Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 16 (2005) 3469–3479

Tetrahedron: *Asymmetry* report number 88

Chiral monomeric organorhenium(VII) and organomolybdenum(VI) compounds as catalysts for chiral olefin epoxidation reactions

Fritz E. Kühn,* Jin Zhao and Wolfgang A. Herrmann*

Lehrstuhl für Anorganische Chemie der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany

Received 1 August 2005; accepted 13 September 2005
Available online 11 November 2005

Abstract—Several attempts have been made to transform the organometallic Re(VII) compound MTO and the $(MoO_2)^{2+}$ moiety to chiral epoxidation catalysts by addition of chiral organic ligands. Being very efficient epoxidation catalysts in achiral reactions, it was hoped that these compounds could be transformed into chiral epoxidation catalysts by adding chiral Lewis base ligands. The major flaw of most of these attempts, however, was the weak coordination of the chiral Lewis base ligands to the metal center, which led either to high ees only at the very beginning of the catalytic reaction (low conversion) or to generally low enantiomeric excesses. The heterogenisation of the Mo(VI) complexes was, at least in some cases, successfully achieved but with the same drawbacks with respect to the ees as in the homogeneous phase. Currently, attempts are being made to synthesize organometallic Re(VII) and Mo(VI) complexes with stronger interactions between the metal containing moiety and the chiral ligand(s).

Contents

1. Introduction 3469
2. Chiral organorhenium(VII) oxides and their epoxidation capabilities 3470
3. Chiral organomolybdenum(VI) oxides and their epoxidation capabilities 3472
4. Summary and outlook 3477
References 3478

1. Introduction

Chiral epoxidations are currently of high interest for the synthesis of non-racemic chiral intermediates in the pharmaceutical and chemical industry to generate enantiomerically pure products.[1] In 1979, Schurig et al. achieved the enantioselective epoxidation of prochiral alkyl-substituted olefins with a Mo(VI) complex bearing a chiral ligand, but the enantioselectivity was quite low.[2] In 1980, Katsuki and Sharpless reported on the asymmetric epoxidation of allylic alcohols mediated by a titanium(IV) complex using (+)-(*R*,*R*)- or (−)-(*S*,*S*)-tartrate as chiral ligands.[3] While the enantioselectivity was very high, the titanium complex had to be applied in stoichiometric amounts. Later, a reduction of the catalyst: substrate ratio of ca. 1:20 to 1:10 was achieved and an X-ray structure of the titanium tartrate catalysts was published.[4] More recently, non-functionalized olefins have been examined as substrates for epoxidation and high enantiomeric excesses have been achieved only with chiral salene manganese(III) catalysts.[5,6]

The success of organorhenium(VII) and organomolybdenum(VI) complexes in racemic epoxides reactions,[7–11] however, led to the belief that some derivatives of these complexes could be applied as chiral catalysts. In parallel, attempts have been made to improve the catalytic performance of 'inorganic' molybdenum(VI)

* Corresponding authors. Tel.: +49 (0)89 289 13080; fax: +49 (0)89 289 13473; e-mail: fritz.kuehn@ch.tum.de

0957-4166/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2005.09.021

moieties with chiral donor ligands in order to obtain better chiral catalysts.

This review summarizes the attempts to achieve chiral olefin epoxidation catalysts based on Re(VII) and Mo(VI) system, with a special emphasis on classical organometallic compounds, that is, complexes containing at least one M–C bond.

2. Chiral organorhenium(VII) oxides and their epoxidation capabilities

The success of the organorhenium(VII) oxides as olefin epoxidation catalysts started with the preparation of methyltrioxorhenium(VII) (MTO, see Fig. 1) by Herrmann et al.[12] Although the compound was already known previously from the work of Beattie and Jones,[13] only the straightforward and high yielding preparation published in 1988,[12] and its further improvements during the following years,[14–17] enabled a detailed examination of the reaction chemistry and the potential catalytic applications of MTO. It was quickly discovered that MTO is an extremely efficient olefin epoxidation catalyst in the homogeneous phase.[18] Particularly, important steps were the isolation of one of the catalytical active species[19] formed by the reaction of MTO with hydrogen peroxide and the kinetic examination of the MTO catalyzed olefin epoxidation.[20,21] While it was also found that derivatives of cyclopentadienyltrioxorhenium(VII)[22] are either not soluble or not reactive enough[25] to be successfully applied as catalysts, alkyl-,[23,24] alkenyl-,[25] alkynyl-,[26] and aryl-derivatives[27–30] of MTO seemed to have higher potential in this field. However, most of these complexes are either thermally unstable or difficult to obtain in good yields. Therefore, different approaches were chosen to get to chiral organorhenium(VII) oxides.

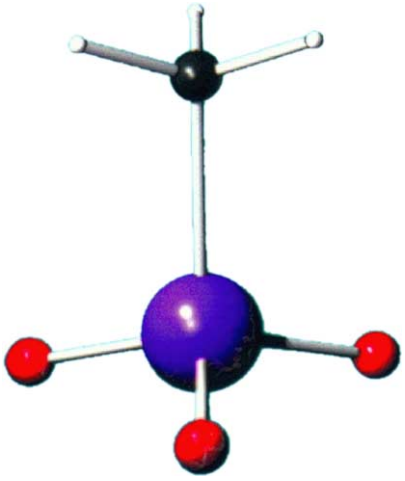


Figure 1. Methyltrioxorhenium(VII) (MTO).

The first fully characterized derivative of MTO was described in the literature in 1997.[31] An adduct of Töger's base [(5*R*,11*R*)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[*b*,*f*]-[1,5]diazocine] was synthesized by simple reaction of Tröger's base with MTO in diethyl ether at −45 °C (Fig. 2 and Eq. 1). However, as could already be assumed from the quite long Re–N bond distance [258.9(5) pm], the interaction between the chiral N-base ligand and MTO is weak. The ^{1}H, ^{13}C, and ^{17}O NMR spectra, recorded in $CDCl_3$ solutions of the MTO-Tröger's base adduct clearly showed an equilibrium between free MTO and the adduct, with free MTO being the far more dominant species even at low measurement temperatures. Accordingly, when applying these compounds in the catalysis of prochiral olefins, no enantiomeric excesses could be found. Nevertheless, the

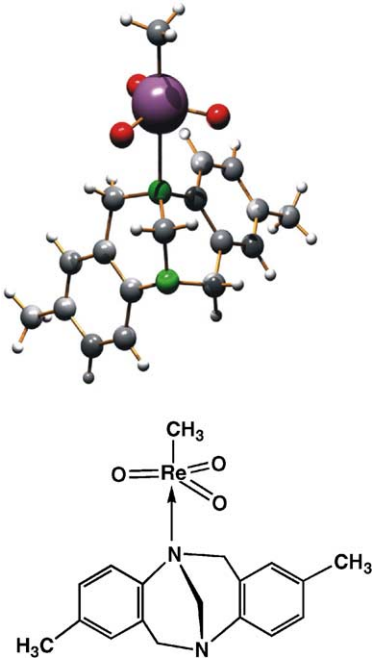
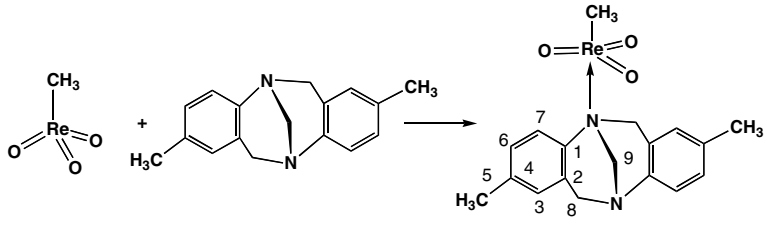
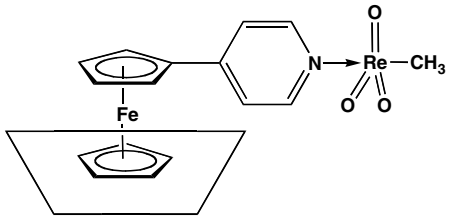


