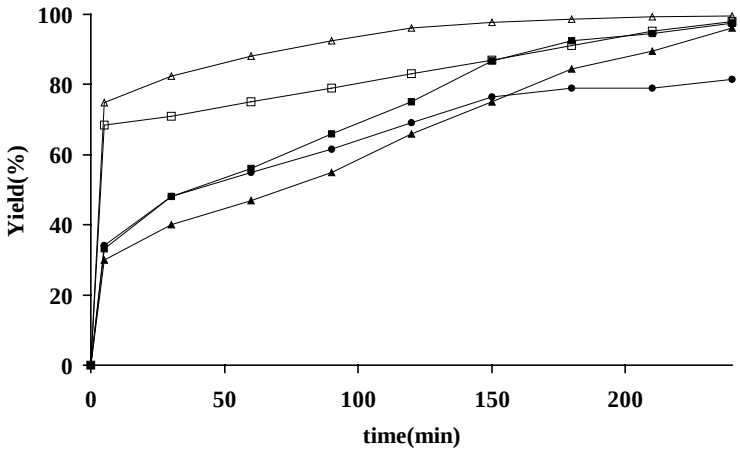


Figure 1. Time dependent yield of cyclooctene epoxide in the presence of compounds **4** (circles), **5** (closed squares), **6** (closed triangles), $CpMo(CO)_3Me$ (open squares) and $CpMo(CO)_3Cl$ (open triangles) as catalysts at 55°C with 1% catalyst charge.

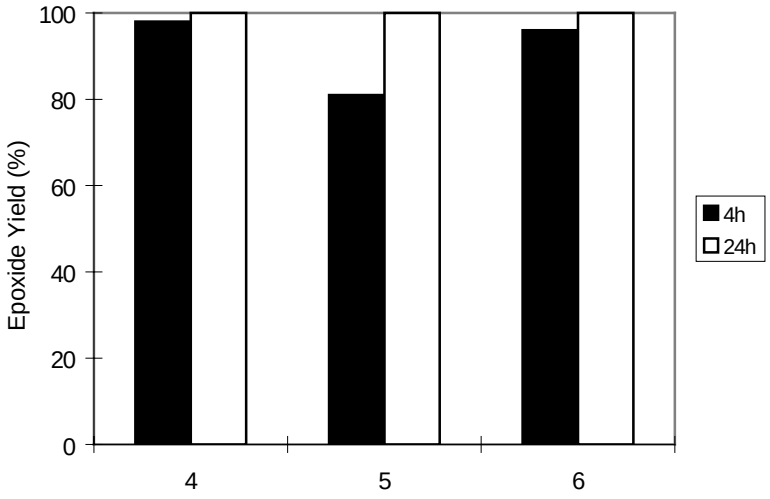


Figure 2. Cyclooctene epoxide yield after 4 (black) and 24h (white) for compounds **4**-**6** (1%) at 55°C.

Compounds **4**-**6** show similar activities in the beginning. The initial turnover frequencies (TOFs) for 1 mol % catalyst after 5 min reaction time are ca. 410 1/h for compound **4**, ca. 400

1/h for compound **5** and ca. 360 1/h for compound **6**. Under the same conditions the TOF for $CpMo(CO)_3Cl$ is ca. 900 1/h and for $CpMo(CO)_3CH_3$ ca. 820 1/h. These differences in the initial TOFs reflect the Lewis acidity at the metal center and are in good accord with the ^{95}Mo NMR results (see above). The most Lewis acidic metal center (compound **4**) is also the most active catalyst when enough substrate is available and a comparatively low amount of competitor (*t*-BuOH) is present. Accordingly, $CpMo(CO)_3CH_3$, being more electron deficient than compounds **4** – **6** shows a higher initial activity, as reflected by its TOF. The same holds for the most active and most electron deficient system examined here, $CpMo(CO)_3Cl$.[14] When the catalytic reaction, however, is followed over a longer period of time, the overall situation changes somewhat. The yield obtained with compounds **5** and **6** is higher after 4 h than that obtained with compound **4**. Compounds **5** and **6**, however, behave rather similar with respect to the increase of their product yield. Compound **6** is a somewhat more sluggish catalyst than compound **5**. This (small) difference probably originates from the slightly lower Lewis acidity of compound **6**, due to the closer proximity of the siloxane group to the molybdenum atom. Compound **4**, being the most active compound on the onset of the reaction falls back behind even compound **6** after ca. 3 h reaction time. A possible explanation for this observation may be the lower steric hindrance of compound **4** around the Mo center. Its steric situation at the Mo atom resembles more that of $CpMo(CO)_3CH_3$ and $CpMo(CO)_3Cl$ than that of compounds **5** and **6**. Accordingly, in a region where less substrate (and more *t*-BuOH) is present, its epoxidation curve form parallels that of $CpMo(CO)_3CH_3$ and $CpMo(CO)_3Cl$ and not that that of catalysts **5** and **6**. This might be due to the fact that the sterically less hindered derivative **4** reacts more easily with *t*-BuOH, blocking the substrate access more efficiently and slowing down the reaction more strongly. In the case of the (at Mo) sterically more hindered compounds **5** and **6** the coordination of *t*-BuOH is hindered more strongly and has accordingly a smaller impact on the catalytic activity. Anyway, after long reaction times (24 h) all catalysts reach quantitative epoxide yields.

It could be also assumed, however, that the similar final epoxide yield of the catalytic reactions with different catalysts is due to the formation of a common catalytic species in all

cases (possibly due to the loss of the organic ligands). For such a decomposition reaction, however, we found no spectroscopic evidence. Full details would be beyond the scope of this work and will be presented elsewhere. One relatively obvious piece of evidence against the decomposition hypothesis, however, is the performance of the catalyst compounds if a second charge of substrate is added to the reaction mixtures after 24 h reaction time. In this case the initial catalytic activities of the different catalyst compounds show again significant differences, paralleling the observations made during the first runs and therefore rendering the possibility of a common catalytic species as quite unlikely.

Additionally, it is interesting to compare the behaviour of a related complex of formula $(C_5H_4(C(=O)\text{-}N(H)\text{-}(CH_2)_3Si(OEt)_3)Mo(CO)_3Cl$ (**7**),[42] which was recently reported by Gonçalves *et al.*, displaying only 1/10 of the initial activity of $CpMo(CO)_3Cl$.[42] The initial activity of complexes **4**-**6** is about half of that of the Cl and CH_3 complexes under the same conditions (see Figure 1). The product yields reached with compound **7** as the catalyst after 4 h reaction time is still significantly lower (35 %) than that of all the compounds described in this work (see also Fig. 1 and Fig. 2).

A catalyst loading of 0.1% was also tested for compound **5** and an initial TOF of ca. 6000 1/h was obtained, demonstrating the high catalytic potential of the synthesized compounds. Furthermore, the catalyst activity is maintained for several catalytic runs (see also above). However, the increasing amount of *t*-BuOH being present reduces the reaction velocity increasingly. Increasingly longer reaction times are necessary to achieve the same product yields. Due to the tiny applied catalyst amounts a re-isolation and cleaning of the catalyst proves to be difficult.

The successful heterogenization and application in heterogeneous catalytic epoxidation of compounds **4**-**6** is discussed elsewhere in full detail.[48] It has to be noted that their catalytic activity after heterogenization on MCM-41/48 is largely maintained (TOFs > 2800 1/h). No significant leaching is observed and a separation of the (heterogenized) catalyst from *t*-BuOH is much easier than in homogeneous phase. However, the long-term activity suffers somewhat from the deposition of organic material in the pores of the carrier.[48]

8.4. Experimental Section

8.4.1. Synthesis and characterization

All preparations and manipulations were performed using standard Schlenk techniques under an atmosphere of Argon. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately (THF) or kept over 4 Å molecular sieves. TBHP was purchased from Aldrich as 5.0-6.0 mol % solution in decane and used after drying over molecular sieves to remove the water (< 4 % when received). Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra of isolated compounds were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets. ^{1}H-, ^{13}C- , ^{95}Mo-, and ^{29}Si-NMR spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer; Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit HP 3396 Series II. Compound **1**, (3-cyclopentadienylpropyl)trimethoxysilane, $(MeO)_3Si(CH_2)_3C_5H_5$ and compound **2** (3-iodopropyl)trimethoxysilane, $I(CH_2)_3Si(OMe)_3$ were synthesised according to literature procedures [8d]. (Iodomethyl)triethoxysilane, Compound **3**, $ICH_2Si(OEt)_3$ was prepared by a straightforward adaptation of a literature procedure [13] from commercially available (chloromethyl) triethoxysilane, $ClCH_2Si(OEt)_3$.

[σ-Methyl-η^5-(trimethoxysilylpropyl)cyclopentadienyl] tricarbonyl molybdenum (**4**)

$Mo(CO)_6$ (1.33 g, 5 mmol) was added to a deep orange solution of sodium(trimethoxysilylpropyl)cyclopentadienyl (1.56 g, 6.25 mmol) in 30 ml THF, which was prepared by stirring (3-cyclopentadienylpropyl)trimethoxysilane (1.425 g, 6.25 mmol) with Na sand (0.23 g) at room temperature for 12h. After refluxing for 18h, the obtained deep orange solution of $NaMo(CO)_3C_5(CH_2)_3Si(OCH_3)_3H_4$ was cooled to room temperature and then treated dropwise with 0.35 ml (5.6 mmol) of methyl iodide. After stirring at room temperature for 12h, all solvent was removed from the reaction mixture in oil pump vacuum

until a sticky deep brown residue remained. This residue was extracted with *n*-hexane three times and the obtained orange red solution was chromatographed on Florisil (60 – 100 mesh) with *n*-hexane as solvent. The yellow fraction is eluted with *n*-hexane and diethyl ether (1:1) and collected. After removal of all solvent, Compound **4** was obtained as brown yellow oil. Yield (1.68 g, 80%). $C_{15}H_{22}O_6MoSi$ (422). calcd: C 42.65, H 5.21; found: C 42.81, H 5.38. IR (Kbr, ν cm^{-1}): 3010 (w, ν CH of Cp-ring), 2941, 2841 (w, ν CH_2), 2014 and 1919 (vs, ν CO), 1192 (w, ν Si-O), 1088 (m, ν Si-O), 819 (m, ν Si-O); ^{1}H-NMR ($CDCl_3$, 400 MHz, rt): δ (ppm) = 5.12, 5.13 (d, 4H, $C_5(CH_2)_3Si(OCH_3)_3$***H_4***$Mo(CO)_3CH_3$), 3.53 (9H, $C_5(CH_2)_3Si$***$(OCH_3)_3$***H_4 $Mo(CO)_3CH_3$), 2.21 (t, 2H, C_5***CH_2***$(CH_2)_2Si(OCH_3)_3H_4Mo(CO)_3CH_3$),1.54 (m, 2H, C_5CH_2 ***CH_2***$CH_2Si(OCH_3)_3H_4Mo(CO)_3CH_3$), 0.65 (t, 2H, $C_5CH_2CH_2$***CH_2***Si $(OCH_3)_3H_4Mo(CO)_3CH_3$), 0.29 (s, 3H, $C_5(CH_2)_3Si(OCH_3)_3H_4Mo(CO)_3$***$CH_3$***); ^{13}C-NMR ($CDCl_3$, 100.28 MHz, rt): δ (ppm) = 115.33, 92.57, 89.96 (***C_5***$(CH_2)_3Si(OCH_3)_3H_4Mo(CO)_3CH_3$), 50.52 ($C_5(CH_2)_3Si$ ***$(OCH_3)_3$***$H_4Mo(CO)_3CH_3$), 31.29 (C_5***CH_2***$(CH_2)_2Si(OCH_3)_3H_4Mo$-$(CO)_3CH_3$), 24.83 (C_5CH_2 ***CH_2***$CH_2Si(OCH_3)_3H_4Mo(CO)_3CH_3$), 9.00 ($C_5CH_2CH_2$***$CH_2$***$Si(OCH_3)_3H_4Mo(CO)_3CH_3$), -19.41 ($C_5(CH_2)_3Si(OCH_3)_3H_4Mo(CO)_3$***$CH_3$***); ^{95}Mo-NMR($CDCl_3$, 26.07 MHz, rt): δ (ppm) = –1715; ^{29}Si-NMR ($CDCl_3$, 79.42 MHz, rt): δ (ppm) = -42.95; FAB-MS (70 eV) m/z (%); M^+ = 422.

