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Review

Synthesis and catalytic applications of chiral monomeric organomolybdenum(VI) and organorhenium(VII) oxides in homogeneous and heterogeneous phase

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Contents

Abstract

In recent years several attempts have been made to introduce chirality into organometallic Re(VII) compounds of formula $RReO_3$ and related organometallic complexes containing the $(MoO_2)^{2+}$ moiety for applications in chiral catalysts. The earliest synthetic procedures applied the addition of chiral organic Lewis base ligands, most conveniently taken from Nature's chiral pool. The major flaw of most of these attempts, however, was the weak coordination of the chiral Lewis base ligands to the metal center, which leads either to high ees only at the very beginning of the catalytic reaction (low conversion) or to generally low optical yields. The heterogenization 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 homogeneous phase occurred. More recent attempts include the addition of chiral ligands via covalent bonds to the metal center and subsequent heterogenization. The stability of the complexes depends in these latter cases crucially on the strength of the metal–carbon interactions involved and the ees obtained also reflect intramolecular mobility of such ligands. The main target of these examinations with respect to applications in catalysis were olefin epoxidation and related reactions.

Keywords: Chirality; High oxidation state; Homogeneous catalysis; Immobilisation; Rhenium; Molybdenum

1. Introduction

The demand for enantiopure chiral compounds rises continuously, facilitated among other reasons, by the increasing number of government regulations and health concerns as well as the need for efficiency in industry. Enantiomerically pure complexes are used mainly in pharmaceuticals but also in three other sectors: flavor and aroma chemicals, agricultural chemicals, and specialty materials. Demand from the drug industry in particular is fuelled by regulations governing chiral active pharmaceutical ingredients (APIs) and the recognition that enantiomers of a chiral compound can have dramatically different biological activities [1]. It follows then that chiral epoxidations are currently of high interest for the synthesis of non-racemic chiral intermediates in the pharmaceutical and chemical industry to generate such enantiomerically pure products [2]. The chiral epoxide functionality, for example, is a key structural unit present in many biologically active compounds as well as in important natural products [3]. Asymmetric catalysis is a particularly elegant and efficient method to achieve the introduction of such functional groups into larger organic compounds [4].

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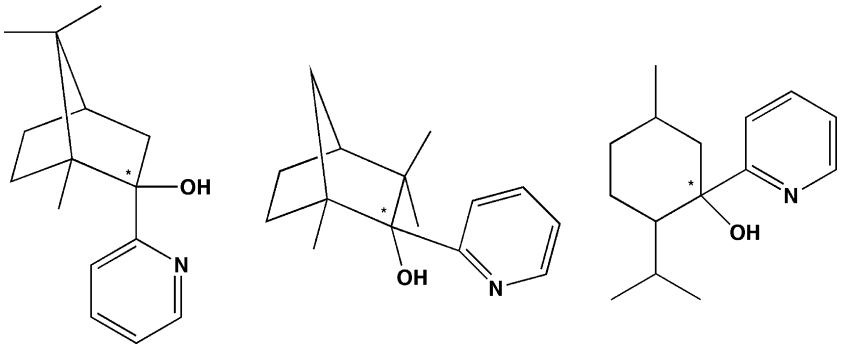


Fig. 1. Examples for chiral 2′-pyridinyl alcohols as ligands.

The success of non-chiral organorhenium(VII) and organomolybdenum(VI) complexes in racemic epoxides reactions [5–9] however, led to the belief that some chiral derivatives of these complexes might be applied equally efficiently as chiral catalysts. It was discovered [10], that methyltrioxorhenium (MTO) was an extremely active epoxidation catalyst in the homogeneous phase and this prompted a spate of inquiry into its chiral applications. The application of chiral Mo(VI) complexes in olefin epoxidations dates back some years before the application of MTO and its derivatives. This interest was born out of the application of homogeneous Mo(VI) catalysts in the Halcon and Arco processes [11,12].

The goal of this review is to chronologically summarize attempts at the synthesis of chiral monomeric organomolybdenum(VI) and organorhenium(VII) oxides in both homogeneous and heterogeneous phases as well as their applications in various reactions. The aim is to show that the work so far done in this interesting field merits the belief that the synthesis of such compounds and their varied applications to fields from pharmaceuticals, fine chemicals and agricultural science to applications in value-added industrial processes can be achieved.

2. Molybdenum(VI) catalysts

Molybdenum(VI) complexes with different types of chiral ligands, among them diisopropyltartrates, lactamides and several other hydroxyacid amides have been applied in chiral epoxidations since the 1970s. *N*-Alkyl ephedrines [13], methyl pyrolinols and diisopropyl tartrates [14] were among the ligand species applied. Chiral ligands which were easy to make and stable in oxidation reactions were searched for. Ligands that would also allow the possibility of varying the steric characteristics easily through simple substitutions, were found in the class of 2′-pyridyl alcohols, which were known to be easily accessible [15,16] and from which Mo-complexes of the type MoO_2L_2 (L-2′-pyridyl alcoholate) that were useful as catalysts for epoxidation, could be prepared.

In 1999 Bellemin-Caponnaz and others demonstrated this by applying the ligand 2-[(−)menthol-pyridine] to such a complex [17]. The conversion was about 20% and an ee of 25% using 1-hexene as substrate, was obtained.

In 2000, Herrmann et al. [18] made use of chiral precursors (Fig. 1) to form enantiomerically pure 2′-pyridinyl alcoholates which were subsequently applied as chiral ligands in Mo(VI) complexes. The complexes were examined for their catalytic activity and good conversions, in the range of 70%, were observed. The enantioselectivities were more dependant on the ligands and were observed between 4 and 26%, with the bulkier norbornane ligands giving the highest optical inductions.

Then in 2001, Gonçalves and coworkers [19] reported Mo(VI) dioxo complexes ligated by pyridyl alcoholate ligands and used for olefin epoxidation. Mono-substituted complexes

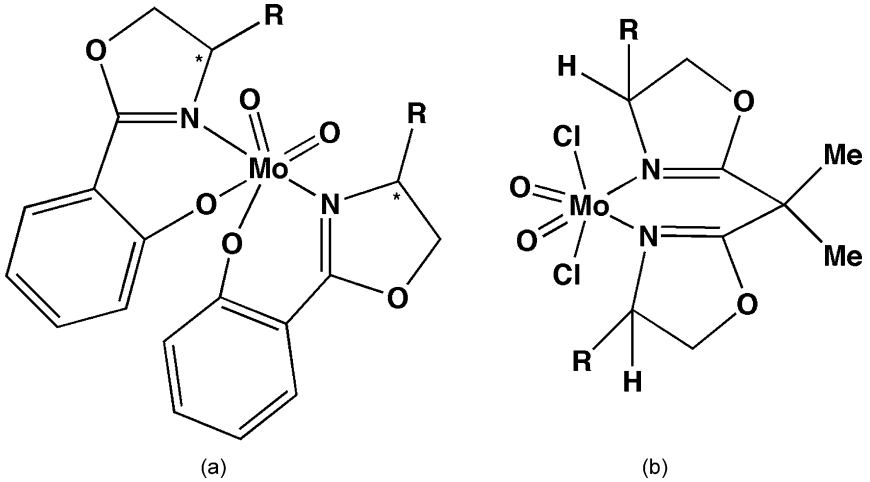


Fig. 2. Different binding modes of bidentate ligands to the Mo–O_2 moiety.

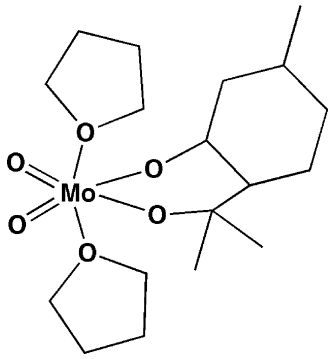


Fig. 3. Mo(VI) complex **1**.