Figure 2. The adduct of MTO with Tröger's base [(5*R*,11*R*)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[*b*,*f*]-[1,5]diazocine], the first chiral derivative of MTO characterized by X-ray crystallography.[31]



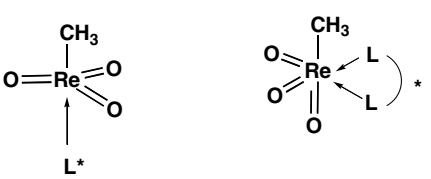
(1)

approach of adding a Lewis base to MTO was found to be an important improvement for MTO catalyzed olefin epoxidations. Applying a 10–12-fold excess of (non-chiral) Lewis base led to an activity increase and a considerable reduction of diol byproduct formation, even in the case of the most sensitive olefins.[32–38] The labile Re–N interactions, even in the case of bidentate Lewis bases, were considered as the main reason for these systems being unsuccessful in chiral applications. Either complexes with more stable Re–N interactions had to be prepared or significant excesses of often comparatively expensive chiral Lewis bases were required for successful application. Since the regio- and diastereoselective catalytic epoxidation of acyclic allylic alcohols with MTO as the catalyst had been achieved by applying urea hydrogen peroxide (UHP) and zeolite lattices,[39,40] the heterogenization of MTO attached to a ferrocenylpyridine linker on β-cyclodextrine (β-CD) was attempted in order to obtain a chiral environment around MTO (Scheme 1).[41] The monodentate ferrocene derivative adheres to an inclusion model in which the ferrocene penetrates deeply into the β-CD cavity in an axial mode, while the MTO substituent protrudes out. Also while both 1,1-bis(4-pyridinylethinyl) ferrocene and ferrocene-4-pyridylacetylene form stable adducts with MTO,[42] the inclusion complex with β-CD was not active as a catalyst for the heterogeneous epoxidation.[41]

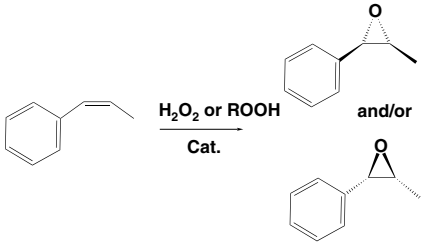


Scheme 1.

Another attempt to utilize chiral N-base adducts of MTO as catalysts in chiral epoxidation was made by Corma et al.[43] (*S*)-2-Aminomethylpyrrolidine, (*R*)-(+)-phenyl ethylamine, and L-prolinamide were used as chiral ligands (Scheme 2). The enantiomeric excesses obtained with *cis*-β-methylstyrene (Eq. 2), 1-methylcyclohexene and α-pinene, respectively, as substrates and hydrogen peroxide as the oxidant at −5° → −55 °C were between 4% and 36% with conversions between 9% and 59%. Unfortunately, the highest enantiomeric excesses were not associated with the highest conversions (the highest values of ca. 36% ee were reached with *cis*-β-methylstyrene as the substrate and (*R*)-(+)-1-phenylethylamine as the catalyst:oxidant ratio of 1:100 in CH_2Cl_2 at −5 °C with conversions of ca. 10% and a reaction temperature of −5 °C after 7 h). Based on ^1H NMR experiments performed at low temperature (down to −40 °C), it was argued that a weak base ligand-MTO coordination, resulting in incomplete MTO coordination did not seem to be the reason for the unsatisfactory ees obtained. Instead 'intrinsical stereochemical features of the newly formed chiral complex'[43] were deemed responsible.

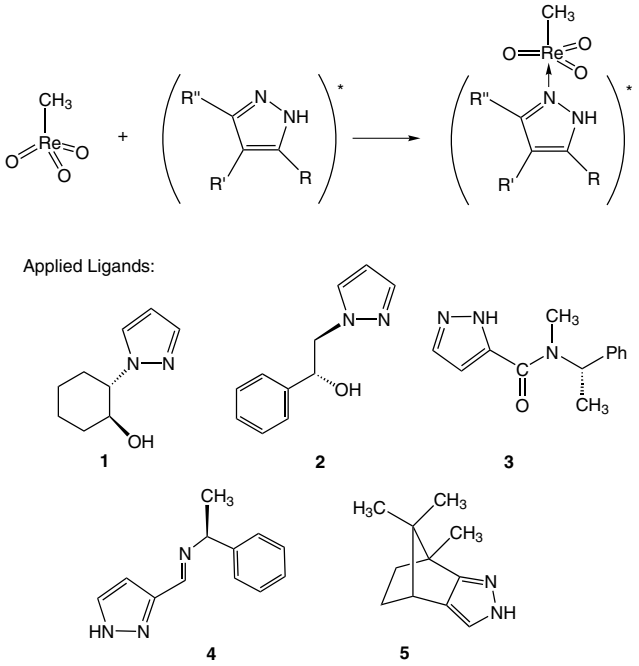


Scheme 2.



(2)

More recently, chiral Lewis base ligands based on pyrazole (Scheme 3, **1**–**5**) have been applied as ligands for MTO (Scheme 3, Table 1). Again, the ees obtained with *cis*-β-methylstyrene were quite low (6–27%) and associated with low conversions (6–22%). As in the case described above, the highest ees were usually associated with the lowest conversions.[44] The weak coordination of the Lewis base ligand was assumed to be the reason for the unsatisfactory performance of the catalyst molecules. Glycolate complexes of MTO (Scheme 4, **6**–**15**) were found to reach somewhat higher enantiomeric excesses (up to 41%), but the conversions remained low (5–30%). In this case, the sensitivity of the catalyst to water induces ligand removal as well as ligand exchange with other diols.[44] The epoxidation reactions were conducted in all cases below 0 °C (Table 2).

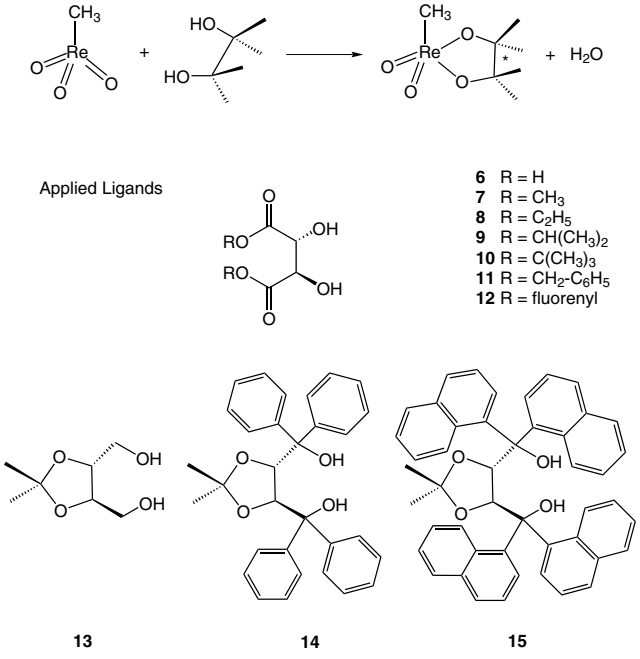


Scheme 3.

Table 1. Application of chiral pyrazole based ligands in the catalytic epoxidation of *cis*-β-methylstyrene with MTO/H_2O_2 in CH_2Cl_2[44]

Ligand	Conversion (%)	Enantiomeric excess (ee)
1	6	27
2	9	12
3	14	10
4	22	15
5	22	6

The reaction was carried out at −30 °C with a catalyst:substrate: oxidant ratio of 1:100:200. The ligand:MTO ratio was 12:1. The conversions are listed for a reaction time of 1 h. The numbering of the ligands refers to Scheme 3.



Scheme 4.