[σ-propyltrimethoxysilane-η^5-cyclopentadienyl] tricarbonyl molybdenum **(5)**

$NaMo(CO)_3C_5H_5$ (1.34 g, 5 mmol) in 30 ml THF was treated with (3-iodopropyl) trimethoxysilane (1.63 g, 5.63 mmol). After stirring the reaction mixture at room temperature for 12 h, all solvent was removed in oil pump vacuum until a sticky deep brown residue remained. This residue was extracted with *n*-hexane three times and the obtained orange red solution was chromatographed on Florisil (60 – 100 mesh) with *n*-hexane as solvent. The yellow fraction is eluted with *n*-hexane and diethyl ether (1:1) and collected. After removal of all solvent, Compound **5** was obtained as brown yellow oil. Yield (1.69 g, 83%). $C_{14}H_{20}O_6MoSi$ (408). calcd: C 41.18, H 4.90; found: C 41,56 H 5.09. IR (KBr, ν cm^{-1}): 3015 (w, ν CH of Cp-ring), 2941, 2841 (w, ν CH_2), 2011 and 1915 (vs, ν CO), 1195 (w, ν Si-O),

1088 (m, ν Si-O), 814 (m, ν Si-O); ^{1}H-NMR ($CDCl_3$, 400 MHz, rt): δ (ppm) = 5.26 (s, 5H, $C_5H_5Mo(CO)_3(CH_2)_3Si(OCH_3)_3$), 3.55 (s, 9H, $C_5H_5Mo(CO)_3(CH_2)_3Si(OCH_3)_3$), 1.63 (m, 4H, $C_5H_5Mo(CO)_3(CH_2)_2CH_2Si(OCH_3)_3$), 0.77 (m, 2H, C_5H_5Mo-$(CO)_3(CH_2)_2CH_2Si(OCH_3)_3$); ^{13}C-NMR ($CDCl_3$, 100.28 MHz, rt): δ (ppm) = 6.21 ($C_5H_5Mo(CO)_3CH_2(CH_2)_2Si(OCH_3)_3$)), 15.77 ($C_5H_5Mo(CO)_3$ $(CH_2)_2$ $CH_2Si(OCH_3)_3$), 29.36 ($C_5H_5Mo(CO)_3CH_2CH_2CH_2Si(OCH_3)_3$), 50.30 ($C_5H_5Mo(CO)_3(CH_2)_3Si(OCH_3)_3$), 92.53 ($C_5H_5Mo(CO)_3(CH_2)_3Si(OCH_3)_3$); ^{95}Mo-NMR ($CDCl_3$, 26.07 MHz, rt): δ (ppm) = –1693.4; ^{29}Si-NMR($CDCl_3$, 79.42 MHz, rt): δ (ppm) = -42.02; FAB-MS (70 eV) m/z (%); M^+ = 408

[σ-methyltriethoxysilane-η^5-cyclopentadienyl] tricarbonyl molybdenum **(6)**

$NaMo(CO)_3C_5H_5$ (1.34 g, 5 mmol) in 30 ml THF was treated with (iodomethyl)triethoxysilane $ICH_2Si(OEt)_3$ (1.71 g, 5.63 mmol). After stirring the reaction mixture at room temperature for 12 h, all solvent was removed in oil pump vacuum until a sticky deep brown residue remained. This residue was extracted with *n*-hexane three times and the obtained orange red solution was chromatographed on Florisil (60 – 100 mesh) with *n*-hexane as solvent. The yellow fraction is eluted with *n*-hexane and diethyl ether (1:1) and collected. After removal of all solvent, Compound **6** was obtained as brown yellow oil. Yield (0.99g, 47%). $C_{15}H_{22}O_6MoSi$ (422). calcd: C 42.65, H 5.21; found: C 42.86 H 5.16. IR (KBr, ν cm^{-1}): 3011 (w, ν CH of Cp-ring), 2969, 2926, 2857 (w, ν CH_2, ν CH_3), 2022 and 1937 (vs, ν CO), 1166 (w, ν Si-O), 1102,1083 (m, ν Si-O), 810 (m, ν Si-O); ^{1}H-NMR ($CDCl_3$, 400 MHz, rt): δ (ppm) = 5.41 (s, 5H, $C_5H_5Mo(CO)_3CH_2Si(OCH_2CH_3)_3$), 3.80 (q, 6H, $C_5H_5Mo(CO)_3CH_2Si(OCH_2CH_3)_3$), 1.21 (t, 9H, $C_5H_5Mo(CO)_3CH_2Si(OCH_2CH_3)_3$), -0.41 (s, 3H, $C_5H_5Mo(CO)_3CH_2Si(OCH_2CH_3)_3$); ^{13}C-NMR ($CDCl_3$, 100.28 MHz, rt): δ (ppm) = -34.40 ($C_5H_5Mo(CO)_3CH_2Si(OCH_2CH_3)_3$), 18.32 ($C_5H_5Mo(CO)_3CH_2Si$-$(OCH_2CH_3)_3$), 58.19 ($C_5H_5Mo(CO)_3CH_2Si(OCH_2CH_3)_3$), 92.62 ($C_5H_5Mo(CO)_3CH_2Si$-$(OCH_2CH_3)_3$); ^{95}Mo-NMR ($CDCl_3$, 26.07 MHz, rt): δ (ppm) = –1645; ^{29}Si-NMR ($CDCl_3$, 79.42 MHz, rt): δ (ppm) = -38.71; FAB-MS (70 eV) m/z (%); M^+ = 422

8.4.2. Catalytic reactions with compounds 4-6 as catalysts

Cyclooctene epoxidation: compounds **4-6** as catalyst (73 μmol, 1mol %) were added to the reaction vessel and TBHP (2.65 mL, 5.5 M-6.0 M in *n*-decane) was added, the mixture was stirred until a change of colour from yellow to pale yellow occurred showing that the carbonyl compounds were oxidised to the corresponding oxides, then *cis*-cyclooctene (800 mg, 7.3 mmol) and mesitylene (1g, internal standard) were added. The course of the reactions was monitored by quantitative GC analysis. Samples were taken and diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

8.5. Conclusion

A series of complexes of the type $CpMoR(CO)_3$ and $RCpMo(CO)_3CH_3$ (R = $(CH_2)_3Si(OMe)_3$ or $CH_2Si(OEt)_3$) was prepared and spectroscopically characterized. They show high catalytic activity in the epoxidation of cyclooctene, and perform in the same order of magnitude with respect to yields and activities as their methyl and chlorine analogues $CpMo(CO)_3Me$ and $CpMo(CO)_3Cl$, demonstrating that siloxane functional groups in the attached ligands do not reduce the catalytic olefin epoxidation activity significantly in homogeneous phase. The successful heterogenization of these compounds by means of their siloxane ligands on MCM-41/48 has already been achieved and is described elsewhere. [48]

8.6. References

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9. Heterogenization of organometallic molybdenum complexes with siloxane functional groups and their catalytic application

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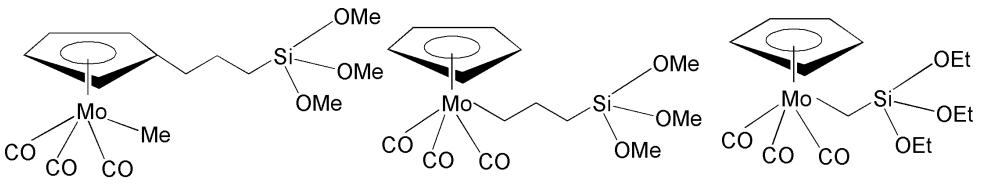
9.1. Abstract

η^5-$CpMo(CO)_3R$ complexes containing siloxane functional groups [$(CH_2)_3Si(OMe)_3$ or $(CH_2)Si(OEt)_3$] attached to either the cyclopentadiene ligand or directly to Mo were grafted on the mesoporous materials MCM-41 and MCM-48 by reaction of the OR (R = Me, Et) moieties in the silane ligand and surface silanol groups (Si-OH). For sake of comparison mesoporous materials modified with silane groups were reacted with $Na^+[CpMo(CO)_3]^-$. The XRD, N_2 adsorption-desorption, and TEM analysis provide strong evidence that the mesoporous structure of the supporting material retains its long range ordering throughout the grafting process, despite significant reductions in surface area, pore-volume and pore size. The appearance of strong IR bands around 2016 and 1956 cm^{-1} on the grafted samples also show that the η^5-$CpMo(CO)_3R$ complexes have been successfully grafted. Elemental analysis reveals that the grafted samples contain 0.3-3.5 wt. % Mo. ^{29}Si CP MAS-NMR spectra give clear evidence for a reduction of the Q_3 and Q_2 sites in number. The formation of new peaks around -49.8, -57.9, and -66.2 ppm (T_1, T_2, and T_3) indicates esterification of silanol groups by the methoxy groups of the silane ligand. Both the *in situ* and *ex situ* prepared samples show good catalytic activity for the epoxidation of cyclooctene.

9.2. Introduction

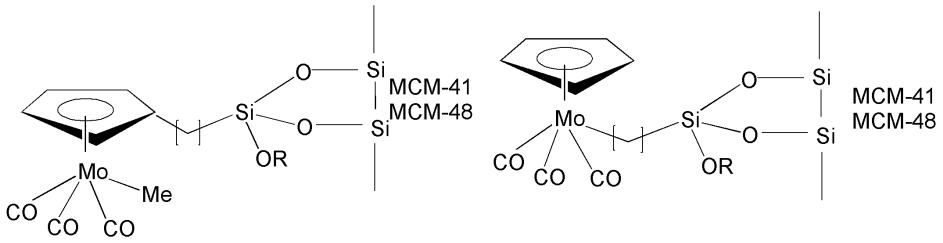
A variety of Molybdenum(VI) complexes is known to be versatile catalysts for the oxidation of organic substrates.[1] During the last decade several well defined homogeneous epoxidation catalysts have been developed and described.[2] As mentioned in chapter 6 and 7, cyclopentadienyl molybdenum complexes of formula Cp'MoO_2Cl were found to be efficient homogeneous catalysts for epoxidation of alkenes with TBHP as the oxidant.[3] Furthermore, it became clear that the direct application of their carbonyl precursor compounds of formula $CpMo(CO)_3Cl$ leads to equally efficient catalysts, since the carbonyl complexes are *in situ* oxidized – also by TBHP - to their oxo congeners. The carbonyl precursor compounds can be stored for long time without any problems while the oxides are somewhat more sensitive.[3] Additionally, Cp'$Mo(CO)_3R$ complexes (R = alkyl) and their oxidized congeners are also known and have already been successfully utilized as homogeneous catalysts or catalyst precursors.[4] However, industrial interest is still to a significant degree focused on heterogeneous catalysts due to their advantages, e. g. easier product/catalyst separation.[5] Among the various supporting materials studied, the mesoporous silicates known as MCM-41 and MCM-48[6] with regular pore size, large surface areas, large number of surface silanol groups, and high chemical and thermal stability, are potential and promising candidates as both catalysts and catalyst supports.[7]

Different approaches have been used in order to obtain heterogeneous molybdenum catalyst for olefin epoxidation.[9-13] During the last decades organometallic complexes with silane functional groups, either attached directly to the metal centre or to a cyclopentadienyl ligand have been reported [14] These functional groups often contributed a considerable kinetic stabilization to the resulting complexes.[14] The introduction of an alkoxy silane group in the organometallic complexes, has received additional attention, owing to the ease of heterogenization of these transition metal complexes by using organic or inorganic supports.[3,12-14] Recently we have successfully synthesized and characterized a series of cyclopendadienyl molybdenum complexes containing a siloxane functional group.[15]



1 **2** **3**

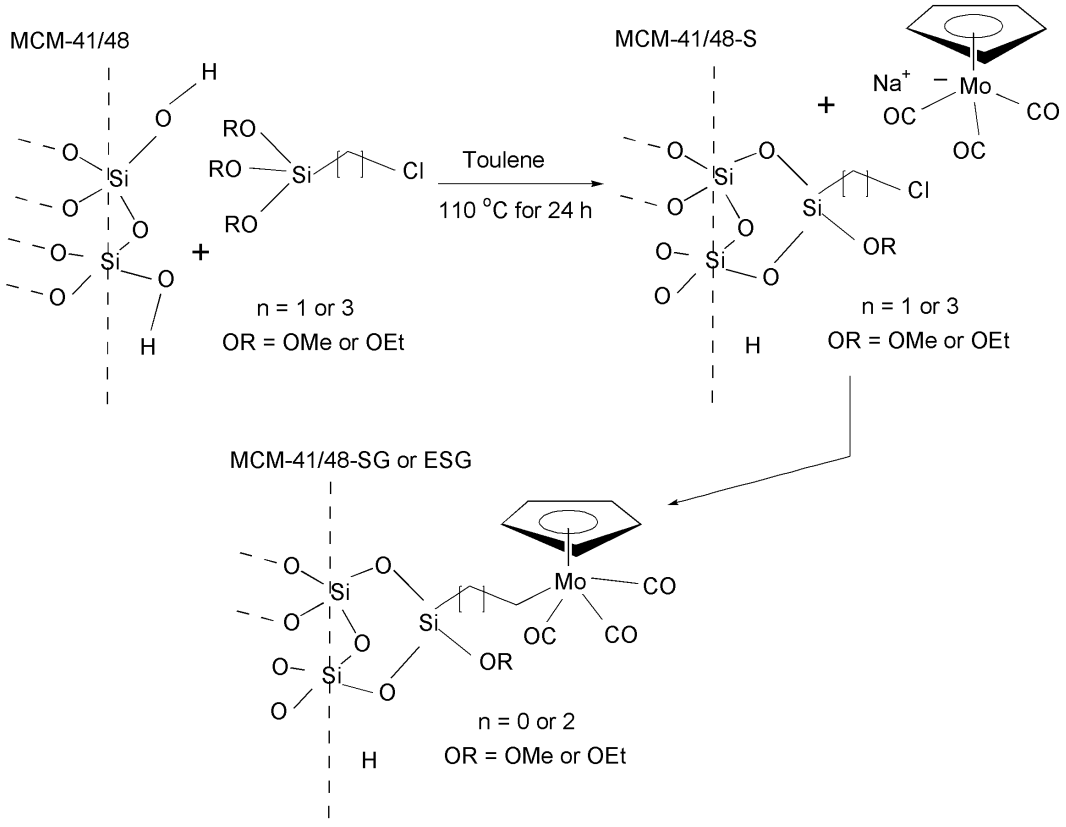
Figure 1



n = 3 and R = Me

n = 1, 3; R = Me, Et

Figure 2



Scheme 1

In this work such complexes (compounds **1-3**, see Fig. 1) are reported to be turned into 'surface organometallic catalysts' by fixing them to MCM-41 and MCM-48 (Fig. 2). Additionally, the *in-situ* synthesis of surface fixed $CpMoR(CO)_3$ by functionalization of the mesoporous framework with $Cl(CH_2)_3Si(OMe)_3$ or $ClCH_2Si(OEt)_3$ followed by the reaction of $Na^+[CpMo(CO)_3]^-$ with the chloride ion of the silane functional group on MCM-41 and MCM-48 is presented (Scheme 1).

9.3. Results and Discussion

9.3.1. Synthesis and Textural Characterization

The compounds **1-3** are prepared as described previously.[15] They are slightly air sensitive and very good soluble both in non polar (e. g. *n*-hexane) and polar (e. g. THF) solvents. The IR spectra (KBr) of compounds **1-3** show strong absorption bands at 2016, 1956 and 1963 cm^{-1}, respectively from terminal carbonyl groups. The ^1H, ^{13}C and ^{29}Si NMR spectra as well as elemental analysis confirm the purity of the complexes.[15] The treatment of the complexes **1-3** with calcined and dehydrated MCM-41 and MCM-48 lead to the modified materials which are respectively designated as SM-41CpSG, SM-48CpSG, SM-41MoSG, SM-48MoSG, SM-41MoESG and SM-41MoESG (see Fig. 2). The *in situ* grafting of a CpMo complexes is carried out by silylation of MCM-41 and MCM-48 followed by treatment with $Na^+[CpMo(CO)_3]^-$ (see Scheme 1) which are represented as SM-41SG, SM-48SG, SM-41ESG and SM-48ESG.