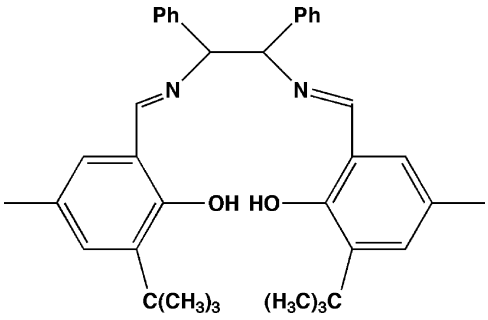


Fig. 5. Ligand **2**.

were more active than those with two chiral ligands. Another class of suitable [19] chiral chelating ligands; C_2-symmetric bis(oxazolines) were used in the same year [20] by Romão et al. for the epoxidation of *trans*-β-methylstyrene. Using *tert*-butyl hydroperoxide (TBHP) as oxidant at 55 °C, up to 86% conversion was achieved although ees were very low, only ranging from 4 to 6%. Teruel and colleagues [21] also applied chiral oxazoline ligands attached to MoO_2 building blocks (Fig. 2a), but the oxazolines applied were attached to the metal by a covalent Mo–O bond in contrast to other occasions [20]. Using styrene as substrate, toluene as solvent and TBHP as oxidant, conversions from 25 to 30% were reached within 18 h at 35 °C. Selectivity was below 50% and ees were still negligible (ca. 2%). Kühn and coworkers [22] also synthesized complexes of the type MoO_2Cl_2L (L = oxime), $MoO_2(THF)_2L$ (L = *cis*-*p*-methane-3,8-diol) and $MoO_2Cl(THF)L$ (L = 8-phenylthioneo- and isoneomenthol). Conversions of 63–82% were obtained with the substrate *cis*-β-methylstyrene, with TBHP as oxidising agent and toluene as solvent (55 °C). The observed ees were on an average low, with 24% in the best case (**1**) (Fig. 3) at 72% conversion.

The first sugar ligands were attached to the $(MoO_2)^{2+}$ moiety by Rao and coworkers [23] in 2001, to make compounds of the formula MoO_2L (L = sugar) (Fig. 4). These were applied in olefin epoxidation by Kühn et al. [24]. The TOF was high (13,000 1/h in the best case) when cyclooctene was the substrate although the velocity of reaction slowed down over time. When esterification was used to protect the –OH group in the sugar ligand tridentate coordination of the ligand took place due to Lewis acid catalysed deacetylation. In the case of *cis*-β-methylstyrene ees of up to 30% were achieved.

In 2004 Herrmann published [25] further results in continuation of their work published in 2000 [18]. A number of chiral 2^I pyridinyl alcohols were used as ligands for the MoO_2 moiety. When TBHP or cumylhydroperoxide were used as oxidants and *trans*-β-methylstyrene was the substrate, ees of up to 23% and conversions up to 58% (temperatures 50–70 °C) were reached [25]. Following also their previous [21] work, Teruel et al. published further research, in 2004, which made it possible to explain the good activity and low enantioselectivity of the oxazoline ligated complexes [26]. They proposed a reaction mechanism for olefin epoxidation catalysed by seven-coordinate molybdenum species with hemilabile ligands. In the same year, Singh and coworkers [27] also synthesized a chiral Mo(VI) compound with bidentate oxazoline ligands, similar to that of Teruel (after 24 h at room temperature, catalyst:styrene:oxidant ratio 1:40:60) and obtained yields of up to 70%. Kühn et al. used a tetradentate chiral Schiff base (Fig. 2b) and obtained ees of up to 26% at 0 °C with toluene with *cis*-β-methylstyrene [28]. Gonçalves and coworkers [29] also prepared chiral 1,4-diazabutenes of the type R–N=CPh–CPh=N–R; (1*R*,2*R*)-*N*,*N*^{I}-dibenzylidenecyclohexane-1,2-diamine and hexa-coordinate Mo(VI) complexes. These complexes were applied as cata-

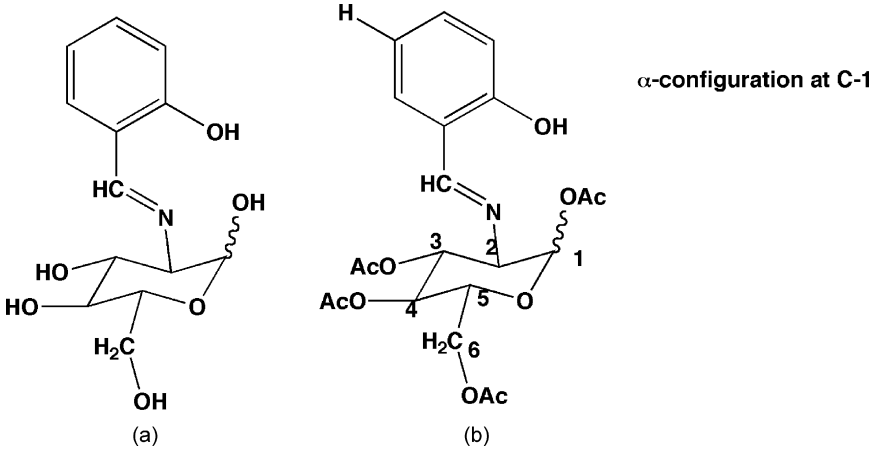


Fig. 4. Examples of protected (a) and unprotected (b) sugars.

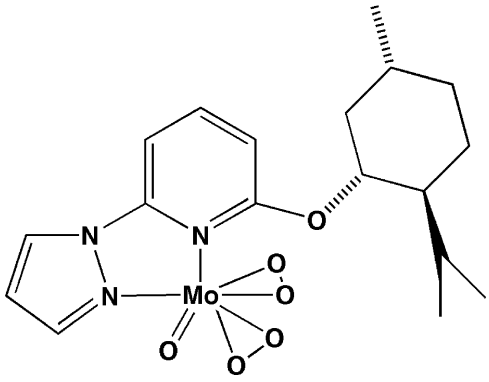


Fig. 6. Complex **3**.

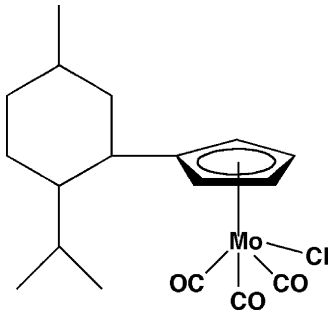


Fig. 8. (−)MenthylCpMo(CO)$_3$Cl.

lysts for epoxidation using *cis*- and *trans*-β-methylstyrene by *tert*-butylchloroperoxide. The reactions proceeded with high retention of configuration and high selectivity to the epoxide, but only for *cis*-β-methylstyrene a high 77% ee at room temperature was obtained (24% conversion). Increasing the reaction temperature increased the epoxide yields but good enantiomeric excesses (ca. 65%) could only be achieved at low conversions (ca. 12%). Shi and coworkers [30] used both mono and tetradentate compounds for the asymmetric epoxidation of *cis*-1-propenylphosphonic acid with 30% aqueous hydrogen peroxide affording (1*R*, 2*S*)-(−)-(1,2)-epoxypropyl phosphonic acid. The reaction was strongly influenced by the ligands, and solvents used as well as the reaction temperatures. For example in a complex with a tetradentate salene ligand (**2**) (Fig. 5), as with all other examined complexes, better ees were obtained in non-coordinating solvents such as methylene chloride than in a solvent like ethanol. The ee observed for a Mo(VI) complex bearing ligand **2** was 69% at 30% conversion after 24 h reaction time.

Not much work was reported on the attachment of chiral organometallic complexes of Mo(VI) on solid surfaces and their catalytic applications. Some reviews on heterogenization of homogeneous catalysts, like the state of the art for anchoring on zeolites [31,32] and on polymers [33] were published. Only recently in 2005, Kühn et al. grafted optically active Mo(VI) dioxo complexes bearing hydrosalene derivatives as ligands on surfaces of MCM41 and MCM48 [34]. The ees obtained (using *cis*- and *trans*-β-methylstyrene) were up to 31% with conversions of up to 55% at room temperature and TBHP as the oxidising agent. At 55 °C the conversions went to 90% but ees dropped to below 20%. As in the case of the Re(VII) complex MTO [35] (see below) the inclusion compound of ferrocenyldiimine dioxomolybdenum complexes with heptakis-2,3,6-tri-*O*-methyl-β-cyclodextrin was reported by Gonçalves and coworkers [36]. This inclusion was reported to be particularly useful for those cycles in which the catalyst has high initial activity but this activity decreases during the reaction due to decomposition. This procedure was also thought to be a possible solution to the problem of many potentially promising Mo(VI)-complexes being untried due to their poor solubility in common solvents.