Table 2. Application of chiral diols in the catalytic epoxidation of *cis*-β-methylstyrene with MTO/H_2O_2 in CH_2Cl_2[44]

Diol applied	Conversion (%)	Enantiomeric excess (ee)
6	30	5
7	0	0
8	10	11
9	5	18
10	7	15
11	10	15
12	8	16
13	5	41
14	5	15
15	5	14

The reaction was carried out at −25 °C, with a catalyst:substrate: oxidant ratio of 1:100:150. The ligand to MTO ratio was 12:1. The conversions are given after 1 h reaction time. The numbering of the ligands refers to Scheme 4.

There have been claims presented in a patent[45] that MTO and (*S*)-1-phenyl-1-dimethylaminoethane could be applied to yield 22% of the epoxide in 86% enantiomeric excess after a 4 h reaction time in a catalytic epoxidation reaction. These results, however, have to be taken with some care as they could not be reproduced with any prochiral substrate in our laboratories. Furthermore, similar results have, to the best of our knowledge, not been published in a refereed scientific journal.

3. Chiral organomolybdenum(VI) oxides and their epoxidation capabilities

The application of chiral molybdenum(VI) complexes in olefin epoxidations dates back some years before the application of MTO and its derivatives. The interest in molybdenum-based olefin epoxidation catalysts is quite old and closely associated with the application of homogeneous Mo(VI) catalysts in the Halcon and Arco processes.[46,47] However, most of the chiral Mo(VI) complexes are not organometallic in a strict sense, that is, they do not contain a Mo–C bond. For the $Mo(VI)O_2$ moiety, however, a broad variety of ligand sets have been applied usually using bidentate, tridentate, or tetradentate chiral ligands. Some of these ligands were chiral, but the number of papers where such chiral compounds have been applied for chiral olefin epoxidation is nevertheless quite limited. To the best of our knowledge, not a single Mo compound containing a Mo–C bond has yet been applied in chiral olefin epoxidation reaction as the catalyst. Therefore, we give herein a brief overview on the work dedicated to Mo(VI) oxo complexes, which contain one or more chiral ligands, but which are not connected to the metal by a Mo–C bond.

Molybdenum(VI) complexes with different types of chiral ligands, among them diisopropyltartrates, lactamides and several other hydroxyacid amides have been applied in chiral epoxidations already in the 1970s and 1980s.[2,48–52] *N*-Alkyl ephedrines,[48] methyl pyrolinols,[49] and diisopropyl tartrates were among the ligand species applied. The enantiomeric excesses obtained, however, were low. One of the difficulties in this area was the development of suitable chiral ligands that are stable to oxidation and straightforward to synthesize, with the possibility of changing electronic and steric characteristics by simple variation of the ligand starting material. One class of ligands that meets these pre-requisites are 2′-pyridyl alcohols, which are readily accessible by the reaction of 2-lithiopyridine with either symmetrical or unsymmetrical ketones.[53,54] Molybdenum complexes of the type MoO_2L_2 (L = 2′-pyridinyl alcoholate) (and their W derivatives) were found to be useful catalysts for the epoxidation of unfunctionalized olefins using organic hydroperoxides or molecular oxygen as oxidants.[55,56] Applying 2-[(-)-menthol-pyridine] as the chiral ligand L (see Chart 1, formula **A**) attached to MoO_2L_2 led to a conversion of ca. 20% and an ee of 25% in the case of 1-hexene as a substrate.[57] Using the chiral monoterpenes (+)-camphor, (−)-camphor, (−)-fenchone, and (−)-menthone as synthetic ligand precursors (Chart 1, formulae **B**–**D**), enantiomerically pure 2′-pyridinyl alcoholates could be obtained (Chart 1, formula **E**, Fig. 3, Table 3) and were applied as chiral N,O-ligands in molybdenum(VI) complexes, which exhibited good catalytic activity and substantial asymmetric induction in the epoxidation catalysis of *trans*-

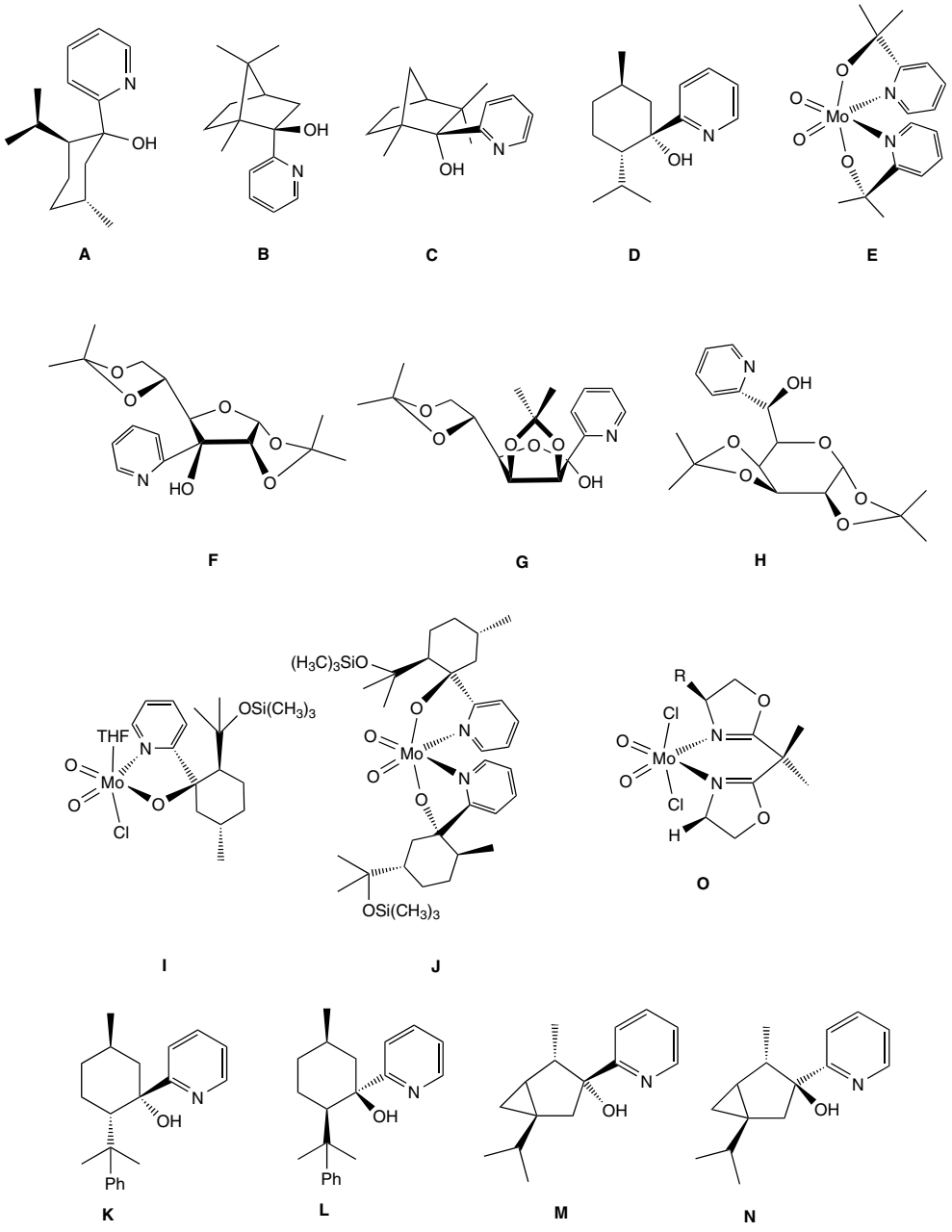


Chart 1.

methylstyrene.[58] Chiral 2′-pyridinyl alcohols (Chart 1, formulae **F**–**H**, Fig. 3b) derived from isopropylidene-protected carbohydrates were also used as ligands for the MoO_2 moiety. The usual precursor for such reactions is $MoO_2(acac)_2$. Using TBHP (*tert*-butylhydroperoxide) or cumylhydroperoxide (Table 3), respectively, as the oxidant and *trans*-β-methylstyrene as the substrate ees of up to 23% with conversions between 20% and 58% have been reached at reaction temperatures of 50–70 °C. The higher ees were reached with cumylhydroperoxide.[59] Gonçalves et al. reported further on the comparison of Mo(VI) dioxo complexes ligated by one or two pyridyl alcoholate ligands (see Chart 1, formulae **I**, **J**) applied also for olefin epoxidation.[60] The monosubstitute complex was found to be more active than the complex bearing two chiral ligands (reaction conditions: 55 °C, catalyst:substrate 1:100, 24 h, solvent decane). In spite of being chiral, both complexes do not discriminate between enantiomerically pure forms of the substrates α-pinene and limonene. Ring opening activity was observed for α-pinene oxide, producing campholenic aldehyde and epoxy campholenic aldehyde.