The powder XRD pattern of the parent MCM-41 (Fig. 3a), and the corresponding grafted Mo samples (SM-41CpSG, SM-41MoSG, SM-41MoESG, SM-41SG and SM-41ESG) are depicted in Fig. 3b-3f. In each case all four reflections are observed in the 2 θ range 2-8°, with an indexing corresponding to a hexagonal cell showing the (100), (110), and (200) and (210) planes. Fig. 3A-3F show the XRD pattern of parent MCM-48 and the corresponding samples with the grafted Mo complexes (SM-48CpSG, SM-48MoSG, SM-48MoESG, SM-48SG and SM-48ESG), which exhibit a main reflection corresponding to the (211) plane along with a shoulder peak derived from the (220) plane, typical for cubic cells. These peaks together with

the sextet pattern observed between the 2θ angles 3°–6°, are characteristic of a cubic mesoporous MCM-48 structure. Compared to parent MCM-41 and MCM-48, the grafted samples show a decrease in the relative intensities of the XRD reflections and there is a clear shift to higher 2 θ values. These changes originate from a contraction of the unit cells of the grafted samples, because of the immobilization of the bulky organosilane groups on the channels of MCM-41 and MCM-48 by reaction with surface silanol (Si-OH) groups.[12] The intensity reduction is mainly due to contrast matching between the silicate framework and organic moieties located inside the channels of the mesoporous molecular sieves.[12] The results clearly indicate that the structure of the mesoporous materials remains intact through the grafting procedure.

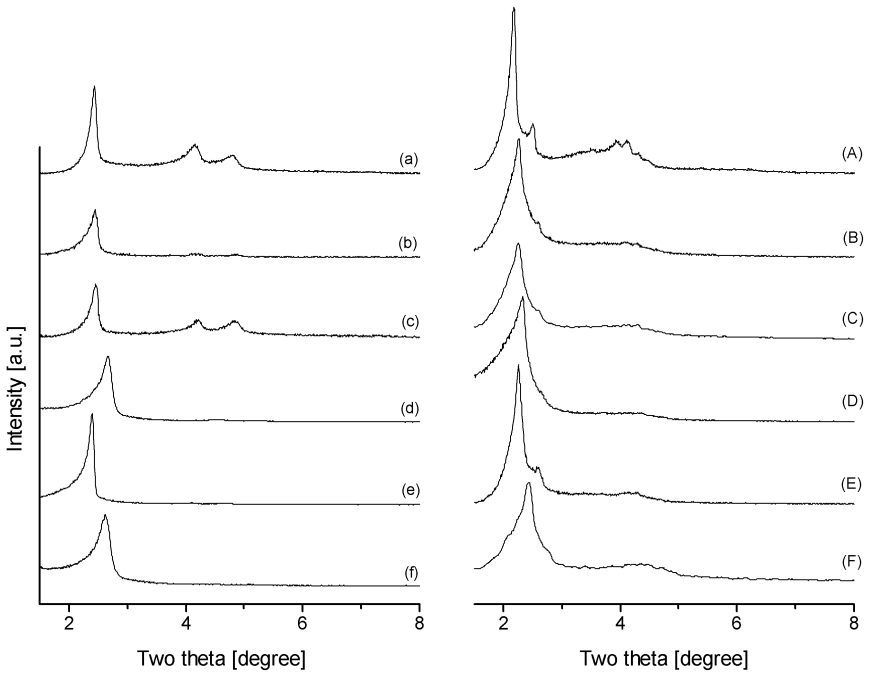


Figure 3. Powder XRD pattern of (a, A) SM-41, SM-48; (b,B) SM-41CpSG, SM-48CpSG; (c, C) SM-41MoSG, SM-48MoSG; (d, D) SM-41MoESG, SM-48MoESG; (e, E) SM-41SG, SM-48SG and (f, F) SM-41ESG, SM-48ESG.

The low temperature N_2 adsorption/desorption isotherm of parent MCM-41 and MCM-48 are of type (IV) according to the IUPAC[16] and characteristic for mesoporous solids. A well-

defined sharp inflection is observed between the relative pressure (p/p_0) of 0.3-0.4 due to capillary condensation of nitrogen inside the primary mesoporous channels. Compared to parent mesoporous samples, the modified samples (Fig. 4) exhibit a decrease in N_2 uptake due to the presence of bulky organometallic complexes grafted on the mesoporous channels.

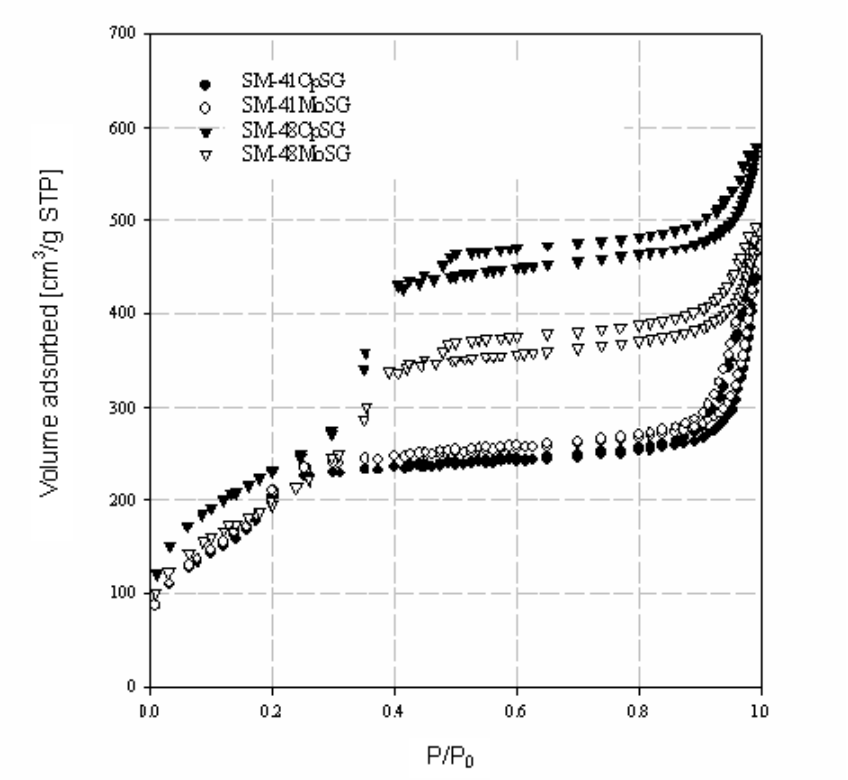


Figure 4. N_2 adsorption/desorption isotherms of complexes **1** and **2** grafted on MCM-41 and MCM-48.

The calculated textural parameters using XRD and adsorption/desorption isotherms are summarized in Table 1. The parent MCM-41 and MCM-48 samples exhibit narrow pore size distributions with average pore diameters of 2.7 and 2.4 nm, respectively. The grafted materials exhibit a broader pore size distribution and display also a decrease in surface area and unit cell volume. The decrease of the unit cell value and the broad distribution of pore size evidences that the organometallic complexes in the grafted mesoporous samples are mainly located on internal surfaces of the mesoporous materials.[12]

Table 1. Textural properties of MCM-41/MCM-48 and of the grafted samples.

Sample	Mo wt. %	Interplane distance (nm)[a]	Unit cell parameter (nm)[b]	BET surface area (m^2g^{-1})	Pore diameter (nm)
MCM-41	__	3.80	4.39	839	2.74
SM-41CpSG	2.3	3.62	4.18	620	2.5-3.1
SM-41MoSG	1.7	3.60	4.16	640	2.3-3.1
SM-41MoESG	0.3	3.31	3.82	__	__
SM-41SG	1.03	3.69	4.26	726	1.9-2.1
SM-41ESG	0.94	3.37	3.89	__	__
MCM-48	__	3.97	9.72	1043	2.41
SM-48CpSG	3.41	3.90	9.55	790	2.24-3.5
SM-48MoSG	1.83	3.92	9.60	680	2.27.3.5
SM-48MoESG	0.4	3.81	9.33	__	__
SM-48SG	1.18	3.90	9.55	840	2.1
SM-48ESG	1.27	3.65	8.94	__	__

a: d_{100} for MCM-41 and d_{211} for MCM-48.

b: $\bar{a} = 2d_{100}/\sqrt{3}$ for MCM-41; $\bar{a} = d_{hkl}(h^2+k^2+l^2)^{1/2}$ for MCM-48.

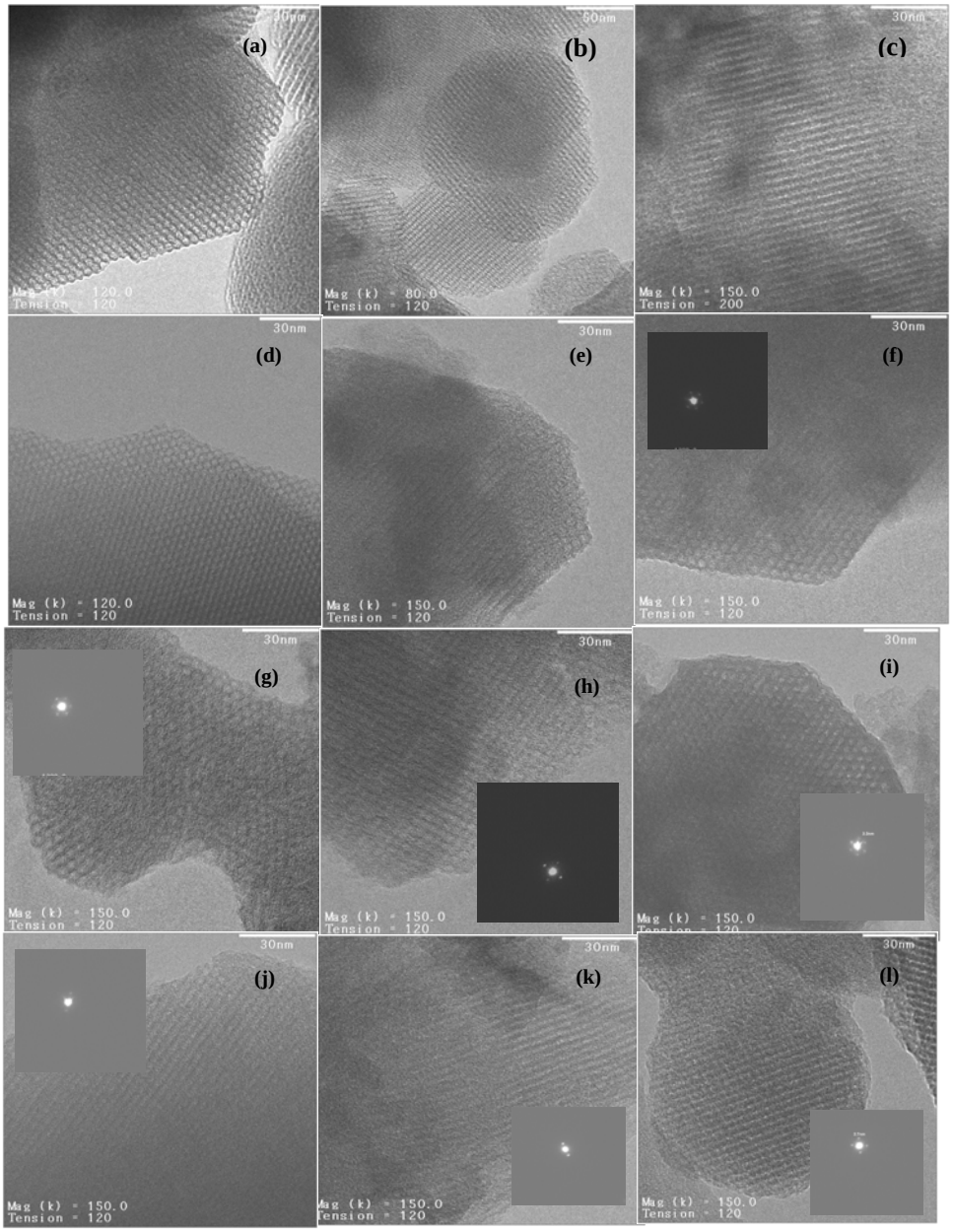


Figure 5. TEM images of (a)SM-41, (b) SM-48, (c) SM-41SG, (d) SM-48SG, (e) SM-41CpSG, (f) SM-41MoSG, (g) SM-48CpSG, (h) SM-48MoSG (i) SM-41MoESG (j) SM-48MoESG (k) SM-41ESG and (l) SM-48ESG.

The TEM images (see Fig. 5) of the grafted samples are providing strong evidence that the mesoporous structure of the support retains long range ordering[6,7] throughout the grafting process and that the channels remain accessible. The ED pattern of grafted samples shows the reflection of the (100) and the (110) planes, which further support the presence of long range ordering in the samples. Elemental analyses (EAs) of the grafted samples of compounds **1**–**3**

reveal (Table 1) a Mo loading of 0.3-3.5 wt. %. The complexes containing methoxy silane enable somewhat higher Mo complex loading on the surfaces than the complex containing ethoxy ligands. This may be due to the higher reactivity of the methoxy groups with silanol moieties in the mesoporous channels in comparison to the ethoxy groups. Furthermore, it is evident that direct grafting is more efficient and leads to higher Mo complex loading on the surface than *in situ* grafting. EA further confirms clearly the decrease of Cl on the SM-41SG and SM-48 SG samples in comparison to the SM-41S and SM-48S samples. Therefore it is clear that a considerable amount of Cl is utilized for the reaction with the $Na^{+}[CpMo(CO)_3]^{-}$ salt.