Besides their work on MTO [37] (see below) and chiral derivatives, Burke, Carreiro and Yong-En also published work in March 2006 that dealt with a Mo(VI) complex

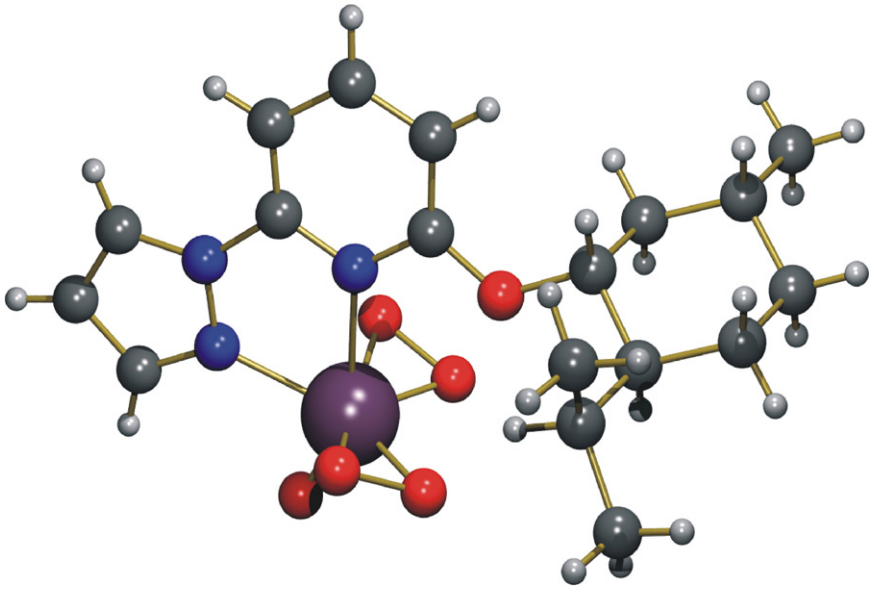


Fig. 7. View of 2-(1-pyrazolyl)-6-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyloxy]-pyridine oxodiperoxomolybdenum(VI) [36].

Table 1
Catalytic epoxidation of simple olefins using **3** [36]

Serial no.	Olefin	Conversion (%)	ee (%)	Conditions
1	Styrene	31	2	100 °C, 1 h
2	Styrene	86	1	100 °C, 17 h
3	*trans*-β-Methylstyrene	28	0	100 °C, 5 h
4	4-Methylstyrene	37	5	100 °C, 1 h
5	4-Methylstyrene	44	6	100 °C, 6 h
6	4-Methylstyrene	49	–	100 °C, 17 h

Using TBHP as oxidant and toluene as solvent.

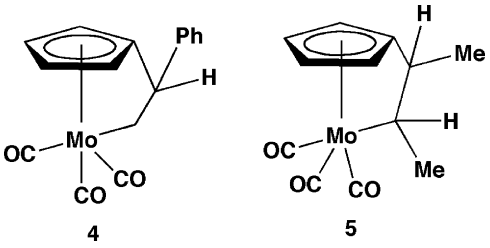
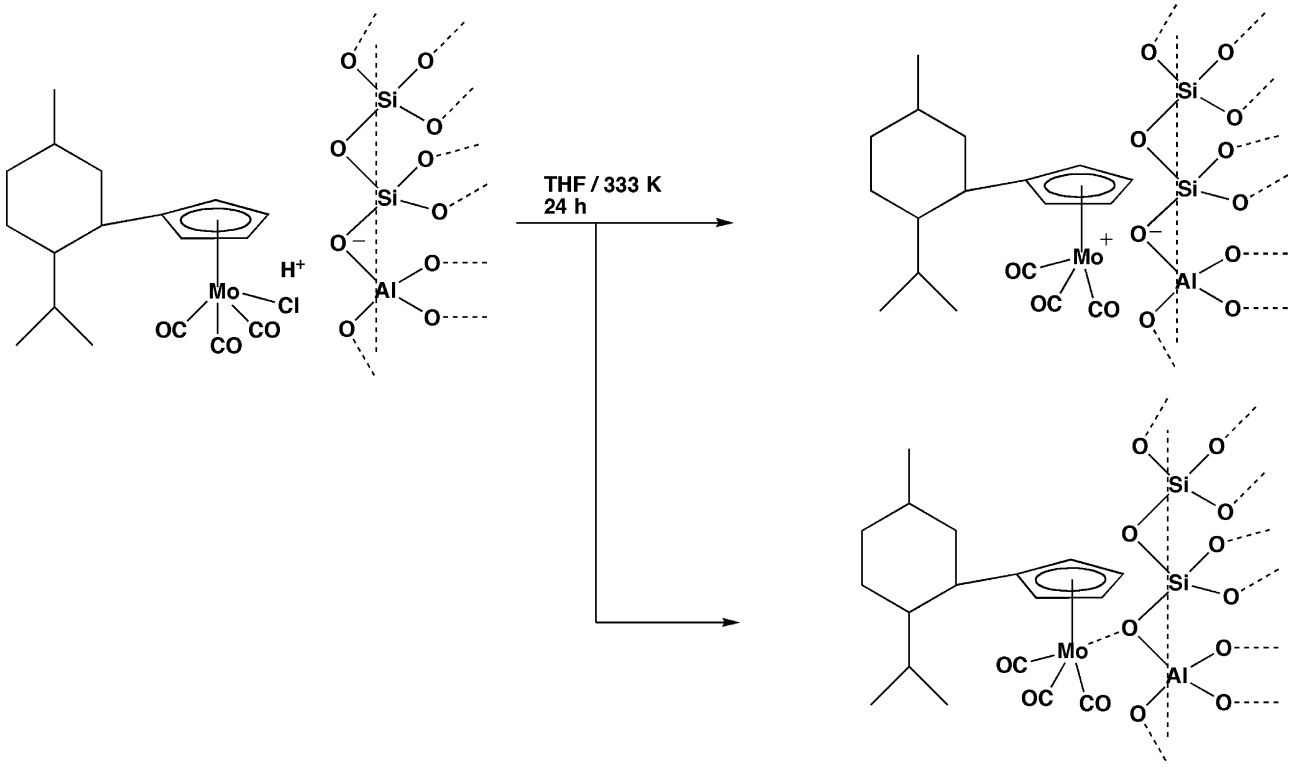


Fig. 9. Complexes **4** and **5**.

(**3**) (Fig. 6) used in chiral reactions [38]. 2-(1-Pyrazolyl)-6-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy] pyridine-oxodiperoxomolybdenum(VI) was obtained via reaction of 2-(1-pyrazolyl)-6-menthylpyridine in methanol and MoO_3 along with H_2O_2 and a few drops of CH_2Cl_2. The product crystallised as yellow needle like structures on refrigeration of the mother liquor and was subsequently purified to give a yield of 42%. X-ray crystal analysis shows that the chiral product exhibits a pentagonal-pyramidal geometry with the sevenfold coordinated molybdenum (Fig. 7). However, the catalytic epoxidation of simple olefins resulted in very low enantioselectivities as summarized in Table 1.

The interest in molybdenum compounds continued with a bid to further improve enantioselectivity. In April 2006 a paper by Kühn and coworkers reported a chiral menthyl cyclopentadienyl molybdenum tricarbonyl chloro molybdenum complex [39]. The production of the chiral catalysts took place in two stages. Stage *one* included the reaction of $Mo(CO)_3(EtCN)_3$ with (−)menthylCpH so that (−)menthylCpMo$(CO)_3$H was produced in the form of a brown solution. After stirring for 2 h the solution was heated to about 330 K and the brown oil so obtained once again dissolved in CH_2Cl_2. In stage *two*, CCl_4 was added to the hydride turning the solution dark red and on evaporation of the solvent an oily brown residue was received. After silica/gel chromatography and subsequent elution the product is obtained as an orange solid (Fig. 8) in a yield of about 26%. The reason for this relatively low yield is the incomplete reaction of $Mo(CO)_6$ and propionitrile to obtain the hydride. The complex was successfully immobilised on MCM-41 and MCM-48 (Scheme 1) and tested as a catalyst for the epoxidation of *cis*-cyclooctene, styrene and *trans*-β-methylstyrene in the presence of TBHP at 55 °C using chloroform as solvent. In the case of styrene, selectivity to the epoxide is generally low, resulting in ring-opening of the epoxide ring under diol formation. For *trans*-β-methylstyrene both homogeneous and heterogeneous catalysts lead to ees of around 20%. For the homogeneous catalyst this ee remains constant throughout the reaction time and favors the RR^I enantiomer. However, for the heterogeneous catalyst the RR^I enantiomer is originally favoured but over a



Scheme 1. Immobilisation of (−)menthylCpMo$(CO)_3$Cl on MCM-41/48 supports.

longer reaction time the SS^I enantiomer predominates, possibly due to the acid sites present on the supporting materials. Soon after Kühn et al. followed with a review, reporting on monomeric cyclopentadiene molybdenum oxides and their carbene precursors—and the applications of both in epoxidation reactions [40].