Another class of chiral chelating ligands that seems to meet the requirements for being utilized for the purposes outlined here are the C_2-symmetric bis(oxazolines), which are easily prepared from readily available amino alcohols.[61] A broad variety of complexes containing the $(MoO_2)^{2+}$ moiety, being ligated either by a tetradentate bis(oxazoline) ligand (Chart 1, formula **O**, R = ^{i}Pr,

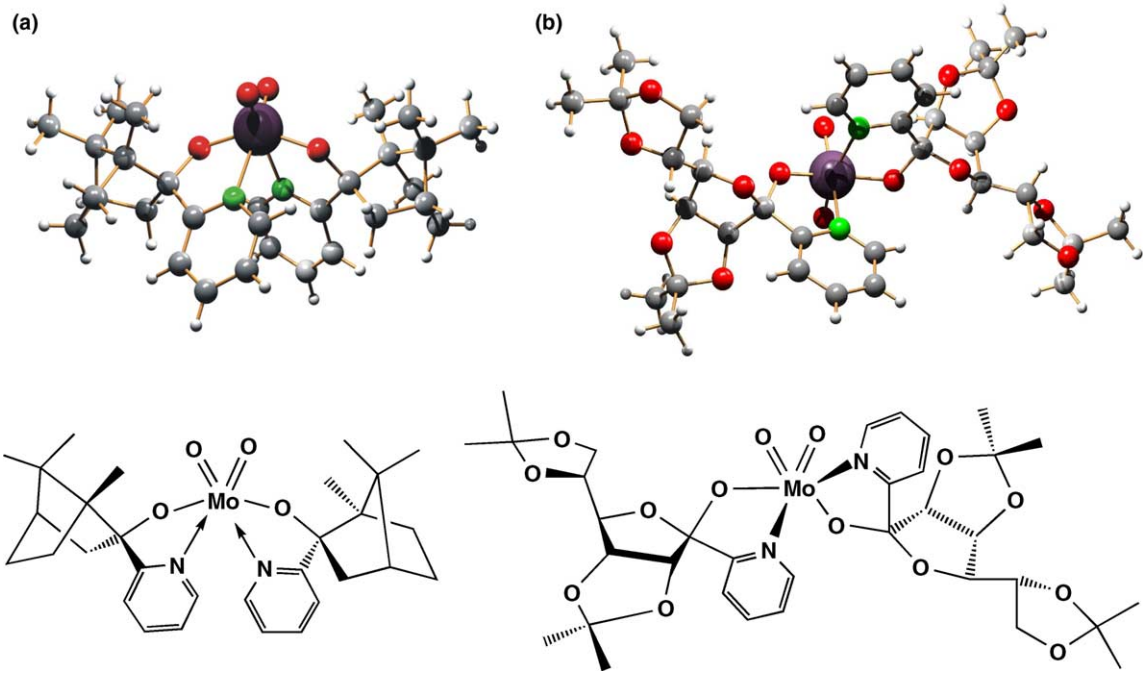


Figure 3. (a) The X-ray crystal structure of MoO_2[(+)-campy]$_2$ [(+)-campy = (1*R*,2*R*,4*R*)-1,7,7-trimethyl-2-(2′-piridinyl)bicyclo[2.2.1]hetptan-2-ol] as ball-and-stick model;[58] (b) The X-ray crystal structure of MoO_2[(manpy)]$_2$ [(manpy) = (1*S*)-1-(2′-pyridinyl)2,3:5,6-di-*O*-isopropyliden-D-mannofuranose] as ball-and-stick model.[59]

Table 3. Application of the ligands **B**–**D** in Mo(VI) complexes of type **E** in the catalytic epoxidation of *trans*-β-methylstyrene with TBHP as the oxidant in $CHCl_3$[58]

Chiral ligand (complex type)	Conversion (%)	Enantiomeric excess (ee)
B (**E**)	76	26
C (**E**)	71	15
D (**E**)	81	4
F (**E**)	38	0
G (**E**)	29	8
H (**E**)	32	7
K (**I**)	66	2
L (**I**)	75	16
M (**I**)	59	12
N (**I**)	81	11
N (**J**)	51	23

The reaction was carried out at 50 °C, with a catalyst:substrate ratio of 1:100. The conversions are given after 16 h reaction time. For the complexes of formula **E** bearing ligands **F**–**H**, under otherwise identical conditions, the conversions and ees are given after 6 h reaction time.[59] For the complexes of the type **I** and **J**, bearing ligands **K**–**N**, 55 °C reaction temperature, 4 h reaction time and toluene as solvent have been applied.[62]

^{t}Bu, Ph), containing a $C(CH_3)_2$ bridge or by two bidentate pyridyl alcoholate ligands (similar to those described in the previous section, see Chart 1, formulae **K**–**N**) was synthesized by Romão et al. and applied to the epoxidation of *trans*-β-methylstyrene. The catalytic reactions were performed with TBHP as oxidant and at reaction temperatures of 55 °C.[62] The bis(oxazoline) complexes showed good catalytic activities (up to 86% conversion) but had very low enantiomeric excesses (4–6%). Complexes of the type $MoO_2Cl(THF)L^*$ (L^* = chiral 2′-pyridyl alcoholate, Chart 1, **I**), which were examined for the sake of comparison, also exhibited high catalytic activity (up to 81% conversion within 16 h) and enantiomeric excesses up to 18%. Complexes with two chiral 2′ pyridyl alcoholate ligands, similar to those described by Herrmann et al.[58] (see above), were found to yield comparable results with respect to the enantiomeric excesses of those with only one chiral 2′ pyridyl ligand (ees up to 23%) although the conversions