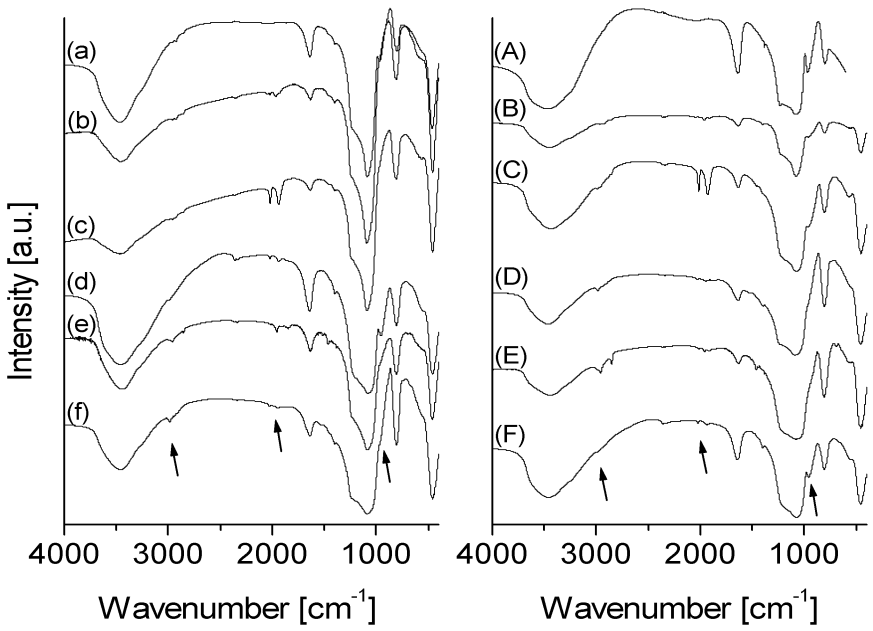


Figure 6. FT-IR spectrum of (a, A) SM-41, SM-48; (b,B) SM-41MoSG, SM-48MoSG; (c, C) SM - 41CpSG, SM-48CpSG; (d, D) SM-41MoESG, SM-48MoESG; (e, E) SM-41SG, SM-48SG and (f, F) SM-41ESG, SM-48ESG.

Fig. 6 depicts the FT-IR spectra of parent calcined mesoporous MCM-41, MCM-48 and grafted samples. The bands at 1206, 1060, and 794 cm^{-1} are attributed to stretching vibrations of the mesoporous framework (Si-O-Si). New, comparatively small bands around 2016 and 1956 cm^{-1} can be assigned to terminal carbonyl (CO) group vibrations of the grafted

compounds. Additional bonds appear in the range of 2949 and 2853 cm^{-1} due to C-H stretching vibrations, originating from the CH_2 groups present in the silane ligand. In order to transfer the Mo precursor in the formal oxidation state +II to the catalytic active species in the formal oxidation state + VI, the SM-41CpSG and SM-41MoSG samples are treated with TBHP. The FT-IR spectra recorded prior to and after oxidation are shown in Fig. 7. After the treatment with TBHP the bands around 2016 and 1956 cm^{-1} disappear and new bands around 914 and 964 cm^{-1} are formed, indicating the oxidative conversion of the Mo-CO groups into Mo=O species[3,11,17]. The oxidative decarbonylation method has already been successfully applied for the oxidation of $Cp'Mo(CO)_3X$ and $Cp'Mo(CO)_3R$ complexes, both in homogeneous[3,4] and heterogeneous phase[11].

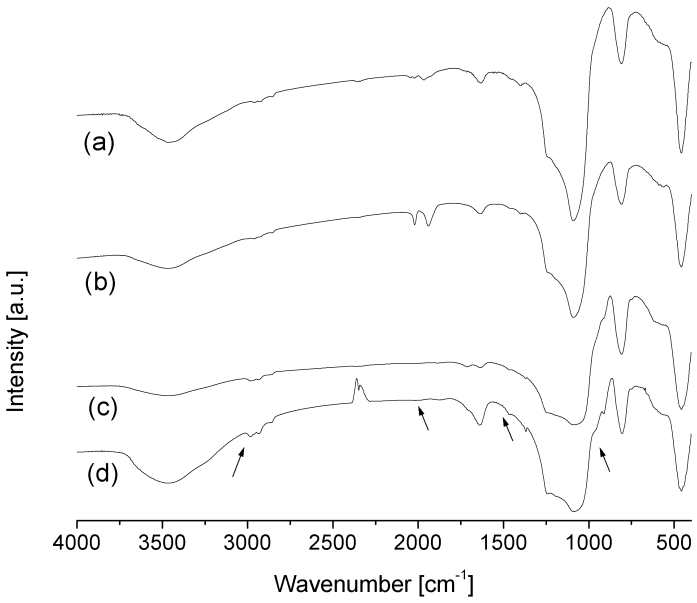


Figure 7. FT-IR spectrum of (a) SM-41MoSG, (b) SM -41CpSG, (c) SM-41MoSG-TBHP treated and (d) SM-41CpSG-TBHP treated samples.

The parent MCM-41 and the grafted samples were examined by solid-state ^{29}Si CP MAS NMR spectroscopy. The parent MCM-41 exhibits two broad elaborate resonances in the ^{29}Si CP MAS NMR spectrum at δ = -113.0 and -103.8 ppm, assigned to Q^4 and Q^3 species of the silica framework, respectively, [$Q_n = Si(OSi)_n(OH)_{4-n}$] (Fig. 8).[12]

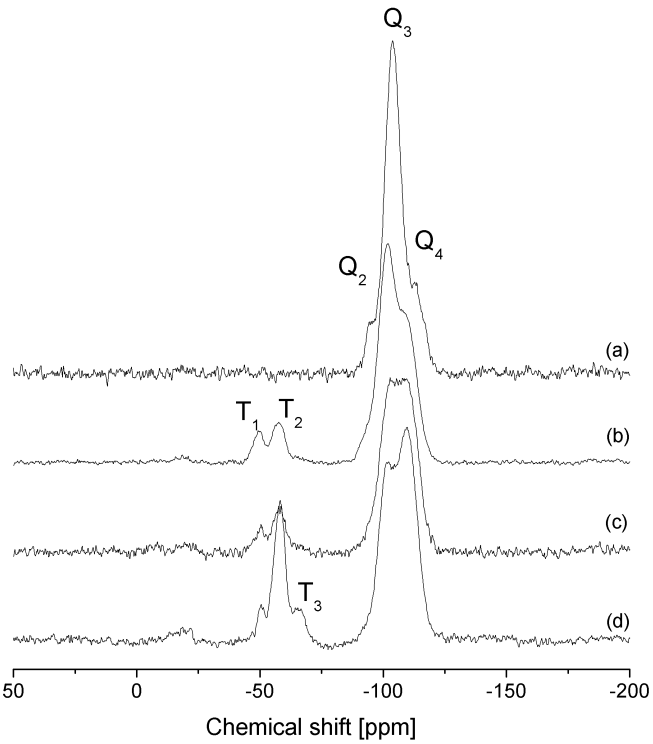


Figure 8. ^{29}Si CP MAS NMR spectrum of (a) SM-41; (b) SM-41CpSG; (c) SM -41MoSG and (d) SM-41SG.

A weak shoulder is also observed at δ = -94.5 ppm for the Q_2 species. The grafting of complex **1-3** and the *in situ* grafting of η^{5}-CpMo complex on mesoporous materials results in the reduction of the Q_2 and Q_3 resonances, and a concurrent increase of the Q_4 resonance. This is consistent with an esterification of the isolated silanol groups (single and geminal) by nucleophilic substitution at the silicon atom in the organic ligand.[12] However, Fig. 8 also shows considerable un-reacted silanol groups remaining after the grafting. The ^{29}Si CP MAS NMR spectra also exhibit two additional signals at δ = -49.8 and -57.9 ppm assigned to T_1 and T_2 organosilica species, respectively, [T_m = $RSi(OSi)_{m-}(OR)_{3-m}$]. A weak, broad signal at δ = -66.2 ppm can be assigned to a T_3 environment. The amount of T_1 and T_2 is much higher in the case of SM-41MoSG than in the case of SM-41CpSG, which suggests that the Mo loading is much higher in the former case than in the later. This observation is in good agreement with the EAs (Table 1).

9.3.2. Catalytic Applications

The grafted samples are tested as heterogeneous catalysts in olefin epoxidation, with cyclooctene being the substrate and TBHP as the oxidizing agent. The results are summarized in Table 2.

Table 2. Oxidation of cyclooctene with various CpMo complexes grafted on MCM-41/MCM-48

Catalysts	1st run				3rd run				TOF
	4h		24 h		4h		24 h		
	Con.	Sel.	Con.	Sel.	Con.	Sel.	Con.	Sel.	
SM-41SG	36	98	68	100	13	50	31	44	2800
SM-48SG	32	88	66	99	8	100	33	80	4850
SM-41ESG	13	100	35	82	14	71	28	64	2900
SM-48ESG	13	97	63	92	17	64	47	64	3150
SM-41CpSG	66	58	95	79	17	100	46	98	10100
SM-48CpSG	88	82	100	100	21	100	73	90	8100
SM-41MoSG	50	39	95	87	24	85	57	91	8400
SM-48MoSG	97	100	100	100	25	61	80	70	10200
SM-41MoESG	10.7	52.9	32.5	73.2	7.1	100	26.8	88.9	4900
SM-48MoESG	20.6	44.6	45.6	77.9	10.1	100	28.8	95.4	6300

The SM-41SG and SM-48SG materials show about 65-68 % cyclooctene conversion with nearly 100 % epoxide selectivity after 24 h reaction time. In the cases of SM-41CpSG, SM-41MoSG, SM-48CpSG, and SM-48MoSG 95-100 % conversion and about 100 % selectivity are obtained. The initial activities (based on the TOFs) are highest for SM-41CpSG, SM-41MoSG, SM-48CpSG and SM-48MoSG. These materials have longer hydrocarbon bridges between the Mo atoms and the surface Si-O groups than the ESG-materials, thus reducing the influence of the electron donor abilities of the surface on the Lewis acidity of the catalytic centers (see Fig. 1 and Scheme 1). The slightly more pronounced steric bulk of the remaining ethoxy groups (after the heterogenization reaction) in case of the ESG materials may also contribute to the generally somewhat lower initial activity of these catalysts. The prehistory (heterogenization method) of the complexes, however, seems also to have a certain impact on the catalytic activities (the MoSG and MoESG materials are more active than the SG and ESG materials). The reasons for this observation, however, are not yet completely understood and still under investigation. All the catalysts, however, show TOFs in the same order of magnitude as the respective homogeneous catalysts **1**-**3**, thus indicating that the reaction is not diffusion limited. This is in good agreement with the results obtained by TEM and BET analysis where the pore channels are found to remain accessible after grafting with the complexes **1** to **3**. After the first catalytic run the catalyst was washed several times with dichloromethane to remove physisorbed molecules and the reaction was repeated several times. The catalysts are found to be active even after several catalytic runs, however, the catalytic activity decreases. The observed decrease in activity is very likely due to the chemisorptions of organic molecules on the surface, such preventing the access of substrate and oxidant molecules to the active Mo species. This was confirmed by TG-MS analysis of SM-48MoSG before and after reactions (Fig. 9). The TG-MS spectrum of SM-48MoSG before reaction shows about 10 % weight loss up to 1000 °C, due to decomposition of complex **2** present in the channels of the mesoporous molecular sieves. However, SM-48MoSG after reaction displays a weight loss of about 23 %, being 13 % higher than that of the original sample. This increase in weight is attributed to a considerable amount of

chemisorbed coke present on the grafted samples after reaction. In order to avoid the thermal destruction of the active Mo complex, the (chemisorbed organic) cokes are not removed by calcination.

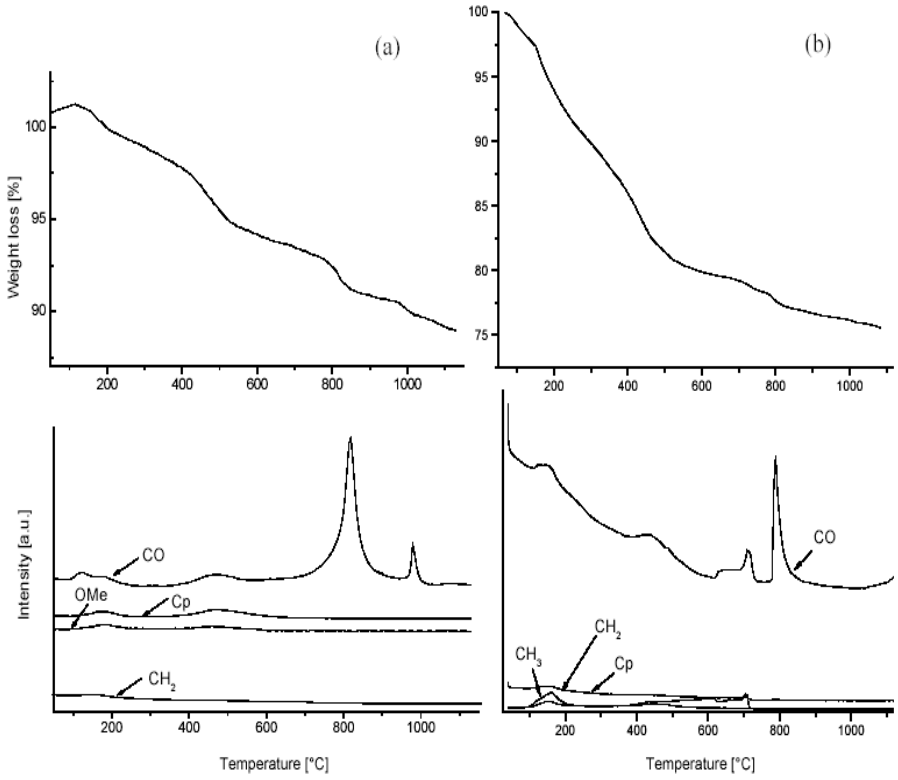


Figure 9. TG-MS spectrum of SM-48MoSG (a) before reaction and (b) after reaction.

In order to examine the extent of leaching, which could also account for the activity loss, control experiments were performed. The catalytic reaction is interrupted after a 50 % conversion of the substrate, the solution is filtered off at reaction temperature and the filtrate is examined for its catalytic activity. This activity, however, is negligible (<< 5 % epoxide yield (i.e. within the measurement error) in the 24 h after filtration), thus demonstrating that catalyst leaching does not play a significant role.