Then in May 2006 another paper dealing with chiral ansa-bridged η^5-cyclopentadienyl molybdenum complexes [41] was reported by Kühn et al. It had been recognized that Mo(II) tricarbonyl complexes of the general composition $CpMo(CO)_3R$ could be easily oxidised to the catalytically active Mo(VI) compounds with TBHP and they are more easy to store and handle than their $CpMoO_2R$ congeners in most cases, thus, the carbonyls are usually directly utilized as catalysts precursors without isolating the dioxo complexes. This is particularly straightforward since both $CpMo(CO)_3R$ catalyst precursors and their substrates are oxidised by the same oxidising agent (TBHP). As soon as Mo(VI) species are present the substrate oxidation begins. Yellow crystals of (*S*)-[Mo(η^5-C_5H_4CHPh-η^1-CH_2)$(CO)_3$] (**4**) in a yield of 75% and orange red crystals (at −30 °C) of thermally unstable (*R*, *S*)-[Mo(η^5-C_5H_4CHMe-η^1-CHMe)$(CO)_3$] (**5**) in a yield of 60%, were two such compounds obtained (Fig. 9). **4** shows the ^{95}Mo NMR signal at −1728 ppm while **5** displays its Mo peak at −1696 ppm. The four protons of the Cp rings in the complexes appear as four multiplets in the ^{1}H NMR spectrum. **4**, being stable in air, was studied in detail and an X-ray crystal structure (Fig. 10) was obtained. The ligands are disposed in a distorted four-legged piano stool fashion similar to that established for analogous tricarbony cyclopentadienyl group VI metal complexes [42–44]. The angles between contiguous legs range from 76.67(9) to 81.06(8) of structure. The cyclopentadienyl ligand is bound in a pentahapto fashion, as inferred from the total value of the angles at the ring (540°) distances, which range from 228.7(2) to 233.8(2) ppm. The carbonyl ligands show a linear arrangement, with Mo–C–O angles ranging from 175.3(2) to 177.8(2). The C–O bond lengths lie between 114.4(3) and 115.3(3) ppm and the average Mo–C_{CO} bond length of 199.7 ppm (with bond lengths ranging from 198.6(2) to 201.6(2) ppm) are usual for terminal CO groups.

The compounds were tested for their activity in the asymmetric epoxidation of unfunctionalized trans olefins—specifically for *trans*-β-methylstyrene using TBHP as oxidant. For the epoxidation of *trans*-β-methylstyrene both compounds exhibited

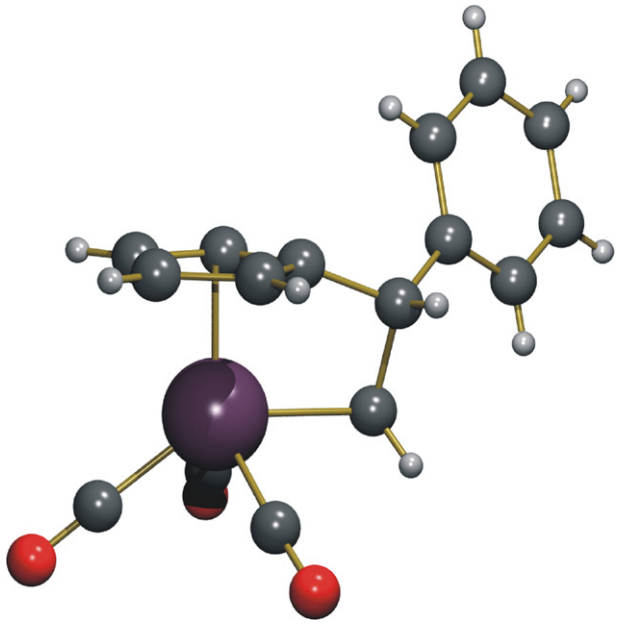


Fig. 10. View of (*S*)-[Mo(η^5-C_5H_4CHPh-η^1-CH_2)$(CO)_3$] [39]. The biatomar ligands coordinating to the molybdenum atom are carbonyls.

good selectivity towards the epoxide. The conversion reaches 66% after 4 h and 50%, respectively. The enantiomeric excess obtained was up to ca. 20%. Compared to **4**, **5** showed better chiral induction—most likely because of the two chiral centers being located in close proximity to the Mo. In the case of compound **5** the initial ee is ca. 21% (after 5 min), going down to ca. 8% after 4 h. In the case of compound **4** the initial ee is ca. 14%, going down to ca. 4% after 4 h. The comparatively low ee values obtained in the work, were thought likely to be due to the breaking of the carbon–metal under the oxidative conditions leading to a significant decomposition of the catalyst and accordingly to the disappearance of the chiral centers during the course of the catalytic reaction. A promising way to obtain higher ee values might be the use of chiral ansa-bridged η^5-cyclopentadienyl complexes with lower ring tension (e.g., a five- or six-membered ring) in the ansa bridge.

Continuing with this research, the group published in August 2006, work on oxazoline dioxomolybdenum(VI) complexes [45]. Dioxomolybdenum(VI) complexes with the general formula $[MoO_2X_2(N,N)]$ (X = Cl, $OSiPh_3$) containing a chiral

Table 2
Catalytic epoxidation of olefins by compounds [43] **6–8**

Serial no.	Olefin	Catalyst	Conversion (%)	ee (%)	Conditions
1	*trans*-β-Methylstyrene[a]	6	24	2	40 °C, 10 m
2	*trans*-β-Methylstyrene[b]	6	23	3[c]	55 °C, 24 h
3	*trans*-β-Methylstyrene[d]	7	76	<1	55 °C, 24 h
4	*trans*-β-Methylstyrene[b]	8	23	13	55 °C, 10 m
5	*trans*-β-Methylstyrene[e]	8	67	<1	55 °C, 24 h
6	Cyclooctene	8	100	–	55 °C, 24 h

[a] DCM/TBHP.
[b] Toluene/TBHP.
[c] (1*S*,2*S*)-configuration.
[d] None/TBHP.
[e] None/cumeneOOH.

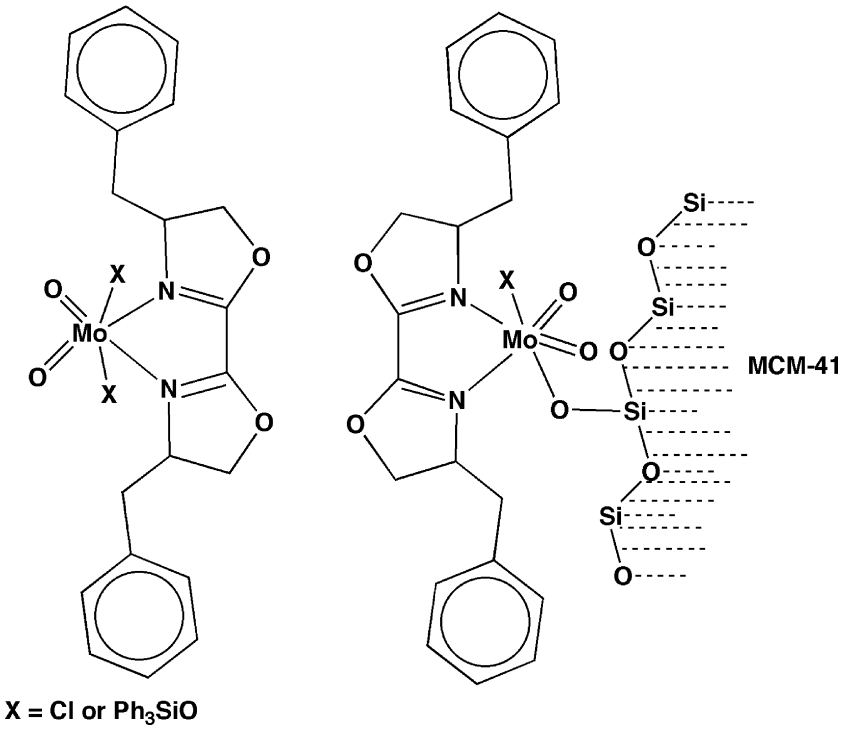


Fig. 11. Chiral Mo(VI) complexes and their immobilisation on MCM-41.

bidentate oxazoline ligand (N,N = 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline]) (Fig. 11) were prepared and characterised by ^{1}H NMR, IR spectroscopy and thermogravimetric analysis. Immobilisation of the complexes on mesoporous silica MCM-41 and an evaluation of the catalytic properties of the different systems in olefin epoxidation processes using TBHP as the oxidant are given in Table 2.