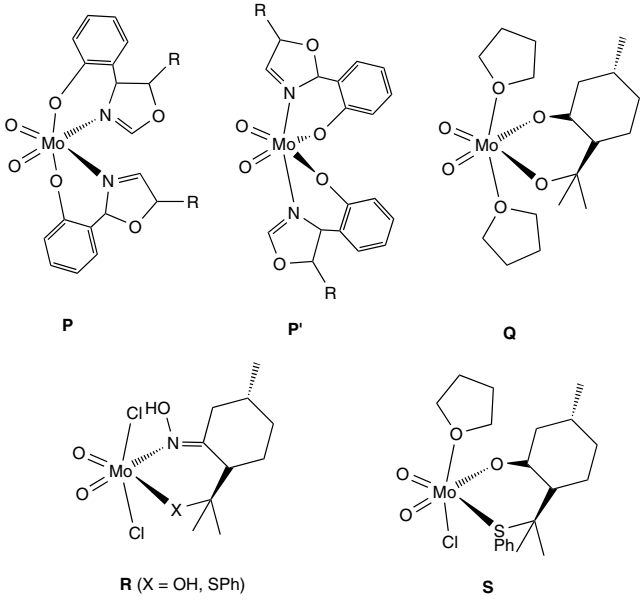
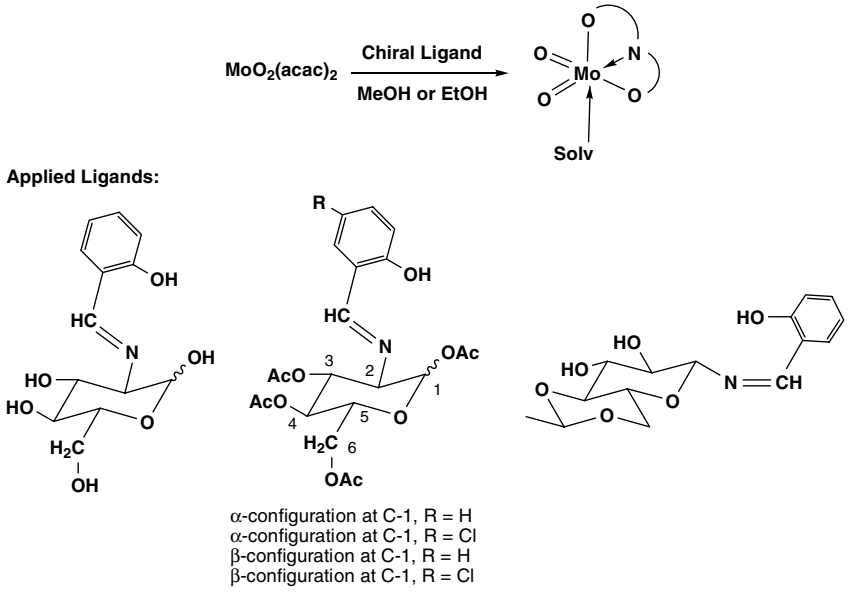


Chart 2.

obtained were somewhat lower (ca. 50% after 16 h). Soon afterwards, Teruel et al. also applied chiral oxazoline ligands attached to the $(MoO_2)^{2+}$ building block.[63] In contrast to the work mentioned above,[62] the oxazolines applied in this work were not linked by a bridge, but were attached to the metal by an additional covalent Mo–O bond (Chart 2, formulae **P** and **P′**, showing the N-*cis* and N-*trans* isomers, R = Et, ^{i}Pr). Therefore, two (bidentate) oxazolines are connected to the molybdenum atom. Using styrene as a substrate, toluene as solvent and TBHP as the oxidant conversions of 25–30% could be reached within 18 h at 35 °C. The selectivity toward the epoxide was, however, low (<50%) and the enantiomeric excess negligible (ca. 2%). In further work, Teruel et al. described that the good activity and low enantioselectivity (with (*R*)-limonene as the substrate) of the oxazoline ligated complexes originate from the lability of the two oxazoline ligands, not being strongly attached to the metal center. Based on X-ray crystallography and NMR spectroscopy, they proposed a reaction mechanism for olefin epoxidation catalyzed by seven-coordinate molybdenum species containing hemilabile ligands.[64] Oxazolinylpyridine ligands, found to be non-labile, were described as enabling a better stereoselective control in the catalyzed organic reaction. Sing et al. also synthesized transition metal complexes containing bidentate oxazoline ligands among them also a chiral Mo(VI) dioxo compound[65] identical to the one described by Teruel et al. (see above). Tested in catalysis at room temperature, the performance of the Mo(VI) catalyst, however, was not good [after 24 h at room temperature, catalyst:substrate (styrene):oxidant 1:40:60, solvent toluene[65]].

Chiral dioxomolybdenum(VI) complexes of the types $MoO_2Cl_2(L^*)$ (L^* = oxime), $MoO_2(THF)_2L^*$ (L^* = *cis*-*p*-menthane-3,8-diol) and $MoO_2Cl(THF)L^*$ (L^* = 8-phenylthioneomenthol and 8-phenylthioisoneomenthol) have been prepared, starting from $MoO_2Cl_2(THF)_2$ by the reaction with the appropriate ligands (See Chart 2, formulae **Q**–**S**). After 3 h reaction time, conversions between 63% and 82% of the substrate cis-β-methylstyrene were reached with TBHP being the oxidizing agent in toluene at 55 °C. The enantiomeric excesses, however, were very low in most cases, amounting to 24% in the best case (formula **Q**) at 72% conversion.[66]

The first sugar derived chiral ligand attached to the $(MoO_2)^{2+}$ moiety was reported by Rao et al.[67] and more compounds of formula $MoO_2(L^*)$(Solv) (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 see Scheme 5 and Fig. 4) were prepared, starting from $MoO_2(acac)_2$ and applied in olefin epoxidation by Kühn et al.[68] Depending on the position of the potential coordination sites of the ligand L, the reaction led to selective inversion at C1 of the sugar ligand in order to reach an optimal coordination geometry. When esterification was used to protect the –OH groups of the sugar ligand, Lewis acid catalyzed deacetylation took place to allow a tridentate coordination of the ligand. The coordination of two bidentate ligands was not observed, even if the ligand size would allow it, as in the case of a non-protected ligand. It was assumed that during the epoxidation catalysis, where the examined complexes were used as catalysts, the weakly coordinating alcohol ligand was replaced by TBHP. The TOF at the beginning of the reaction was reported to be quite high in the case of cyclooctene as the substrate. During the course of the reaction, however, the velocity slowed down considerably. It had been assumed that an increasing amount of *tert*-butyl alcohol was competing for the same coordination sites as the TBHP molecules. Furthermore, a



Scheme 5.

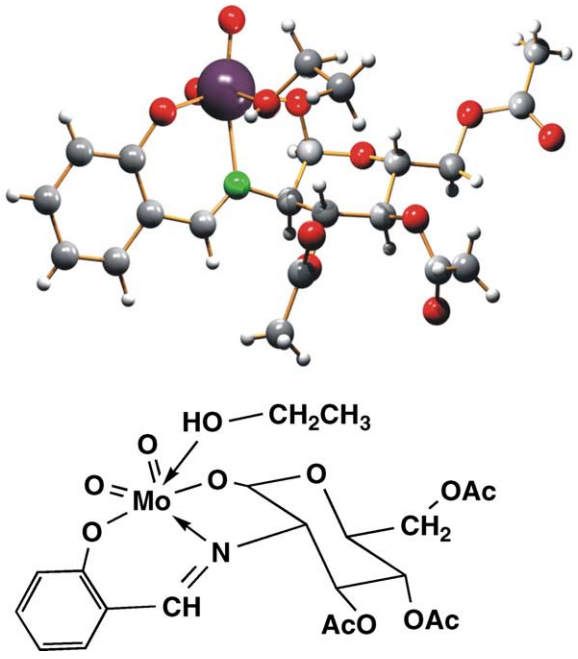
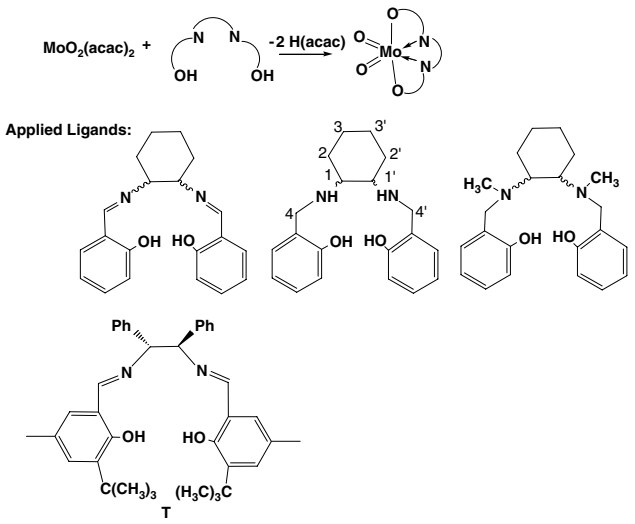


Figure 4. The X-ray crystal structure of $MoO_2(L^*)$(Solv) (with L = *N*-salicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine, Solv = ethanol) as ball-and-stick model.[68]