9.4. Experimental Section

9.4.1. Synthetic Procedures

Mesoporous molecular sieves are synthesized following the procedures described earlier[9] with molar gel compositions of SiO_2 : 0.2NaOH : 0.27 TMAOH : 0.27CTABr : 60 H_2O for MCM-41, and 5.0SiO_2 : 2.5NaOH : 0.87CTABr : 0.13Brij30 : 400 H_2O for MCM-48 respectively. Solvents were dried by standard procedures (THF, with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under argon and kept over 4 A ° molecular sieves. The homogeneous catalysts **1-3** were synthesized as published previously.[15]

9.4.2. Grafting and Characterization Methods

Grafting experiments were carried out using standard Schlenk techniques under argon atmosphere with the following procedure: First the mesoporous molecular sieves MCM-41/48 were pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove physisorbed water. The activated sample was treated with 0.2 mmol of complexes **1-3** in 30 ml dry THF under argon atmosphere. The mixture was stirred at 339 K for 24 h. The resulting solution was filtered off and the pale orange solid was washed repeatedly with CH_2Cl_2 until all physisorbed Cp complex was removed from the surface. The washed samples were dried under vacuum at RT. The material prepared from the complexes **1-3** on MCM-41 and MCM-48 are designated as SM-41CpSG, SM-48CpSG, SM-41MoSG, SM-48MoSG, SM-41MoESG and SM-48MoESG respectively. The *in situ* grafting (Scheme 1) was carried out according to the following procedure: first the mesoporous molecular sieve (MCM-41 or MCM-48, resp.) is silylated with chloropropyl trimethoxy and chloromethyl triethoxy silane using dry toluene (30 ml) as solvent under argon atmosphere at 383 K for 24 h. Then excess silane is removed by filtration followed by washing several times with dichloromethane. The resulting solid is dried under vaccum at room temperature. The samples silylated with chloropropyl trimethoxy silane and chloromethyl triethoxy silane are designated as SM-41S, SM-48S, SM-41ES and SM-48ES respectively. After drying, the silyated samples were treated with 2 mmol of $Na^+[CpMo(CO)_3]^-$ salt in 30 ml dry THF under argon atmosphere. The mixture was again stirred for 24h at 339 K. The *in situ* grafted sample was filtered off and the resulting orange solid was washed repeatedly with CH_2Cl_2 to remove all physisorbed CpMo salt. The washed

samples were dried under vacuum at room temperature. The samples prepared by the *in situ* method are named SM-41SG, SM-48SG, SM-41ESG, and SM-48ESG.

Microanalyses were performed at the Mikroanalytisches Laboratorium of the Technische Universität München (M. Barth and co-workers). IR spectra were measured with a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Powder XRD data were collected with a Phillips X'pert diffractometer using Cu-Kα radiation filtered by Ni. Nitrogen adsorption-desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41/48 was degassed at 723 K overnight to a residual pressure of ca. 10-24 mbar. A lower degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume (VP) was estimated from the N_2 uptake at $p/p_0 = 0.95$, using the liquid nitrogen density of 0.8081 gcm^{-3}. The pore size distribution curves (PSD, the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron micrograph (TEM) was recorded on a Philips CM 200 microscope operated at 160 kV. Thermo gravimetric mass spectra analysis (TG-MS) measurements were conducted with a Netzsch TG209 system; typically about 10 mg of sample was heated from 300 to 1473 K at 10 K min^{-1} under argon. ^{29}Si CP MAS NMR spectra were recorded at 59.627 MHz, with a (7.05 T) Bruker Avance 300 spectrometer, with 5.5 μs ^{1}H 90º pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays. ^{13}C CP MAS NMR spectra were recorded at 75.468 MHz with 2.8 μs ^{1}H 90º pulses, 8 ms contact time, a spinning rate of 8 kHz and 5 s recycle delays.

9.4.3. Catalytic reactions

The catalytic behaviour of the grafted samples (ca. 175 mg) was tested by examining the oxidation of cyclooctene (0.8020 g; 8 mmol) at 328 K in a liquid phase batch reactor with

TBHP (5.5 M in *n*-decane; 16 mmol) as the oxidizing agent. A catalyst : oxidant : substrate ratio of 0.0063 : 2 : 1 was applied. The samples were analyzed every 30 min for 4 h and the reaction was terminated after 24 h. The analyses were carried out using a gas chromatograph (HP 5890) using a FID detector. The yields and conversions were calculated according to calibration curves ($r^2 = 0.999$) determined prior to reaction course.

9.5. Conclusions

Successful grafting of the complexes **1-3** by the utilization of a metal- or ligand attached siloxane group on the mesoporous molecular sieves MCM-41 and MCM-48 is achieved without significant loss of ordering. The *in situ* and *ex situ* grafted samples are active and highly selective catalysts for the cyclooctene epoxidation with the oxidizing agent TBHP. The samples **1** and **2**, containing methoxy silane display both higher complex loadings on the surfaces and higher catalytic activity in the epoxidation reaction owing to the higher reactivity of the methoxy functional groups with the siloxane groups of the surface. Catalyst leaching seems not to be a pronounced problem, but significant activity losses occur after several runs, very likely due to coke formation and chemisorption of organic molecules on the surface.

9.6. References

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10. Chiral *ansa*-bridged η^5- Cyclopentadienyl - Molybdenum Complexes: Synthesis, Structure and application in Asymmetric Olefin - Epoxidation

This chapter contains still unpublished results.

10.1 Abstract

Some ansa-bridged η^5-cyclopentadienyl-carbonyl molybdenum complexes were synthesized with stereogenic centers located on the side chain. An exemplary X-ray crystal structure and the catalytic activity for asymmetric olefin epoxidation are reported. In non chiral epoxidation the compounds show a similar high catalytic activity as the related non chiral complexes of composition $CpMo(CO)_3X$. For the asymmetric epoxidation of *cis*-β- methylstyrene the chiral induction is higher than with most other previously examined chiral Mo-based epoxidation catalysts.

10.2. Introduction

Chiral epoxidations are of high interest for the synthesis of chiral intermediates in chemical and pharmaceutical processes to generate enatiomeric pure products.[1,2]

Mimoun et al. reported on the enantioselective epoxidation of prochiral alkyl-substituted olefins in 1979 untilizing a Mo(VI) complex bearing a chiral ligand,[3] but the enantioface selectivity was not high. One year later Katsuki and Sharpless achieved the asymmetric epoxidation of allylic alcohols, mediated by a titanium (IV) complex using (+)-R, R or (-)-S, S tartrate as chiral ligand.[4] In this case the enantioselectivity was very high, but the titanium complex had to be applied in stoichiometric amounts. The reaction was improved later, enabeling a reduction of the catalysts: substrate ratio to ca. 1:10 – 1:20 and X-ray structures of the titanium tartrate catalysts could be presented.[5] More recently, non-functionalized olefins have been applied as substrates, but high enantiometric excesses have only been achieved with

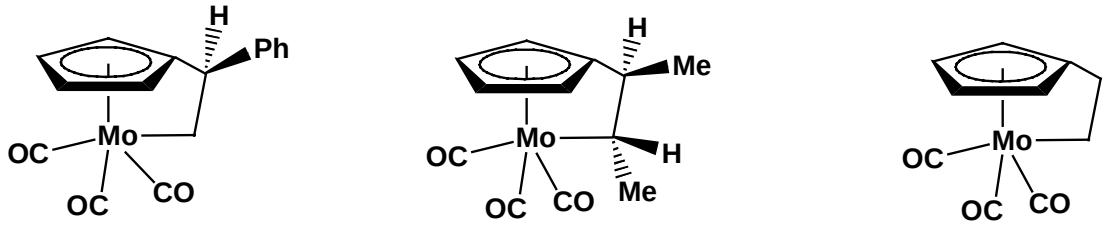
chiral salene manganese (III) catalysts.[6, 7]

Several other attempts to achieve chiral epoxidation, e. g. with Mo, W and Re based catalysts have been made, but usually led only to moderate enantiomeric excesses.[8] The generally good catalytic activities of several molybdenum(VI)-oxo complexes, however, in oxidation reactions make this type of complexes - in principle - promising candidates for asymmetric catalysis by replacing the achiral by chiral ligands.[9]

Although the *ansa*-bridged η^5-cyclopentadienyl complexes of transition metals, in which a distal methyl group of the substituted cyclopentadienyl ligand can undergo a cyclometallation reaction to produce metallacyclic compounds, where the metal center is coordinated to both the η^5-cyclopentadienyl and the η-alkyl group, are relatively rare, some examples with group 6 and 9 metals have been reported [10] and Eilbracht et al. have described several examples of this kind of reaction for a wide variety of spiro-dienes.[11] The resulting ligand can be considered as chelate where the cyclopentadienyl group and the alkyl group are both interacting with the metal center.[12] Recently the formation of some molybdenum and tungsten complexes containing a linked cyclopentadienyl-ethyl ligand has been described and the stabilities of their metal-alkyl bond were investigated. The crystal structure of a tungsten tricarbonyl complex has been determined.[13] More recently it was found that the ansa-bridged Mo tricarbonyl complex **7** (see Scheme 1) possess a comparable catalytic activity to its alkyl- and chloro-analogues of composition Cp'Mo$(CO)_3$X (X = alkyl, or Cl).[9d, 9e] In fact, its epoxidation activity surpasses most other Mo-based epoxidation catalysts (e. g. of the composition $MoX_2O_2L_2$ (X = Cl, Br, Me; L = Lewis base)) significantly and rivals even the very active and well examined Re(VII) epoxidation catalyst methyltrioxorhenium (MTO).[14] The synthetic pathway used for the preparation of ansa-bridged compounds should allow the easy introduction of a chiral ligand instead of an alkyl group. The presence of a chiral group in the immediate surrounding of the metal centre might assist in controlling the stereochemistry of reactions taking place at the metal center and therefore could eventually increase the stereoselection in catalytic reactions and lead to much higher enantiomeric excesses as have been reached in the past with related complexes, where the chirality centre was usually quite

far away from the metal.

In this work we synthesized some ansa-bridged η^5-cyclopentadienyl-carbonyl molybdenum complexes (see scheme 1), in which the stereogenic centers are located on the side chain. An exemplary X-ray crystal structure and preliminary catalytic activity test for asymmetric olefin epoxidation are reported.



(S)-3 **(S,S)-6** **7**

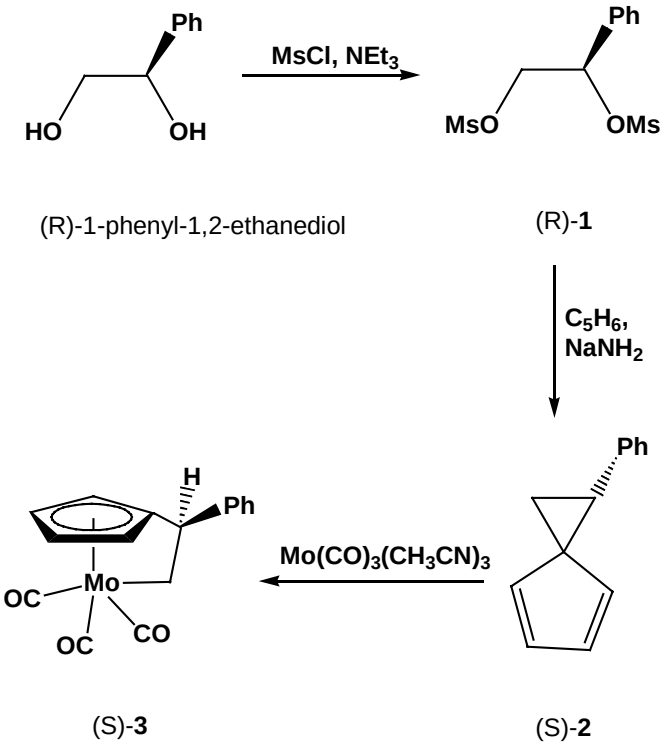
Scheme 1

10.3. Results and Discussion

10.3.1. Synthesis and spectroscopic examinations

The synthesis of chiral derivatives of spirocyclopentadienes **2** and **5** starts from optically active 1, 2-diols according to the literature approaches. Displacement of the methanesulfonate groups by cyclopentadiene in the presence of excess $NaNH_2$ affords the spiroannulated diene with inversion of the configuration at the chiral carbon. [15b] Reaction of a THF solution of the spirocyclopentadienes with the tricarbonyl complex $Mo(CO)_3(CH_3CN)_3$ takes place by a coordination followed by activation of one C_{diene}-C bond and transfer of the terminal R group to the metal center, as reported previously by Eilbracht et al.[11] (See Schemes 2 and 3)

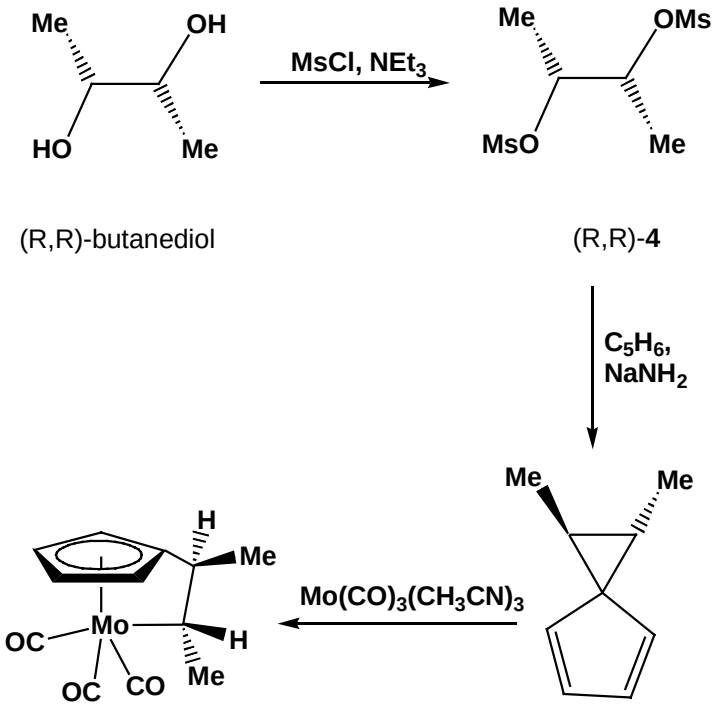
Complex **3** was isolated as yellow crystals in ca. 80 % yield and complex **6** is obtained as orange red needle shaped crystals at -30° C and as an oily solid at room temperature in ca. 70 % yield. Both compounds are stable at room temperature, can be handled in laboratory atmosphere and kept under air for some hours without significant change.