To $MoO_2Cl_2(THF)_2$ was added 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] under nitrogen and the reaction mixture stirred at room temperature, protected from light for 2 h. Complex **6**

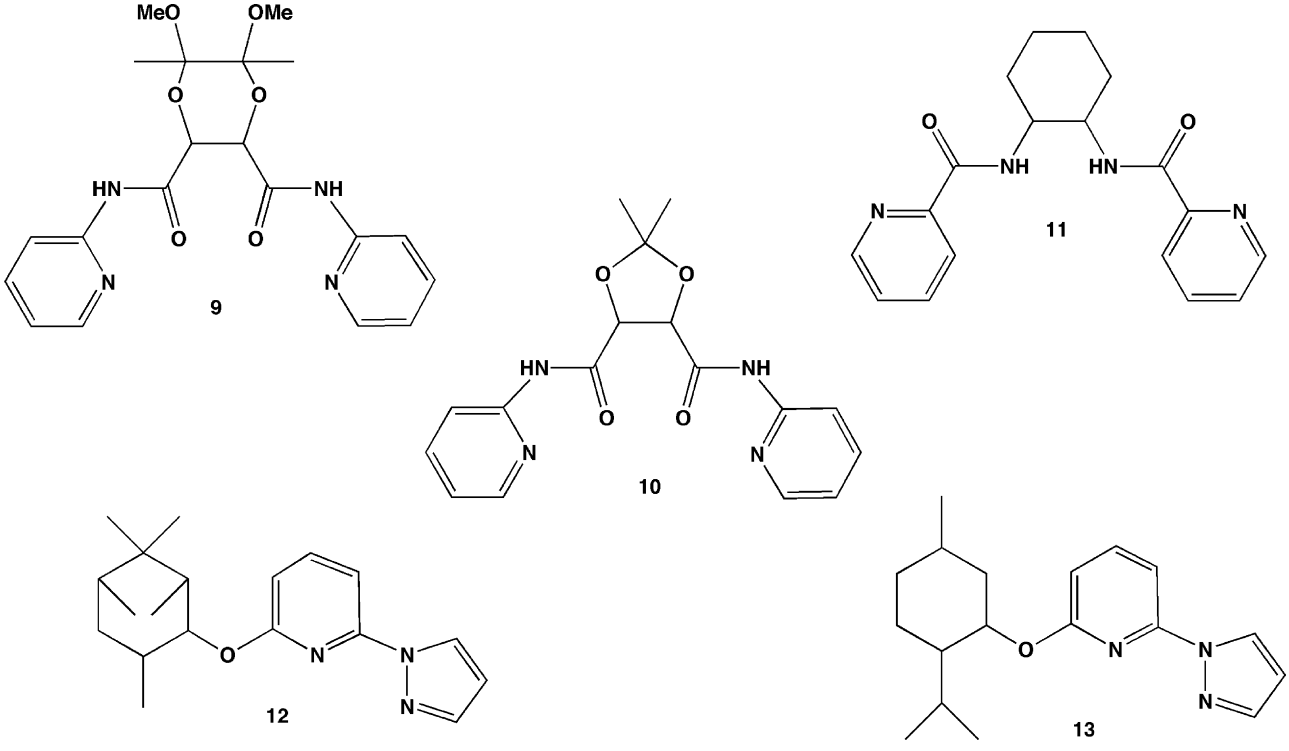


Fig. 12. Ligands **9**–**13**.

Table 3
Mo(VI) catalysed epoxidation of simple olefins with chiral ligands **9–13**

Serial no.	Olefin	Ligand	Conversion (%)	Epoxide selectivity (%)	Conditions
1	Styrene	**9**	56	73	100 °C, 15 h
2	Styrene	**10**	61	90	100 °C, 15 h
3	Styrene	**11**	68	89	100 °C, 15 h
4	4-Methylstyrene	**12**	88	86	100 °C, 12 h
5	Styrene	**13**	13	48	55 °C, 14 h
6	1-Methylcyclohexane	**13**	71	98	100 °C, 15 h

Using TBHP as oxidant and toluene as solvent.

was then obtained as a white solid in a yield of 92%. A suspension of Ag_2MoO_4 in 1,2-dichloroethane and CH_3CN was stirred for 15 min. Ph_3SiCl was then added and the mixture was refluxed under nitrogen for 20 h. **7** was added and the mixture stirred for a further 5 h at room temperature. On filtration, evaporation and drying [$MoO_2(OSiPh_3)_2${2,2′-bis[(4*S*)-4-benzyl-2-oxazoline]}] was obtained as a pale green solid in 80% yield. The immobilisation of **6** on MCM-41 gave **8** as a light green solid. Mo(VI) complexes with the *cis*-dioxo unit typically show two very strong IR bands in the range 905–940 cm^{-1} assigned to the symmetric and asymmetric Mo=O stretching modes, υ(Mo=O). For **6**, the symmetric and asymmetric stretching vibrations are observed at 943 and 911 cm^{-1}, respectively. For **8**, bands corresponding to the υ(Mo=O) modes are visible at 964 and 908 cm^{-1}. In the Si-complex the υ(Mo=O) modes are shifted to higher frequencies (954 and 912 cm^{-1}) indicating a strengthening of the Mo=O bonds when the Mo–Cl bonds are replaced by Mo–$OSiPh_3$. Various catalytic activities have been obtained (Table 2). Elemental analysis and ^{29}Si-MAS NMR spectroscopy of the derivatized material indicated the presence of monopodally anchored species of the type MoO_2[(–O)$_3$SiO]Cl(N,N). The complex [MoO_2Cl_2(N,N)] and the derivatized material exhibited initial activities of 147 and 255 mol mol_{Mo}^{-1} h^{-1}, respectively, in the catalytic epoxidation of cyclooctene using TBHP as the oxidant, both yielding 1,2-epoxycyclooctane quantitatively within 24 h at 55 °C. With *trans*-β-methylstyrene as the substrate, the bis(chloro) complex and the derivatized material gave epoxides as the only products with yields in the range of 56–64% after 24 h, but no catalytic asymmetric induction was observed. **7** was more active than **6** in the epoxidation of *trans*-β-methylstyrene, but the ee observed was low. For the reaction catalysed by **8**, changing the oxidant from TBHP to cumene hydroperoxide greatly improved the catalytic activity but the enantiomeric excess continued to be low.

Burke and colleagues also continued studies on chiral Mo(VI) catalysts and in September 2006 [46] published observations related to epoxidation reactions with five different chiral ligands (**9–13**) as they had already been applied for MTO (see below), on MoO_3 (Fig. 12). The maximum conversion obtained was 88% (using 4-methylstyrene) and a maximum epoxide selectivity of 98% was found (using 1-methylcyclohexene and 1-phenylcyclohexene). The selectivities of the ligands with various substrates are outlined (Table 3). Strictly speaking, however, this MoO_3 based catalyst is not organometallic as it does not display a Mo–C bond, but is included for the sake of completeness.