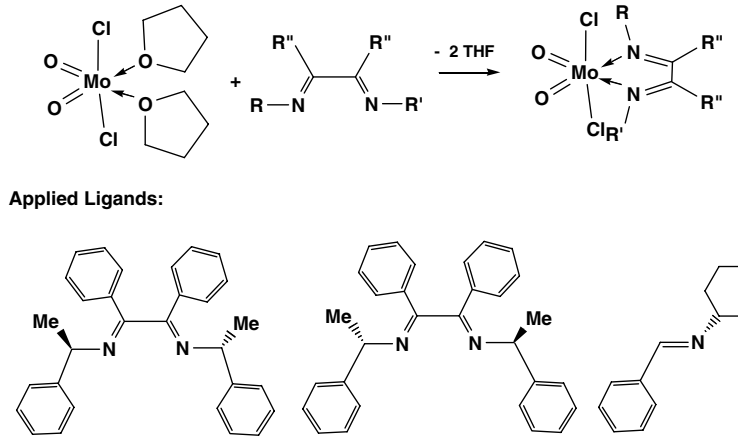


Scheme 6.

significant portion of the tiny amounts of catalyst, used to reach the high TOFs, probably fell victim to decomposition due to traces of water in the catalytic system. The catalytic olefin epoxidation reaction was observed to be much slower with styrene as the substrate, but in the case of *cis*-β-methylstyrene moderate enantiomeric excesses of up to 30% could be reached (in toluene at 0 °C after 24 h with catalyst:substrate:oxidant ratio being 1:100:200). The moderate enantiomeric excesses were assumed to be (at least in part) due to an ongoing ligand exchange in solution, which could be slowed down only at lower temperatures.

Another approach to achieve good enantioselectivities in the chiral epoxidation with Mo(VI) species led to the application of tetradentate chiral salen ligands. Although Mo(VI) dioxo complexes have been prepared and spectroscopically characterized already more than 20 years ago[69–71] it has only been very recently that chiral derivatives have been applied for chiral catalytic reactions.[72–74] Kühn et al. prepared $MoO_2(L^*)$ complexes, with L^* being a tetradentate chiral Schiff base (Scheme 6).[72] In the case of *cis*-β-methylstyrene being the substrate moderate enantiomeric excesses of up to 26% were reached at 0 °C in toluene after 4 h. Shi et al. applied both a chiral tetradentate Mo(VI) compound of formula $MoO_2(L^*)$ and systems containing two bidentate pyridinyl alcoholate ligands (as described above) for the asymmetric epoxidation of *cis*-1-propenylphosphonic acid with 30% aqueous hydrogen peroxide affording (1*R*,2*S*)-(−)-(1,2)-epoxypropyl phosphonic acid 74. It was found that the reaction was strongly dependent on the ligands, the reaction temperature and the solvent. In methylene chloride at 0 °C for 72 h one of the 2′-pyridinyl alcoholate coordinated complexes, namely MoO_2[(+)-campy]$_2$ (the X-ray crystal structure of this compound is shown in Fig. 3a) catalyzed the asymmetric epoxidation in a 100% conversion with an ee of 80%. It was assumed by the authors that the epoxidation could be described as a direct oxygen transfer occurring at the interface of the biphasic H_2O-nonprotic system.[74] The complex bearing the tetradendate salene ligand **T** was found, as with all other examined complexes, to give a better enantiomeric excess in the non-coordinating solvent methylene chloride than in ethanol solvent. The obtained enantiomeric excess was 69% at 30% conversion after 24 h reaction time.

Another attempt to obtain useful chiral epoxidation catalysts based on the $(MoO_2)^{2+}$ moiety was made by Gonçalves et al.[75] Chiral 1,4-diazabutenes (DAB) of the type R*-N=CPh–CPh=N–R* were prepared in quantitative yields by condensation of benzil with two equivalents of (*R*)-(+)-α-methylbenzylamine or (*S*)-(−)-α-methylbenzylamine, using $ZnCl_2$ as a catalyst. The chiral diimine (1*R*,2*R*)-*N*,*N*′-dibenzylidenecyclohexane-1,2-diamine was also prepared by condensation of (1*R*,2*R*)-cyclohexane-1,2-diamine with two equivalents of benzaldehyde using a Dean–Stark adapter for the removal of water. Six-coordinate dioxomolybdenum(VI) complexes of the type $[MoO_2Cl_2L]$ containing the bidentate chiral ligands were prepared (Scheme 7). The complexes were evaluated as catalysts for the asymmetric epoxidation of *cis*- and *trans*-β-methylstyrene by *tert*-butylhydroperoxide at either room temperature or 55 °C. The reactions proceeded with high retention of configuration and high selectivity to the epoxide, but only for *cis*-β-methylstyrene significant ees were obtained. With this substrate and the complex containing (1*R*,2*R*)-*N*,*N*′-dibenzylidenecyclohexane-1,2-diamine, in hand (1*S*,2*R*)-*cis*-β-methylstyrene oxide was obtained in 77% ee at room temperature (24% conversion). Increasing the reaction temperature increased the epoxide yields but good enantiomeric excesses ($\geqslant$65%) could only be achieved at low conversions ($\leqslant$12%).[75]



Scheme 7.

Concerning the attachment on solid surfaces (heterogenisation of homogeneous catalysts) of chiral complexes containing the $(MoO_2)^{2+}$ moiety, the number of recent reports is very limited. Corma et al. presented a review about the state of the art concerning the synthesis, reactions and catalytic applications of some zeolite anchored Mo complexes for epoxidising simple alkenes a decade ago.[76] A review on polymer-supported metal complexes for the alkene epoxidation was published by Sherrington some years later.[77] Corma et al. synthesized enantiopure $MoO_2(acac)L^*$, where L^* is the bidentate O,O-ligands derived from L-*trans*-4-hydroxy-proline.[78] Derivatives bearing a $Si(OEt)_3$ group were heterogenized by anchoring into modified USY zeolites. According to elemental analyses, the metal loading on modified zeolite USY was ca. 1%. The compounds have been, however, applied solely for the epoxidation of allylic alcohols. At room temperature, conversions of up to 93% and enantiomeric excesses of up to 47% have been reached for geraniol being the substrate and conversions up to 98% and ees of up to 64% for nerol after reaction times of 3–4 h. Catalyst leaching was not significant.[78]

Optically active molybdenum(VI) dioxo complexes bearing hydrosalen derivatives as ligands were also grafted on surfaces, in this case on MCM-41 and MCM-48. The heterogenization was achieved by reacting a surface fixed linker molecule (synthesized with a trimethoxyiodo propyl silane), bearing a $R\text{-}CH_2I$ end group with one of salene nitrogen atoms.[79] The heterogenized complexes were found to be applicable for asymmetric epoxidation of *trans*-β-methylstyrene and *cis*-β-methylstyrene with enantiomeric excesses up to 31% at conversions up to 55% at room temperature and TBHP being the oxidizing agent. At higher reaction temperature (55 °C), the conversions went up to ca. 90%, but the ees dropped to below 20%.

As in the case of MTO, which has been mentioned above,[41] the inclusion compound of a ferrocenyldiimine dioxomolybdenum complex with heptakis-2,3,6-tri-*O*-methyl-β-cyclodextrin (TRIMEB) has been described[80] by Gonçalves et al. Upon coordination of the ferrocenyl diimine (FcNN) ligand to the MoO_2Cl_2 moiety, an isomerization from trans, trans to cis, cis with respect to the C=N bonds of the free ligand takes place. The authors assumed that the guest species adhered to an inclusion model in which each ferrocenyl sub-unit penetrates into the CD cavity in axial mode, giving rise to a 2:1 host:guest stoichiometry. The inclusion compound was found to be soluble and catalyzed with high selectivity the liquid phase epoxidation of cyclo-octene using *tert*-butyl hydroperoxide as the oxidant. In general, the catalytic behavior of $MoO_2Cl_2(FcNN)$ is, according to the authors, not detrimentally affected by encapsulation in TRIMEB, although the observed activities were slightly lower. The use of a TRIMEB inclusion complex in molybdenum-catalyzed olefin epoxidation is expected to be particularly advantageous in cases where the 'free' catalyst is initially highly active but loses activity during the reaction due to decomposition. Immobilization in a CD host may, as stated by the authors, help to stabilize the catalyst, and also facilitate subsequent recycling. In addition, the catalytic potential of many molybdenum complexes has not been realized due to their poor solubility in common solvents. Inclusion in TRIMEB may also be one possible answer to this problem.