(R)-1-phenyl-1,2-ethanediol (R)-**1**

(S)-**3** (S)-**2**

Scheme 2



(R,R)-butanediol (R,R)-**4**

(S,S)-**6** (S,S)-**5**

Scheme 3

The composition and spectroscopic data of compounds **3** and **6** were determined by elemental analysis, IR-, and NMR-spectroscopy (^{1}H, ^{13}C, ^{95}Mo) as well as mass spectroscopy (MS). Comparing with the related ligands **2** and **5**, whose ^{1}H-NMR spectra display two multiplets corresponding to an AA'BB' spin system for the substituted cyclopentadienyl ring, the four protons of the Cp ring in complex **3** and **6** appear as four multiples. This feature is also confirmed by their $^{13}C\{^{1}H\}$-NMR spectra, which show five signals for the cyclopentadieny carbon atoms. This result is different from the ^{1}H-NMR spectra of the molybdenum complex containing a linked cyclopentadienyl-ethyl ligand (complex **7,** see Scheme 1), whose Cp ring represents an AA'BB' spin system.[13] The substitution on the side chain with a phenyl or methyl group leads to the observed magnetic inequivalency of the nuclei. In the case of complex **6**, the protons of both bridging CH groups appear as two multiples, the one bound to the metal center being shifted to higher field. The two substituted methyls on the side chain appear as two doublets, the one near to the metal center being shifted to higher field. The coupling constant, $J_{CH3\text{-}CH}$ is 6.8 Hz, which is in accordance with the configuration of trans-protons.[11g] It confirms that after the ring-opening of the spiro ligand through the reaction with the $Mo(CO)_3(CH_3CN)$- complex, the formed complex **6** maintains its original (S, S) ligand configuration.

Interestingly, the two protons of the methylene group on the side chain of complex **3** are diastereotopic because of the presence of a chiral center in the neighborhood, appearing as a quadruplet at -0.11 ppm and at 0.50 ppm, owing to the strong shielding effect of metal center. The ^{1}H-NMR shift of the CH group on the side chain, being connected with the phenyl group, appears as pseudo-triplet at 4.03 ppm. This result also confirms that the phenyl group is neighboring the Cp ring, not the metal center. It further indicates that the C-C bond, which is opposite to the phenyl group has been cleaved, which is also in accordance with the literature known ring-opening of 1, 1 – dimethylspiro[2,4]hepta-4,6-diene by a Mo carbonyl complex.[11g] This molecular disposition was confirmed from the X-ray structure of complex **3** (see below), which further proves that the Mo center coordinates to the less hindered side of the diene system.

The ^{95}Mo chemical shift is not an appropriate tool to distinguish between complexes in different oxidation states, however, it is highly sensitive to structural and electronic variations within a series of closely related mononuclear compounds,[16] allowing insight into the electronic situation at the molybdenum centre. The compounds examined in this work exhibit highly shielded chemical shifts, which can be in general associated with low formal oxidation states. Compounds **3** and **6** display their ^{95}Mo-NMR signal in $CDCl_3$ at -1728 and -1696 ppm, respectively, which are in the same region as that of the complex **7**. [12a]

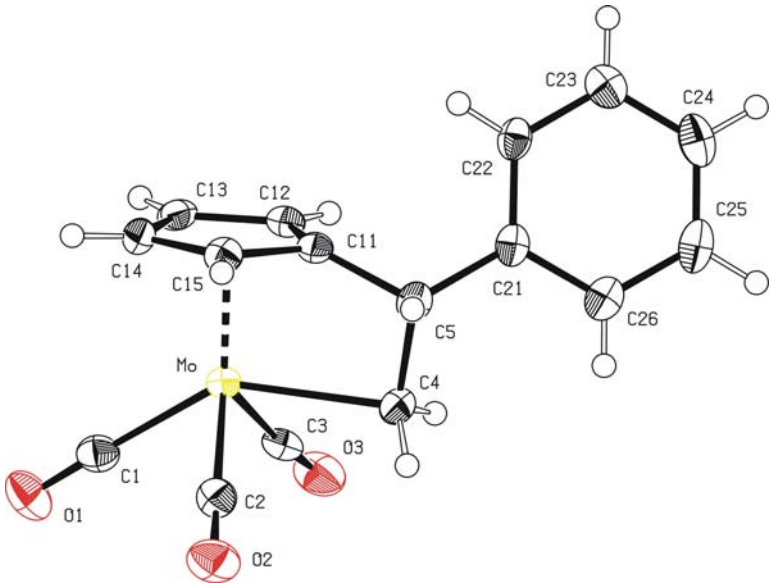


Figure 1 ORTEP style plot of the X-ray crystal structure of compound **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Mo-C1 2.016(2), Mo-C2 1.986(2), Mo-C3 1.988(2), Mo-C4 2.347(2), Mo-C11 2.287(2), Mo-C12 2.295(2), Mo-C13 2.324(2), Mo-C14 2.338(2), Mo-C15 2.323(2); C1-Mo-C2 81.06(9), C1-Mo-C2 81.06(9), C1-Mo-C3 80.05(9), C1-Mo-C4 143.63(9), C1-Mo -C11 155.49(9), C1-Mo-C12 129.14(9), C1-Mo-C13 98.18(9), C1-Mo-C14 96.48(9), Mo-C14-C15 71.84(13), C1-Mo-C15 125.35(9), C2-Mo-C3 104.29(10), C2-Mo-C4 78.12(9), C2-Mo-C11 111.32(9), C2-Mo-C12 147.60(9), C2-Mo-C13 147.67(9), C2-Mo-C14 112.17(9), C2-Mo-C15 94.82(9), C3-Mo-C4 76.67(9), C3-Mo-C11 115.11(9), C3-Mo-C12 93.79(9), C3-Mo-C13 107.41(9), C3-Mo-C14 142.40(9), C3-Mo-C15 150.75(9), C4-Mo-C11 60.88(8), C4-Mo-C12 80.27(8), C4-Mo-C13 115.22(8), C4-Mo-C14 118.92(8), C4-Mo-C15 86.07(8), Mo-C4-C5 97.13(14), C4-C5-C11 100.38(18).

10.3.2. The X-ray crystal structure of compound 3

The X-ray crystal structure of compound **3** has been determined (see Figure 1). The ligands are disposed in a distorted four-legged piano stool fashion similar to that established for analogous tricarbony cyclopentadienyl group 6 metal complexes.[9e, 13, 17] The angles between neighbouring CO-moities range from 76.67 to 81.08°, being typical values for this type of structure. The cyclopentadieny ligand is bound in a pentahapto fashion, as inferred from the total value of the angels at the ring (540°) and the metal ring-carbon distances which range from 2.287(2) to 2.338(2) Å. The carbonyl ligands have, as expected, a lineal arrangement, with Mo-C-O angles ranging from 175.3(2) to 177.8(2)°. The C-O bond lengths of between 1.144(2) and 1.153(2) Å and the averaged Mo-C(CO) bond length of 1.997 Å (with bond lengths ranging from 1.97(1) to 2.002(9) Å) are normal for the terminal CO groups. The slightly elongated Mo-C_{sp3} bond distance of 2.347(2) is in the range for a methyl group bound to a molybdenum center, for example, as reported Mo(η^5-C_5HMe_4)$(CO)_3$Me (2.311(2) Å) [9e], suggesting an electronically relatively saturated metal center due to the presence of the carbonyl groups. The bond angles at the lateral chain are rather different from the expected values for normal tetrahedral angles showing that Mo-C(4)-C(5)-C(11) is a strained four members.[13]

10.3.3. Complexes 3 and 6 in oxidation catalysis

Compounds **3** and **6** were tested as catalysts for the epoxidation of cyclooctene with TBHP.

The details concerning the catalytic reaction are given in the experimental part. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst. A catalyst: oxidant: substrate ratio of 1:200:100 was used in all experiments unless stated otherwise. The catalysts were first stirred with TBHP until a colour change from orange to yellow occurred, indicating the oxidation of the carbonyl complexes to the corresponding dioxo Mo(VI) compounds.[9d, 9e] For cyclooctene no significant formation of by-products (e.g. diol) was observed. Both catalytic reactions show similar time-dependent curves, in which the yield increases steadily in the first two hours of the reaction and then slows down

(first order kinetics), the curves for complexes **7** and $CpMo(CO)_3Me$ were also measured for comparison reasons (Figure 2).

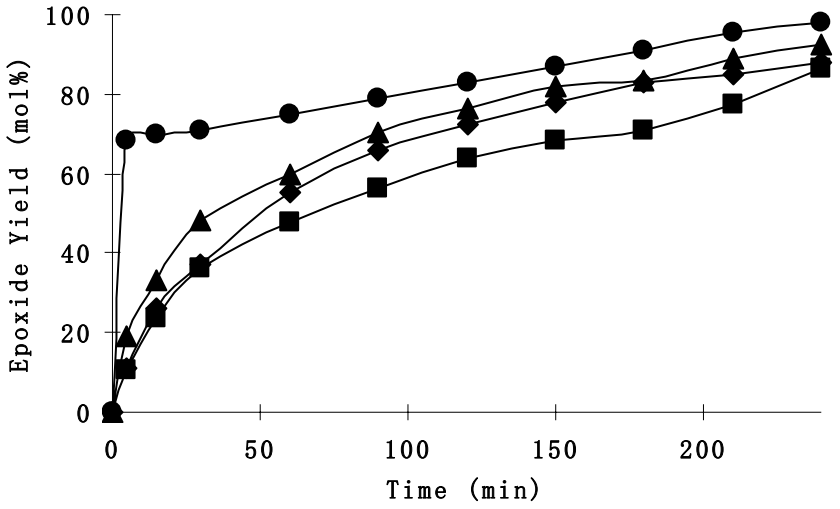


Figure 2 Time dependent yield of cyclooctene epoxide in the presence of compounds **3** (closed squares), **6** (closed diamond), **7** (closed triangles) and $CpMo(CO)_3Me$ (closed circles) as catalysts at 55°C with 1 mol % catalyst charge.

Compounds **3, 6** and **7** show a similar behaviour indicating that introduction of substituents on the side chain between the metal center and the Cp ring does not influence much the electronic situation at the metal centre and therefore also not the catalytic performance. Comparison with $CpMo(CO)_3Me$ indicates that the replacement of a methyl group by a *ansa*-bridge does not strongly influence the overall catalytic performance, but leads to a somewhat slower reaction. This observation may be caused by the more pronounced steric hindrance of the ansa-bridged systems.

Compounds **3** and **6** were also preliminarily tested as chiral catalysts for the asymmetric epoxidation of *cis*- -β-methylstyrene and the chiral induction in our first experiments was ca. 40%, indicating that these chiral complexes allow higher enantiomeric excesses than the previous described MoO_2L_3 and MoO_2L_4 derivatives. [8]

These results, however, have to be regarded with some caution, since the column applied for separation of the enatiomes did not work very well, due to its age. The experiments wil be repeated as soon as a new column is available.

10.4. Experimental Section

10.4.1. Synthesis and Characterization

All preparations and manipulations were performed using standard Schlenk techniques under an atmosphere of Argon. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately (THF) or kept over 4 Å molecular sieves. TBHP was purchased from Aldrich as 5.0-6.0 mol % solution in decane and used after drying over molecular sieves to remove the water (< 4 % when received). Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra of isolated compounds were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets. ^{1}H-, ^{13}C- , and ^{95}Mo- NMR spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer; Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit HP 3396 Series II. Compound (R)-1-Phenyl-1, 2-ethanediol bis (methanesulfonate), (S)-1-Phenyl-spiro[2, 4]hepta-4,6-diene, (R, R)-2, 3-butanediol bis (methanesulfonate) and (S, S)-1, 2-Dimethyl-spiro[2, 4]hepta-4,6-diene were synthesised according to literature procedures.[15]

(R)- [Mo(η^5- C_5H_4CHPh- η^1–CH2)$(CO)_3$] (**3**)

The addition of a THF (ca. 20 ml) solution of the ligand (S)-1-Phenyl- spiro[2, 4]hepta-4,6-diene (0.60 g, 3.3 mmol) to $Mo(CO)_3(CH_3CN)_3$ (0.91 g, 3.0 mmol) at 0° C produces an orange solution, which is stirred overnight at r. t. All volatiles are removed in vacuo, and the sticky residues are extracted with 15 ml hexane (three times) and filtered. The obtained orange red filtrates are concentrated and chromatographed on Florisil (60 – 100 mesh). The orange yellow fraction is eluted with *n*-hexane and collected. After cooling to -30

°C yellow crystal is obtained. Yield (1.68 g, 81%). $C_{16}H_{12}O_3Mo$ (348). calcd: C 55.17, H 3.45; found: C 55.28, H 3.37. IR (Kbr, ν cm^{-1}): 3110 (w, ν CH of Cp-ring), 2961, 2932, 2891 and 2859 (w, ν CH_3 and ν CH_2), 2003.6, 1903.9 (vs, ν CO); ^{1}H-NMR ($CDCl_3$, 400 MHz, rt): δ (ppm) = -0.11 (q, 1H, Mo-C*H*), 0.50 (q, 1H, Mo-C*H*), 4.03 (t, 1H, Cp-C*H*-Ph), 5.29 (m, 1H, Cp), 5.28 (m, 1H, Cp), 5.21 (m, 1H, Cp) and 5.13 (m, 1H, Cp), 7.24, 7.37, 7.36 and 7,35 (m, 5H, C_6H_5); ^{13}C-NMR ($CDCl_3$, 100.28 MHz, rt): δ (ppm) = 222.4 (CO) 151.1, 144.9, 128.5, 128.4, 126.7, 126.1 (C_6H_5), 90.3, 88.6, 88.59, 87.9, 75.1 (C_5H_4), 38.57 (Cp-*C*H), -36.41 (Mo-*C*H_2); ^{95}Mo-NMR($CDCl_3$, 26.07 MHz, rt): δ (ppm) = –1728; FAB-MS (70 eV) m/z (%); M^+ = 348.