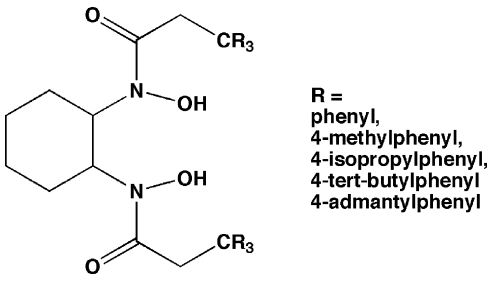
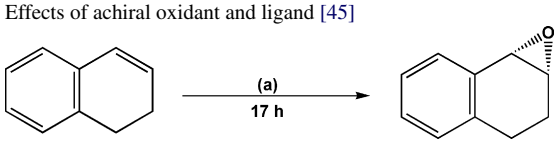


Fig. 13. Various ligands used for Mo-catalyst.

In 2006 Yamamoto and others also published enantioselective olefin oxidation with a chiral bishydroxamic acid complex of Mo as the catalyst [47]. Based on the idea that a Mo(VI) complex of bishydroxamic acid (BHA) in the presence of an organic hydroperoxide would be a strong oxidizing agent, the group went ahead to develop such catalysts using different ligands (Fig. 13) and used them to successfully catalyse asymmetric oxidations of mono-, di- and trisubstituted olefins in mild conditions and obtained epoxides in high yields and selectivities of up to 96% (tritylhydroperoxide as oxidant). Mo–BHA complexes are easy to prepare—the catalyst was air stable and reactions could be carried out at ambient temperatures while the simple aqueous work-up needed to remove any metal residues and BHA acts as a metal scavenger. The effect of some of the different ligands and various oxidants are summarized in Table 4.

Table 4
Effects of achiral oxidant and ligand [45]



Serial no.	Oxidant	Ligand (R=)	Yield[a] (%)	ee[b] (%)
1	TBHP(aq)	4-Methylphenyl	15	42
2	CHP	4-Methylphenyl	72	66
3	THP	4-Methylphenyl	27	96
4	CHP	4-Isopropylphenyl	92	80
5	CHP	4-*tert*-Butyphenyl	82	87

All reactions were carried out in CH_2Cl_2 in the presence of 1.5 equivalent of oxidant and 2 mol% of molybdenum catalyst at RT in air unless indicated.
[a] Yield of isolated product after chromatographic purification.
[b] Determined by chiral HPLC or GC.

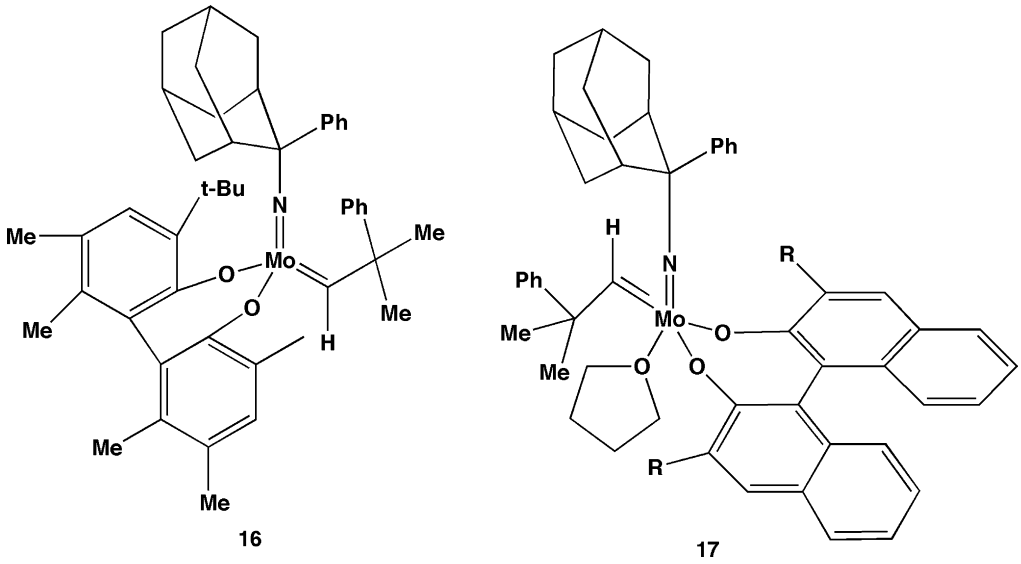


Fig. 14. Complexes **16** and **17**.

In early 2007 Coperet and Basset published a review [48] on catalysts for metathesis and made a brief reference to a chiral polymer-supported Mo imidoalkylidene bisphenoxide asymmetric complex and wrote about its inability to measure up to homogeneous systems. Yet another review by Schrock and Czekelius [49] dealt with the applications of Mo alkylidene and alkylidyne catalysts for the metathesis of alkenes and alkynes. This was followed subsequently with their publication on enantiomerically pure molybdenum(VI) based alkylidene complexes and their applications in chiral olefin metathesis [50]. Alkylimido complexes were tested for their catalytic ability in reactions involving substrates that were challenging for arylimido complexes. The two imido groups that had quarternary carbon bonds to the imido nitrogen were 1-phenylcyclohexylimido (NPhCy) and 2-phenyl-2-admantylimido (NPhAd). The phenyl groups employed were (*S*)-biphen; 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate and (*R*)-trip; (3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-binaphtholate).

Mo(NPhCy)(CHCMe$_2$Ph)[(*S*)-biphen] (**14**) was obtained as an orange powder in a yield of 79%. The Mo–C bond distance is 188.9(2) ppm and the Mo–C–C bond angle is 144.51(16)°. The ^{13}C NMR signal is found at 273.6 ppm.

Mo(NPhCy)(CHCMe$_2$Ph)[(*R*)-trip] (**15**) is a yellow powder obtained in a yield of 99%. The ^{13}C NMR signal is found at 308 ppm suggesting that the alkylidene ligand is in an anti-configuration with the alkyl substituent away from the imido group.

Both complexes are highly soluble in all common solvents but can be isolated via crystallisation from a concentrated *n*-pentane solution at temperatures from −20 to −30 °C.

Two more complexes Mo(NPhAd)(CHCMe$_2$Ph)[(*S*)-biphen] (**16**) obtained as an orange solid in 84% yield and Mo(NPhAd)(CHCMe$_2$Ph)[(*R*)-trip](thf) (**17**) obtained as orange powder in a yield of 98%, were also synthesized (Fig. 14). The NMR characteristics of these were analogous to those of **14** and **15**.

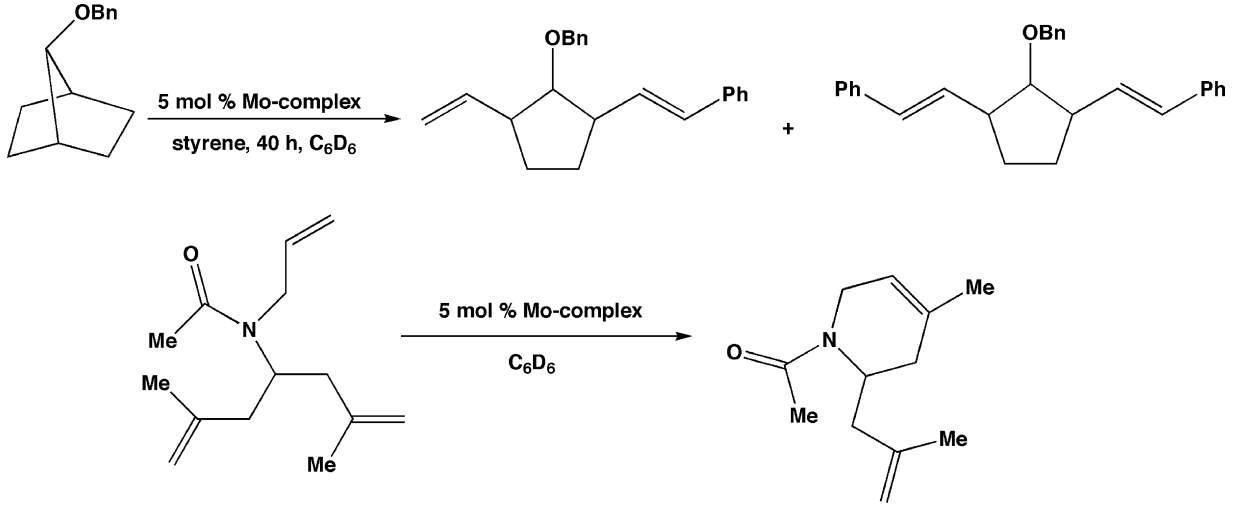


Fig. 15. Some metathesis reactions catalysed by Mo-compounds.