4. Summary and outlook

Several attempts have been made to transfer the organometallic Re(VII) compound MTO and the $(MoO_2)^{2+}$ moiety to chiral epoxidation catalysts by the addition of chiral organic ligands, most conveniently taken from Nature's chiral pool. The major flaw in most of these attempts, however, was the weak coordination of the chiral Lewis base ligands to the metal center, which leads either to high enantiomeric excesses only at the very beginning of the catalytic reaction (low conversion) or to generally low enantiomeric excesses. The heterogenization of the Mo(VI) complexes was, at least in some cases, successfully achieved, but with the same drawbacks with respect to the enantiomeric excesses as in homogeneous phase. The lability of the chiral Lewis base ligands in both the Re(VII) and the Mo(VI) systems, however, is not surprising when considering the general examinations, particularly those of Herrmann et al. with respect to Re(VII) systems[81–86] and of Thiel

et al.[87–90] concerning Mo(VI) systems. Besides the possibility of applying particularly strongly coordinating ligands, which should not be too strong electron donors to maintain the Lewis acidity of the metal center, covalently bonded chiral ligands might be a way out of the notoriously low enantiomeric excesses obtained to date. Some results have been already presented, which give enantiomeric excesses significantly above 50%. Based on these results and still unexamined synthetic possibilities as outlined above, it should be possible to reach high enantiomeric excesses in olefin epoxidation catalysis on a broader scale within the coming decade with both homogeneous and heterogeneous Re(VII) and Mo(VI) catalyst systems.

References

1. Sheldon, R. A. In *Applied Homogeneous Catalysis with Organometallic Compound*; 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; Vol. 1, pp 412–426.
2. Kagan, H. B.; Mimoun, H.; Marc, C.; Schurig, V. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 485–486.
3. Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974–5976.
4. Williams, I. D.; Pedersen, S. F.; Sharpless, K. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6430–6431.
5. Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 9333–9334.
6. Pietikäinen, P. *Tetrahedron* **1998**, *54*, 4319–4326.
7. Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169–180.
8. Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197–3246.
9. Owens, G. S.; Arias, J.; Abu-Omar, M. M. *Catal. Today* **2000**, *55*, 317–363.
10. Kühn, F. E.; Scherbaum, A.; Herrmann, W. A. *J. Organomet. Chem.* **2004**, *689*, 4149–4164.
11. Kühn, F. E.; Santos, A. M.; Herrmann, W. A. *Dalton Trans.* **2005**, 2483–2491.
12. Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394–396.
13. Beattie, R. I.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318–2319.
14. Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R.; Romão, C. C. *Inorg. Chem.* **1992**, *31*, 4431–4432.
15. Herrmann, W. A.; Kratzer, R. M.; Fischer, R. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 2652–2654.
16. Herrmann, W. A.; Kratzer, R. M. *Inorg. Synth.* **2002**, *33*, 110–112.
17. Kühn, F. E.; Romão, C. C.; Herrmann, W. A. In *Science of Synthesis, Category 1 Organometallics*; Imamoto, T., Ed.; Houben-Weyl Georg Thieme: Stuttgart, New York, 2003; Vol. 2, pp 128–130.
18. Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638–1641.
19. Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157–1160.
20. Al-Ajlouni, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243–9250.
21. Espenson, J. H. *Chem. Commun.* **1999**, 479–488.
22. Kühn, F. E.; Herrmann, W. A.; Hahn, R.; Elison, M.; Blümel, J.; Herdtweck, E. *Organometallics* **1994**, *13*, 1601–1606.
23. Herrmann, W. A.; Romão, C. C.; Fischer, R. W.; Kiprof, P.; Meric de Bellefon, C. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185–187.
24. Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Huy, H. T.; Wang, M.; Fischer, R. W.; Scherer, W.; Kiprof, P. *Chem. Ber.* **1993**, *126*, 45–50.
25. Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Huy, H. T. *J. Organomet. Chem.* **1994**, *481*, 227–234.
26. Herrmann, W. A.; Kühn, F. E.; Romão, C. C. *J. Organomet. Chem.* **1995**, *495*, 209–213.
27. Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1989**, *371*, C13–C17.
28. Meric de Bellefon, C. M.; Herrmann, W. A.; Kiprof, P.; Whitaker, C. R. *Organometallics* **1992**, *11*, 1072–1081.
29. Herrmann, W. A.; Kühn, F. E.; Romão, C. C. *J. Organomet. Chem.* **1995**, *489*, C56–C59.
30. Rietveld, M. H. P.; Nagelholt, L.; Grove, D. M.; Veldman, N.; Spek, A. L.; Rauch, M. U.; Herrmann, W. A.; Koten, G. v. *J. Organomet. Chem.* **1997**, *530*, 159–167.
31. Herrmann, W. A.; Kühn, F. E.; Mattner, M. R.; Artus, G. R. J.; Geisberger, M. R.; Correia, J. D. G. *J. Organomet. Chem.* **1997**, *538*, 203–209.
32. Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189–6190.
33. Copéret, C.; Adolfsson, H.; Sharpless, K. B. *Chem. Commun.* **1997**, 1565–1566.
34. Herrmann, W. A.; Ding, H.; Kratzer, R. M.; Kühn, F. E.; Haider, J. J.; Fischer, R. W. *J. Organomet. Chem.* **1997**, *549*, 319–322.
35. Adolfsson, H.; Converso, A.; Sharpless, K. B. *Tetrahedron Lett.* **1999**, *40*, 3991–3994.
36. Kühn, F. E.; Santos, A. M.; Roesky, P. W.; Herdtweck, E.; Scherer, W.; Gisdakis, P.; Yudanov, I. V.; Valentin, C. Di.; Rösch, N. *Chem. Eur. J.* **1999**, *5*, 3603–3615.
37. Adolfsson, H.; Copéret, C.; Chiang, J. P.; Yudin, A. K. *J. Org. Chem.* **2000**, *65*, 8651–8658.
38. Ferreira, P.; Xue, W. M.; Bencze, E.; Herdtweck, E.; Kühn, F. E. *Inorg. Chem.* **2001**, *40*, 5834–5841.
39. Adam, W.; Corma, A.; Martínez, A.; Mitchell, C. M.; Reddy, T. I.; Renz, M.; Smerz, A. K. *J. Mol. Catal. A, Chem.* **1997**, *117*, 357–366.
40. Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *J. Org. Chem.* **1999**, *64*, 3699–3707.
41. Cunha-Silva, L.; Gonçalves, I. S.; Pillinger, M.; Xue, W. M.; Rocha, J.; Teixeira-Dias, J. C.; Kühn, F. E. *J. Organomet. Chem.* **2002**, *656*, 281–287.
42. Santos, A. M.; Kühn, F. E.; Xue, W. M.; Herdtweck, E. J. *Chem. Soc., Dalton Trans.* **2000**, 3570–3574.
43. Sabater, M. J.; Domine, M. E.; Corma, A. *J. Catal.* **2002**, *210*, 192–197.
44. Haider, J. J.; Kratzer, R. M.; Herrmann, W. A.; Zhao, J.; Kühn, F. E. *J. Organomet. Chem.* **2004**, *689*, 3735–3740.
45. Tucker, C. E.; Davenport, K. G. Hoechst Celanese Corporation, USA. US 5618958 A 19970408, 1997.
46. Sheng, M. N.; Zajaczek, G. J. ARCO, GB 1.136.923, 1968.
47. Kollar, J. Halcon, US 3.350.422, US 3.351.635, 1967.
48. Yamada, S. I.; Mashiko, T.; Terashima, S. *J. Am. Chem. Soc.* **1977**, *99*, 1988–1990.
49. Coleman-Kammula, A.; Duim-Kollstra, E. T. J. *Organomet. Chem.* **1983**, *246*, 53–56.
50. Schurig, V.; Hintzer, K.; Leyrer, U.; Mark, C.; Pitchen, P.; Kagan, H. B. *J. Organomet. Chem.* **1989**, *370*, 81–96.
51. Brunner, H.; Zintl, H. *J. Organomet. Chem.* **1991**, *411*, 375–382.
52. Kaneda, K.; Haruna, S.; Imanaka, T.; Hamamoto, M.; Nishiyama, Y.; Ishii, Y. *Tetrahedron Lett.* **1992**, *33*, 6827–6830.
53. Genov, M.; Kostava, K.; Dimitrov, V. *Tetrahedron: Asymmetry* **1997**, *8*, 1869–1876.