(S, S)- [Mo(η ^{5}- C_5H_4CHMe- η ^{1}–CHMe)$(CO)_3$] (**6**)

The addition of a THF (ca. 20 ml) solution of the ligand (S, S)-1, 2-Dimethyl-spiro[2, 4]hepta-4,6-diene (0.35 g, 2.9 mmol) to $Mo(CO)_3(CH_3CN)_3$ (0.80 g, 2.65 mmol) at 0° C produces an orange solution, which is stirred overnight at r. t. All volatiles are removed in vacuo, and the sticky residue is extracted with 15 ml hexane (three times) and filtered. The obtained orange red filtrates are concentrated and chromatographed on Florisil (60 – 100 mesh). The orange yellow fraction is eluted with *n*-hexane and collected. After removal of all solvent, Compound **6** is obtained as orange red oily solid. After cooling to -30 °C thermally unstable orange-red needles are afforded. Yield (1.68 g, 72%). $C_{12}H_{12}O_3Mo$ (300). calcd: C 48.00, H 4.00; found: C 48.17, H 4.18. IR (Kbr, ν cm^{-1}): 3118 (w, ν CH of Cp-ring), 2969, 2938, 2897 and 2854 (w, ν CH_3 and ν CH_2), 1999.5, 1902.4 (vs, ν CO); ^{1}H-NMR ($CDCl_3$, 400 MHz, rt): δ (ppm) = -0.07 (m, 1H, Mo-C*H*), 1.11 (d, *J* = 6.8Hz, 3H, Mo-CH-CH_3), 1.46 (d, *J* = 6.8Hz, 3H, Cp-CH-CH_3), 2.39 (m, 1H, Cp-C*H*), 5.21 (m, 1H, Cp), 5.18 (m, 1H, Cp), 5.16 (m, 1H, Cp) and 5.12 (m, 1H, Cp); ^{13}C-NMR ($CDCl_3$, 100.28 MHz, rt): δ (ppm) = 224 (*C*O), 89.90, 88.65, 87.74, 86.73, 74.26 (C_5H_4), 38.18 (Cp-*C*H), 24.41 (Cp-CH-*C*H_3), 20.79 (Mo-CH-*C*H_3), -17.48 (Mo-*C*H); ^{95}Mo-NMR($CDCl_3$, 26.07 MHz, rt): δ (ppm) = –1696; FAB-MS (70 eV) m/z (%); M^+ = 300.

10.4.2. Crystallography

Crystal structure analysis of compound **3:**[18] $C_{16}H_{12}MoO_3$, M_r = 348.20, pale yellow fragment (0.08 x 0.15 x 0.46 mm^3), orthorhombic, Pbca ba-c (No. 61), a = 7.5948(1), b = 12.7778(1), c = 28.3288(3) Å, V = 2749.16(5) $Å^3$, Z = 8, d_{calc} = 1.683 gcm^{-3}, F_{000} = 1392, μ = 0.957 mm^{-1}. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo- K_α radiation (λ = 0.71073 Å). Data collection were performed at 173 K within the Θ range of 2.2° < Θ < 25.3°. A total of 68508 reflections were integrated, corrected for Lorentz, polarization, and, arising from the scaling procedure, corrected for latent decay and absorption effects. After merging (R_{int} = 0.058), 2497 [2210: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 229 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ and converged with $R1$ = 0.0230 [$I_o > 2\sigma(I_o)$], $wR2$ = 0.0497 [all data], GOF = 1.11, and shift/error < 0.002. The final difference-Fourier map shows no striking features ($\Delta e_{min/max}$ = +0.33/-0.35 $eÅ^{-3}$).

10.4.3. Catalysis reactions with compounds 3 and 6 as catalysts

The catalytic reactions were performed under an air atmosphere, in a reaction vessel equipped with a magnetic stirrer, immersed into a thermostated bath.

Achiral catalytic epoxidation: *Cis*-cyclooctene (800 mg, 7.2 mmol), mesitylene (1g, internal standard), 1 mol % (72 μmol) of compounds **3** or **6** as catalysts were added to the reaction vessel. With the addition of TBHP (2 mL, 5.5 M-6.0 M in *n*-decane) the reaction was started. The course of the reactions was monitored by quantitative GC analysis. Samples were taken and diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate

injected into a chiral GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

Chiral catalytic epoxidation: *cis*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene (100 mg, 0.83 mmol, internal standard), and 1 mol% (17 μmol), 5 mol% and 10 mol% of the compounds **3** or **6** as catalysts and 2 mL toluene as solvent were added to the reaction vessel. With the addition of TBHP (450 μl, 7.5 M in toluene) the reaction started. The course of the reactions was monitored by quantitative GC analysis. The samples were processed as described above. The enantiomeric excess was calculated with the ratio of the peaks corresponding to both epoxides formed.

10.5. Conclusions

The ansa-bridged η^5-cyclopentadienyl-carbonyl molybdenum complexes **3**, **6** and **7** were synthesized and in the case of complexes **3** and **6**, the stereogenic centers are located on the side chain. The X-ray crystal structure of **3** shows a distorted four-legged piano stool fashion similar to that established for analogous trancarbony cyclopentadienyl molybdenum complexes. Compounds **3, 6** and **7** show a similar behaviour indicating that introduction of substitutes on the side chain between metal center and Cp ring does not influence much the electronic situation at the metal centre and therefore also not the catalytic performance. Comparison with $CpMo(CO)_3Me$, indicates that the replacement of a methyl group by a *ansa*-bridge does not very strongly influence on the overall catalytic performance, but leads to a somewhat slower reaction. This observation is probably caused by the more pronounced steric hindrance of the ansa-bridged systems. For the asymmetric epoxidation of *cis*-β-methylstyrene the chiral induction is up to 40% according to preliminary experiments, indicating that these systems may turn out to be the best among the chiral Mo epoxiation catalysts reported to date. .

10.6. References

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11. Summary

The preparation and synthetic application of both MoO_2L_3, MoO_2L_3L' and MoO_2L_4 type complexes and of compounds of general formula $CpMo(CO)_3R$ (Cp = (η^5-C_5R_5)) were achieved. They also could be heterogenized and chiral derivatives were also prepared.

Complexes of the type MoO_2L_3L' (with L = tridentate, sugar derived chiral Schiff base, L' = alcohol; see Figure 1) were prepared by the reaction of the ligands L with $MoO_2(acac)_2$ in alcohols.

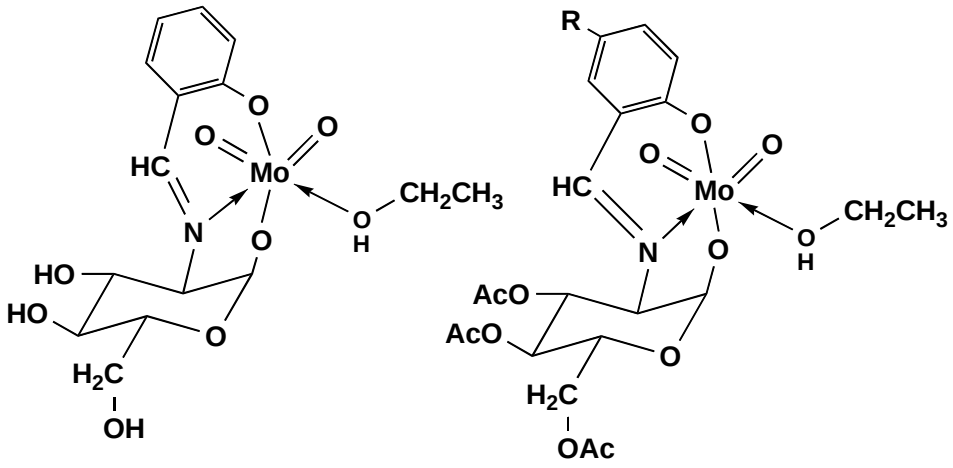

Figure 1. MoO_2L_3L' type compounds, ligated by tridentate, sugar derived chiral Schiff bases.

Depending on the position of the potential coordination sites of the ligand L, the reactions lead to selective inversion at the C1 atom of the sugar ligand in order to reach the optimal coordination geometry. When esterification is used to protect the –OH groups of the sugar ligand, Lewis acid catalyzed deacetylation takes place to allow a tridentate coordination of the ligand. The coordination of two bidentate ligands is not observed, even if the ligand size would allow it. It can be assumed that during the epoxidation catalysis, where the examined complexes can be used as catalysts, the weakly coordinating alcohol ligand is replaced by TBHP. The TOF in the beginning of the reaction is very high in the case of cyclooctene, being an easily oxidizable substrate. During the course of the reaction, however, the velocity

slows down considerably since an increasing amount of *t*-butyl alcohol (oxidation by-product) is competing for the same coordination sites as the TBHP molecules. Furthermore, a significant portion of the tiny amounts of catalyst, used to reach the high TOFs, falls victim to decomposition due to traces of water in the catalytic system. The catalytic epoxidation reaction is – as expected - much slower but nevertheless selective towards the epoxide with styrene being the substrate. In the case of the substrate cis-ß-methylstyrene moderate enantiomeric excesses of up to 30 % can be reached. The moderate enantiomeric excess may be – at least in part – be due to an ongoing ligand exchange in solution, which can be slowed down at lower temperatures. Application of very low reaction temperatures, however, nearly stops the catalytic reaction.

Based on these results, a modified compound of the same general type of MoO_2L_3L' and a tungsten derivative, namely WO_2L_3 (L_3 = tridentate, trans-2-aminocyclohexanol derived chiral Schiff base) were prepared in an analogous way as the compounds described above (see Figure 2). A comparison of the coupling constant of $J_{1,2}$ before and after coordination to the metal, indicates that there is no inversion of configuration from β to α, as it has been observed for the sugar derived Schiff base ligands, but the ligands are, dispite being tridentate, still comparatively weakly attached to the Mo center.

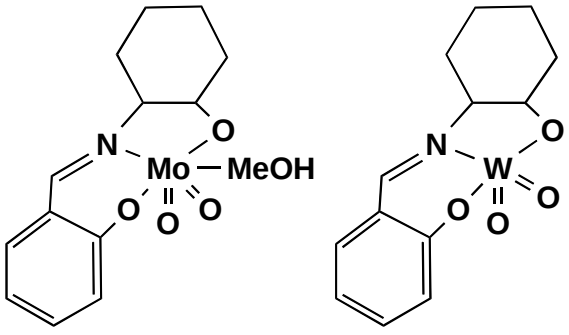

Figure 2. MoO_2L_3L' and WoO_2L_3-type compounds, ligated by a tridentate trans-2-aminocyclohexanol derived chiral Schiff base.

The Mo compounds show only moderate activity for olefin epoxidation, while the W analogue displays quite low epoxidation activity.

In order to further strengthen the ligand-metal binding and in the hope to achieve reasonably good chiral induction, optically active molybdenum (VI) dioxo complexes bearing tetrahydro salen and substituted tetrahydrosalen derivatives ligands were synthesized (general formula MoO_2L_4, for the ligands see Fig. 3) and tested as catalysts for asymmetric epoxidation. With cis-ß-methylstyrene moderate enantiomeric excesses of up to 26% could be reached at 0°C. Using a chiral amine instead of an imine improves neither the catalytic activity nor the chiral induction. Due to the fact that – as in the case of the tridentate ligands described above – only two of the coordinating ligands are connected by stronger bonds (the other interactions are weaker donor-acceptor interactions) the ligands can still partially open in solution, which may be responsible for the unsatisfying enantiomeric excesses in the product epoxides.

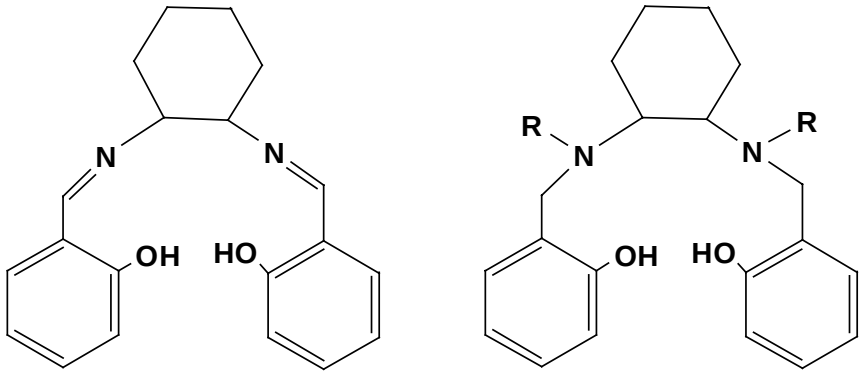

Figure 3. Tetradentate salen ligands, applied for MoO_2L_4 type compounds.