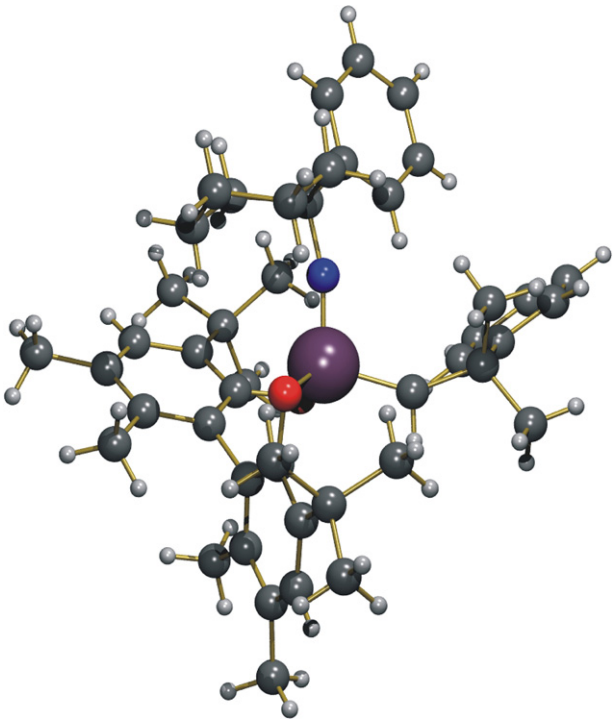


Fig. 16. View of Mo(NPhCy)(CHCMe$_2$Ph)[(*S*)-3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate] (**14**) [48]. Color code: dark gray, carbon; light gray, hydrogen; maroon, molybdenum; red, oxygen; blue, nitrogen.

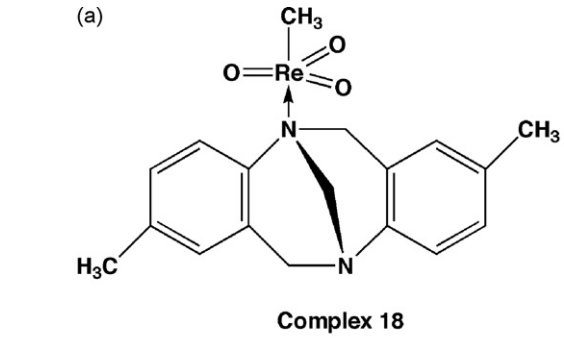
In initial studies the new alkylimido complexes are effective in enantioselective metathesis reactions (Fig. 15). **14** (Fig. 16) provides conversions of over 98% when the reaction proceeds for 20 h at 22 °C.

3. Rhenium(VII) catalysts

The first fully characterised rhenium(VII) chiral compound was synthesized in 1997 [51]. [(5*R*,11*R*)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[*b*,*f*]-(1,5)diazocine] (**18**), was formed when Tröger's base reacted with MTO in diethyl ether at −45 °C (Fig. 17). The Re–N bond distance was 258.9(5) ppm reflecting the weak interaction between MTO and the chiral base ligand. Not unexpectedly an ee could not be determined for this compound when it was applied as catalyst for olefin epoxidation as chirality is not induced.

Following these early attempts, since it was known that the stereoselective epoxidation of acyclic allylic alcohols could be done [52,53], Kühn and coworkers [35], attempted the heterogenization of MTO attached to a ferrocenylpyridine linker on β-cyclodextrine (β-CD) in order to obtain a chiral environment around MTO (Fig. 18). The monodentate ferrocene penetrates into the β-CD cavity while the MTO is oriented outward. Complexes of this type formed with ferrocene adducts [54] were not however, active as catalysts for heterogenous epoxidation reactions.

More recently [55] in 2002 Corma et al. published work that dealt with the utilization of N-base adducts of MTO as epoxidation catalysts. Compounds were synthesized using the chiral ligands (*S*)-2-aminomethyl pyrrolidine, (*R*)-(+)-phenyl



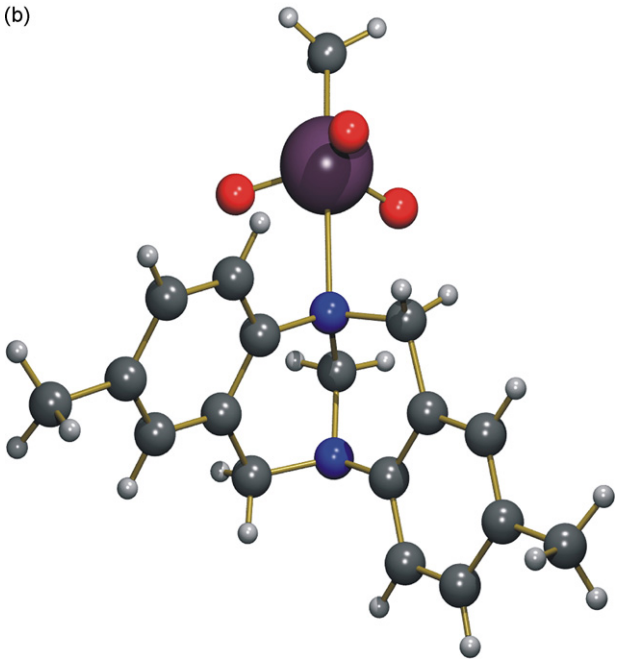


Fig. 17. (a) Complex **18** (b) X-ray crystal structure of [(5*R*,11*R*)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[*b*,*f*]-(1,5)diazocine] (**18**) [51]. Color code: dark gray, carbon; light gray, hydrogen; maroon, rhenium; red, oxygen; blue, nitrogen.

ethylamine, and L-prolinamide. The complexes formed were used in epoxidation reactions with 1-methyl-cyclohexene and α-pinene as substrates with H_2O_2 as oxidant. The ees were between 4 and 36% using at temperatures from −5 to −55 °C (conversions from 9 to 59%). Unfortunately the highest ees were not associated with the highest conversions—the highest ee of 36% (with *cis*-β-methylstyrene substrate and

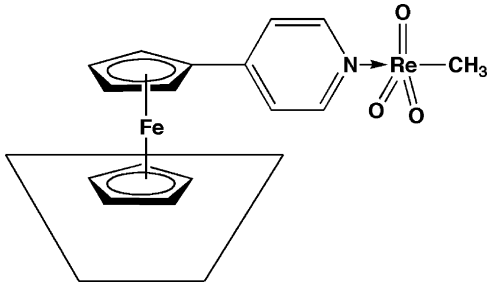


Fig. 18. Heterogenization of ferrocenyl pyridine linker attached MTO on beta-cyclodextrine.