54. Chelucci, G.; Soccolini, F. *Tetrahedron: Asymmetry* **1992**, *3*, 1235–1238.
55. Herrmann, W. A.; Lobmaier, G. M.; Priermaier, T.; Mattner, M.; Scharbert, B. *J. Mol. Catal. A: Chem.* **1997**, *117*, 455–469.
56. Herrmann, W. A.; Fridgen, J.; Lobmaier, G. M.; Spiegler, M. *New J. Chem.* **1999**, *23*, 5–7.
57. Bellemin-Caponnaz, S.; Coleman, K. S.; Osborn, J. A. *Polyhedron* **1999**, *18*, 2533–2536.
58. Herrmann, W. A.; Haider, J. J.; Fridgen, J.; Lobmaier, G. M.; Spiegler, M. *J. Organomet. Chem.* **2000**, *603*, 69–79.
59. Fridgen, J.; Herrmann, W. A.; Eickerling, G.; Santos, A. M.; Kühn, F. E. *J. Organomet. Chem.* **2004**, *689*, 2752–2761.
60. Valente, A. A.; Gonçalves, I. S.; Lopes, A. D.; Rodríguez-Borges, J. E.; Pillinger, M.; Rocha, J.; Garcia-Mera, X. *New. J. Chem.* **2001**, *25*, 959–963.
61. Denmark, S. E.; Nakajima, N.; Nicaise, O. J. C.; Faucher, A. M.; Edwards, J. P. *J. Org. Chem.* **1995**, *60*, 4884–4892.
62. Kühn, F. E.; Santos, A. M.; Lopes, A. D.; Gonçalves, I. S.; Rodriguez-Borges, J. E.; Pillinger, M.; Romão, C. C. *J. Organomet. Chem.* **2001**, *621*, 207–217.
63. Gómez, M.; Jansat, S.; Muller, G.; Noguera, G.; Teruel, H.; Moliner, V.; Cerrada, E.; Hursthouse, M. *Eur. J. Inorg. Chem.* **2001**, 1071–1076.
64. Brito, J. A.; Gómez, M.; Muller, G.; Teruel, H.; Clinet, J. C.; Dunach, E.; Maestro, M. A. *Eur. J. Inorg. Chem.* **2004**, 4278–4285.
65. Kandasamy, K.; Singh, H. B.; Butcher, R. J.; Jasinski, J. P. *Inorg. Chem.* **2004**, *43*, 5704–5713.
66. Gonçalves, I. S.; Santos, A. M.; Romão, C. C.; Lopes, A. D.; Rodríguez-Borges, J. E.; Pillinger, M.; Ferreira, P.; Rocha, J.; Kühn, F. E. *J. Organomet. Chem.* **2001**, *626*, 1–10.
67. Sah, A. K.; Rao, C. P.; Saarenketo, P. K.; Wegelius, E. K.; Kohlemainen, E.; Rissanen, K. *Eur. J. Inorg. Chem.* **2001**, 2773–2781.
68. Zhao, J.; Zhou, X.; Santos, A. M.; Herdtweck, E.; Romão, C. C.; Kühn, F. E. *Dalton Trans.* **2003**, 3736–3742.
69. Gullotti, M.; Pasini, A.; Zanderighi, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, *4*, 902–908.
70. Elias, H.; Stock, F.; Röhr, C. *Acta Crystallogr.* **1997**, *C53*, 862–864.
71. Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189–214.
72. Zhou, X.; Zhao, J.; Santos, A. M.; Kühn, F. E. *Z. Naturforsch.* **2004**, *59b*, 1223–1228.
73. Sun, C.; Wang, X. Y.; Zhang, Z. G.; Shi, H. C. *Chin. J. Org. Chem.* **2004**, *24*, 547–549.
74. Wang, X. Y.; Shi, H. C.; Sun, C.; Zhang, Z. G. *Tetrahedron* **2004**, *60*, 10993–10998.
75. Gago, S.; Rodríguez-Borges, J.; Teixeira, C.; Santos, A. M.; Zhao, J.; Pillinger, M.; Nunes, C. D.; Petrovski, Z.; Santos, T. M.; Kühn, F. E.; Romão, C. C.; Gonçalves, I. S. *J. Mol. Catal. A, Chem.* **2005**, *236*, 1–2.
76. Corma, A.; Iglesias, M.; Obispo, J. R.; Sánchez, F. In *Chiral Reactions in Heterogeneous Catalysis*; Jannes, G., Dubois, V., Eds.; Plenum: New York, 1994.
77. Sherrington, D. C. *Catalysis Today* **2000**, *57*, 87–104.
78. Corma, A.; Fuerte, A.; Iglesis, M.; Sánchez, F. *J. Mol. Catal. A: Chem* **1996**, *107*, 225–234.
79. Sakthivel, A.; Zhao, J.; Raudaschl-Sieber, G.; Hanzlik, M.; Chiang, A. S. T.; Kühn, F. E. *Appl. Catal. A: Gen.* **2005**, *281*, 267–273.
80. Petrovski, Z.; Braga, S. S.; Santos, A. M.; Rodrigues, S. S.; Gonçalves, I. S.; Pillinger, M.; Kühn, F. E.; Romão, C. C. *Inorg. Chim. Acta* **2005**, *358*, 981–988.
81. Herrmann, W. A.; Thiel, W. R.; Kühn, F. E.; Fischer, R. W.; Kleine, M.; Herdtweck, E.; Scherer, W.; Mink, J. *Inorg. Chem.* **1993**, *32*, 5188–5194.
82. Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Kleine, M.; Scherer, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1714–1716.
83. Herrmann, W. A.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1995**, *485*, 243–251.
84. Herrmann, W. A.; Kühn, F. E.; Rauch, M. U.; Correia, J. D. G.; Artus, G. R. J. *Inorg. Chem.* **1995**, *34*, 2914–2920.
85. Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Elison, M.; Artus, G. R. J.; Scherer, W.; Romão, C. C.; Lopes, A. D.; Basset, J. M. *Inorg. Chem.* **1995**, *34*, 4701–4707.
86. Herrmann, W. A.; Correia, J. D. G.; Rauch, M. U.; Artus, G. R. J.; Kühn, F. E. *J. Mol. Catal. A, Gen.* **1997**, *118*, 33–45.
87. Thiel, W. R.; Angstl, M.; Priermeier, T. *Chem. Ber.* **1994**, *127*, 2373–2379.
88. Thiel, W. R.; Priermeier, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1737–1738.
89. Thiel, W. R.; Eppinger, J. *Chem. Eur. J.* **1997**, *3*, 696–705.
90. Glas, H.; Spiegler, M.; Thiel, W. R. *Eur. J. Inorg. Chem.* **1998**, 275–281.