MoO_2L_4 complexes bearing substituted hydrosalen ligands were then heterogenized on the surface of mesoporous MCM-41 and MCM-48 molecular sieves as shown in Fig. 4. The obtained heterogenized compounds were found to be applicable for asymmetric epoxidation of *trans*-ß-methylstyrene and *cis*-ß-methylstyrene, with optical inductions similar to the homogeneous results (ees of up to 31%). The catalytic activity remains virtually unchanged throughout several recycling experiments

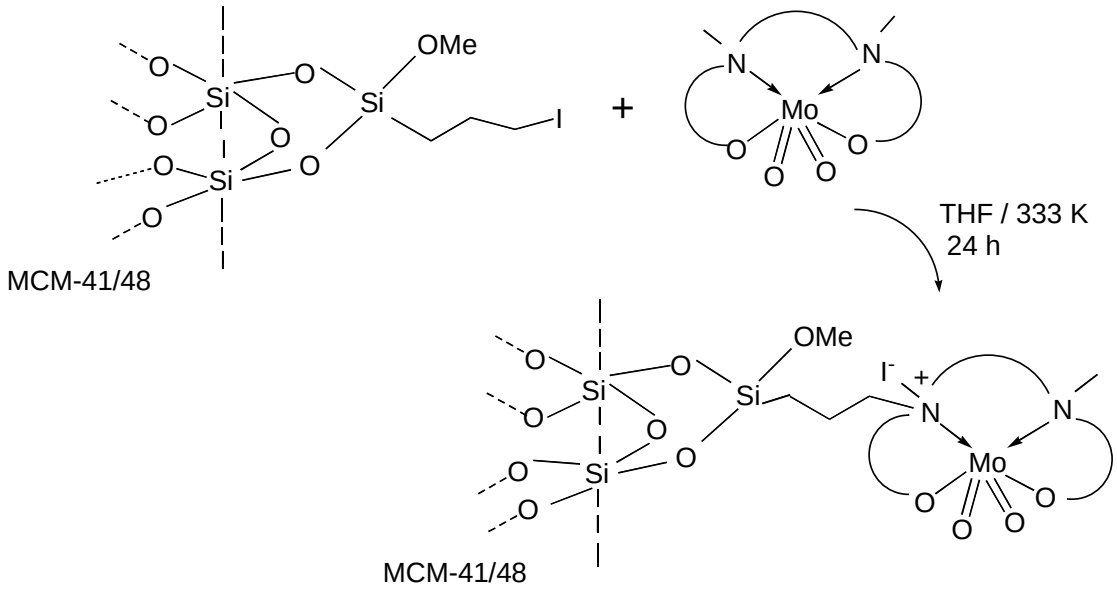

Figure 4. Heterogenization of MoO_2L_4-type compounds.

These results demonstrate the good heterogenizability of these compounds and their stability on the surface (no significant leaching was observed). On the other hand, however, they show that such compounds are not the best choice for chiral catalysis, due to the comparatively low enantiomeric excesses being obtained.

In continuation of the work performed on the synthesis and application of $CpMoO_2Cl$ systems, the precursor compounds for the derivatives of formula $CpMoO_2R$, compounds of composition $CpMo(CO)_3R$ (and also W derivatives) were prepared (for an example see Figure 5). The application of these metal carbonyl complexes directly in epoxidation catalysis showed that they are in situ transformed (by an oxidative decarbonylation) to the catalytically active Mo(VI) congeners. Isolation of these more sensitive oxo and peroxo compounds prior to application in catalysis proved to be unnnecessary, avoiding also material losses. This oxidation, however, does not include the loss of the Cp' and the R ligand, comparable to the situation observed for $Cp'Mo(CO)_3Cl$ complexes. The activity and selectivity of the catalysts is high and they can be reused several times without significant decomposition. The by-

product of the oxidation, *t*-BuOH hampers the catalytic reaction with increasing concentration, as it is known for other Mo(VI) oxidation catalysts (see also above).

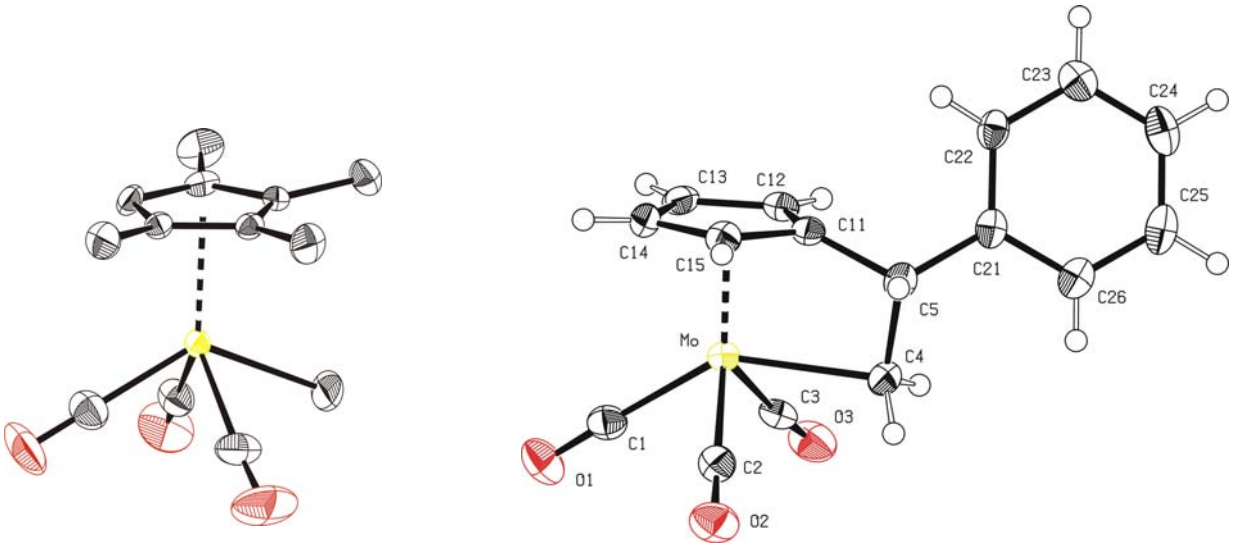

Figure 5: X-ray structure of $(C_5(CH_3)_4H)Mo(CO)_3(CH_3)$ (left side) and of a chiral, ansa-bridged derivative.

It was also possible to synthesize ansa-bridged derivatives, including a chiral derivative (see Figure 5, right structure). Experiments indicate, that the chiral derivative allows higher enantiomeric excesses than the above described MoO_2L_3 and MoO_2L_4 derivatives.

The heterogenation of $CpMo(CO)_3X/R$ complexes was also attempted. Several different methods were applied:

1) Simple grafting of $CpMo(CO)_3Cl$-type compounds (see Figure 6).

2) Synthesis of compounds of the type $(R'O)_3Si\text{-}(CH_2)_n\text{-}(C_5H_4)Mo(CO)_3R$ and $(R'O)_3Si\text{-}(CH_2)_n\text{-}Mo(Cp)(CO)_3$. These complexes were directly reacted with the surface materials to obtain products as described in Figure 7.

All applied materials were fully characterized, the metal loading was determined and the materials were applied as heterogeneous catalysts. All materials were stable against leaching. The achieved loading for the case 1 (< 1 mol% Mo in the materials), however, was much lower than for the other cases (up to 8 % mol% Mo in the materials).

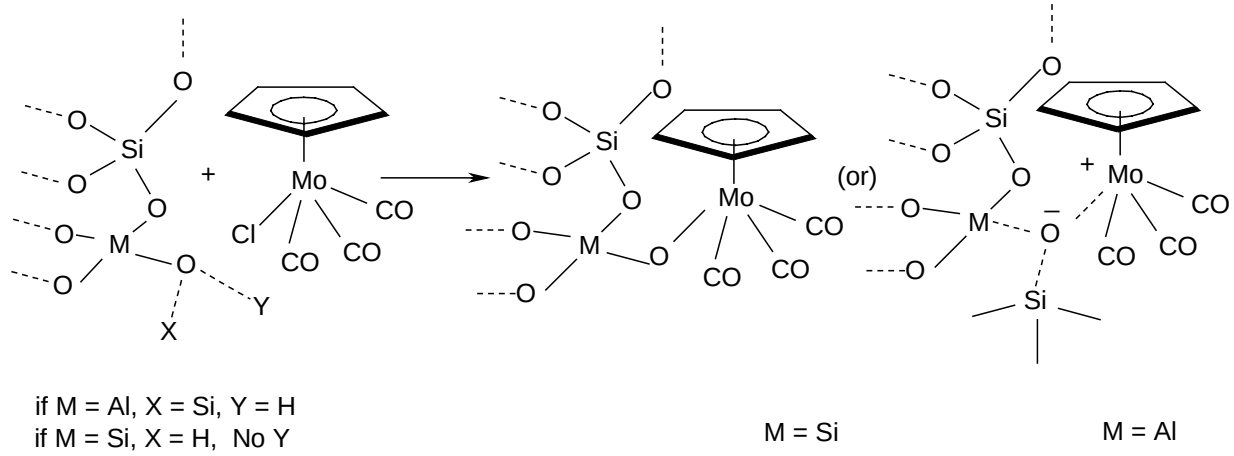

Figure 6. Heterogenization of $CpMo(CO)_3Cl$ by simple grafting.

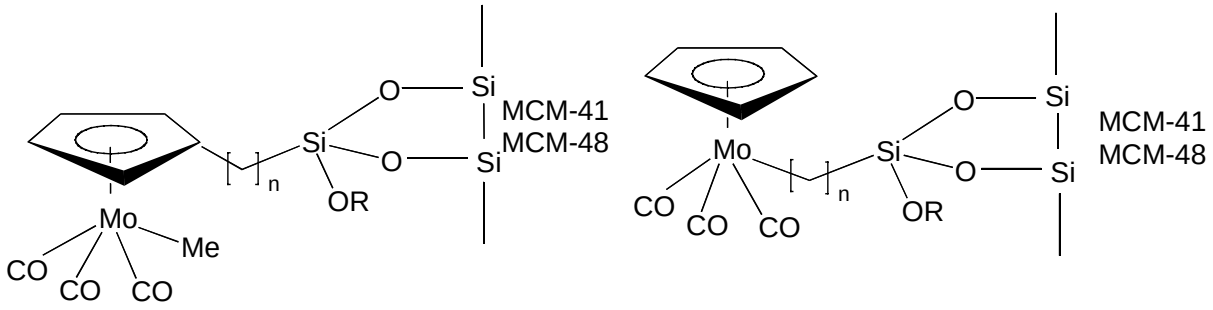

Figure 7. Surface bonding of $(R'O)_3Si\text{-}(CH_2)_n\text{-}(C_5H_4)Mo(CO)_3R$ and $(R'O)_3Si\text{-}(CH_2)_n\text{-}Mo(Cp)(CO)_3$ type compounds.

The catalytic activity, however, as well as the selectivity were quite good in all cases and similar to the homogeneous systems. The highest obtained turnover frequencies were well above 50000 mol/(mol x h). These results place the systems described in this work among the most active olefin epoxidation systems based on organometallic catalysts described in the literature to date.

Additionally, complexes of the type $CpMo(CO)_3X/R$ (X = Cl, R = Me, Cl), have been examined for their catalytic performance in olefin epoxidation in systems containing room temperature ionic liquids (RTILs) of composition $[BMIM]NTf_2$, $[BMIM]PF_6$, $[C_8MIM]PF_6$,

and [BMIM]BF_4 (Figure 8). It was found that the catalytic performance for cyclooctene epoxidation in the presence of RTILs depends strongly on the water content of the system, the catalyst solubility in the RTIL, and the reaction behaviour of the RTIL under the applied reaction conditions. The catalysts can be recycled without significant loss of activity when a reaction system containing [BMIM]NTf_2 and [BMIM]PF_6 in a 4:1 relationship is used. High proportions of [BMIM]PF_6 lead to a ring opening reaction (diol formation), due to HF formation and the presence of residual water.

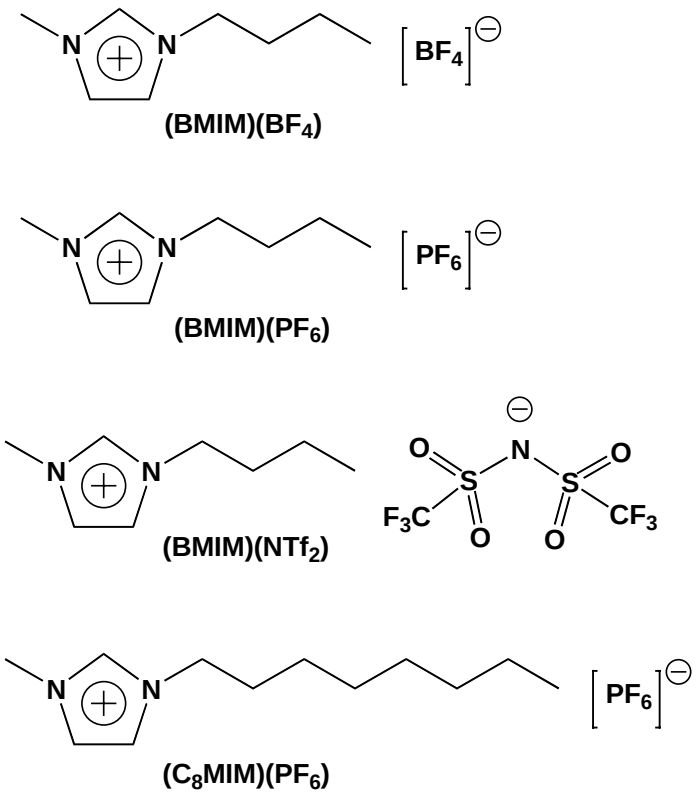

Figure 8. Room temperature ionic liquids, which have been examined as co-solvents for $CpMo(CO)_3X/R$ derived catalysts in the olefin epoxidation.

Curriculum Vitae

Name:	Jin Zhao
Date of Birth:	4. December, 1970,
Place of Birth:	Shenyang, Liaoning Province, P. R. China
Nationality:	Chinese
Civil Status:	Married to Weisong Zhao
Sept. 1977-July 1982	The Guilin Primary School of Shenyang, P. R. China
Sept. 1982-July 1985	The 106th Middle School of Shenyang, P. R. China
Sept. 1985-July 1988	The Twentith High School of Shenyang, P. R. China
Sept. 1988-July 1992	Study of Chemistry for Bachelor Degree at Liaoning University, Shenyang, P. R. China
Sept. 1992-July 1995	Study of Condensed State Physics for Master Degree at the Changchun Physics Institute, Chinese Academy of Science, Changchun, P. R. China
Aug. 1995-Sept. 2000	Research Assistant and lector at the Department of Chemistry of Liaoning University, Shenyang, P. R. China
Sept. 2000- May 2001	Learning German in the Deutsch-Kolleg at the Tongji University, Shanghai, P. R. China
June 2001-Oct. 2001	Learning German at the Goethe-Institut, Goettingen, Germany
Oct. 2001- Feb. 2005	Ph.D. at the Technische Universität München under supervision of Priv. -Doz. Dr. F. E. Kühn in the group of Prof. Dr. Dr. h. c. mult. W. A. Herrmann

Foreign Languages:

English:	Passed the WSK (PETS5, as a state foreign language qualification examination for the application of study abroad) on 9. Sept. 1999
German:	Passed the DSH on 22. Sept. 2001