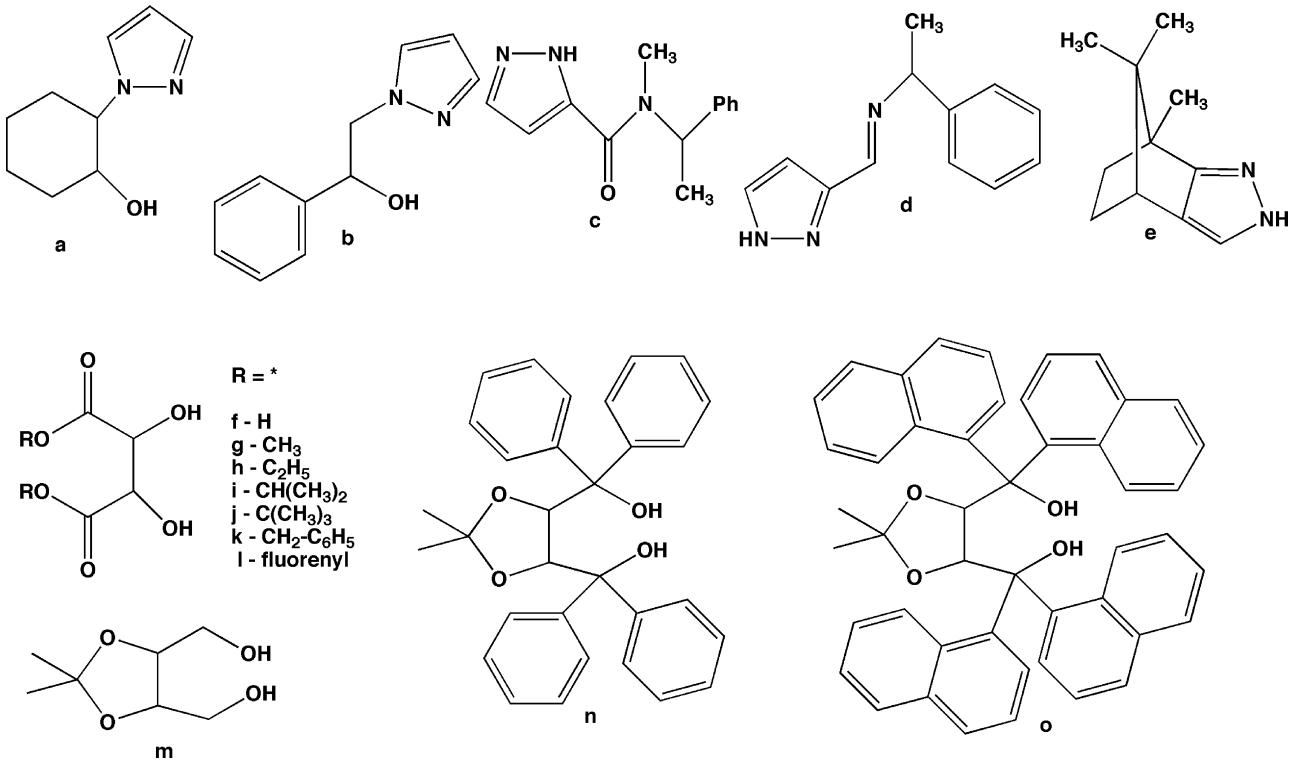


Fig. 19. Various ligands used in synthesis of chiral Re(VII) complexes.

(*R*)-(+)-phenyl ethylamine catalyst) had a conversion of only 10%.

Following these reactions, in 2004, Herrmann and coworkers [56] applied chiral Lewis base ligands (Fig. 19) based on pyrazole, but once again highest ees were associated with low conversions as seen in Table 5.

Burke and colleagues prepared chiral non-racemic 2-substituted pyridine derivatives of MTO and published their observations in May 2005 [37]. Efforts were made at obtaining good enantioselectivities in simple olefin epoxidations with MTO and six different chiral ligands; **9**–**15** and **19** (Fig. 18). Urea-hydrogen peroxide was chosen as the peroxide source to avoid unfavourable competition from water for vacant sites on the metal. On an average the ees obtained were low and lay between 3 and 12% as shown in Table 6. Three types of 2-substituted pyridine systems were explored in the paper. Some of the complexes have been successfully applied [57–59] before (Fig. 20).

Complex **19** obtained in about 48% yield, was the first such ligand to be prepared via the treatment of picolinic acid chloride with menthol alkoxide. Complex **9** was obtained as a white powder on purification in a yield of 63%, from dimethyl(2*R*,3*R*,5*R*,6*R*)-dimethoxy-2,3-dimethyl-1,4-dioxane-5,6-dicarboxylate. The complex **10**

Table 5
Application of chiral pyrazole based ligands (Fig. 15) in catalytic epoxidations [54]

Serial no.	Olefin	Ligand	Conversion (%)	ee (%)	Conditions
1	*cis*-β-Methylstyrene	a	6	27	−30 °C, 1 h
2	*cis*-β-Methylstyrene	b	9	12	−30 °C, 1 h
3	*cis*-β-Methylstyrene	c	14	10	−30 °C, 1 h
4	*cis*-β-Methylstyrene	d	22	15	−30 °C, 1 h
5	*cis*-β-Methylstyrene	e	22	6	−30 °C, 1 h
6	*cis*-β-Methylstyrene	f	30	5	−25 °C, 1 h
7	*cis*-β-Methylstyrene	g	–	–	−25 °C, 1 h
8	*cis*-β-Methylstyrene	h	10	11	−25 °C, 1 h
9	*cis*-β-Methylstyrene	i	5	18	−25 °C, 1 h
10	*cis*-β-Methylstyrene	j	7	15	−25 °C, 1 h
11	*cis*-β-Methylstyrene	k	10	15	−25 °C, 1 h
12	*cis*-β-Methylstyrene	l	8	16	−25 °C, 1 h
13	*cis*-β-Methylstyrene	m	5	41	−25 °C, 1 h
14	*cis*-β-Methylstyrene	n	5	15	−25 °C, 1 h
15	*cis*-β-Methylstyrene	o	5	14	−25 °C, 1 h

Using H_2O_2 in CH_2Cl_2.

Table 6
MTO catalysed epoxidation of simple olefins using chiral ligands[a] **9–13**, **19**

Serial no.	Olefin	Ligand	Conversion (%)	ee (%)	Conditions
1	1-Methylcyclohexane	**10**	90	7	0 °C, 24 h
2	1-Methylcyclohexane	**10**	75	11	Rt, 5 h
3	Styrene	**10**	36	12	Rt, 24 h
4	4-Methylstyrene	**12**	7	12	Rt, 13 h
5	4-Methylstyrene	**13**	17	9	Rt, 13 h
6	1-Methylcyclohexene	**19**	63	9	Rt, 5 h
7	1-Methylcyclohexene	**11**	69	7	Rt, 5 h
8	1-Methylcyclohexene	**9**	61	8	Rt, 24 h

UHP used as a source of H_2O_2.

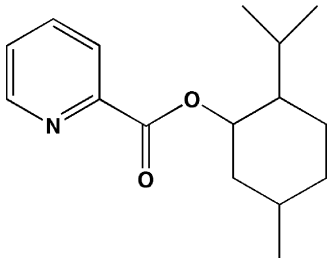


Fig. 20. Ligand **19**.

was prepared from (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylic acid dimethyl-ester and was obtained in a yield of 72%. Complex **11**, used previously for Mo-catalysed asymmetric allylic alkylation reactions [59]—was prepared in an enantiomerically pure form from commercial diaminocyclohexane. The ligands **12** (58%) and **13** (45%) were synthesized by treating 2-bromo-6-(1-pyrazolyl)pyridine (obtained from 2,6-dibromopyridine using the procedure of Jameson and Goldsby [60]) with sodium (l)-mentholate and sodium isopinocampheolate. As seen in Table 6, the selectivity for epoxide formation was ≥85% in all cases.

4. Conclusions and outlook

Considering the work on chiral high oxidation state rhenium and molybdenum organometallic complexes it is quite obvious that the focus has been more towards molybdenum compounds than to rhenium complexes. Several reasons seem to be responsible for this imbalance. One of them is that MTO, by far the best catalyst yet examined in the rhenium(VII) organometallics family cannot be easily derivatized. Branched complexes (particularly at the α-C atom) tend to be both temperature and moisture sensitive as well as difficult to synthesize. The usual approach for introduction of chirality into R–ReO_3 complexes was therefore the attachment of chiral donor ligands, e.g. monodentate chiral N-bases. These donor complexes, however display a notoriously weak Re–donor interaction, leading only to low enantiomeric excesses. Applying the donor ligands in huge excess, as in the case of non-chiral epoxidation catalysis makes the whole process significantly more wasteful and expensive. The weakness of the Re–donor interaction also hampers the immobilisation of the Re(VII) compounds on carrier materials. Bidentate donor ligands are more strongly attached to the Re(VII) center, but also undergo exchange reactions and thereby hinder the catalytic reactions due to their steric demands. Accordingly, they are also not ideally suited for introducing chirality in the R–ReO_3 catalyst systems. A possible way around these problems may be systems, which contain ligands which are not branched at the α-position or that contain intramolecular donor functions that can reversibly open vacant coordination sites, without losing chirality and stability.

In the case of organometallic Mo(VI) a larger variety of systems has been examined. However, even here the synthesis of chiral catalysts is still in its infancy. As in the case of the above discussed Re(VII) systems the usual approach for chirality is via donor ligands, which, so far, have been bidentate in most cases. The ees obtained are still low, however, and the number of applied substrates appears to be somewhat limited. As in the case of Re(VII), the metal donor interaction is comparatively weak and intramolecular rearrangements as well as ligand exchange reactions seem to be quite common, being in disfavour of chirality transfer to prochiral substrates. Nevertheless, some of the applied systems seem to have potential for better chirality transfer in organic reactions. The main advantage of the Mo(VI) systems in comparison to their Re(VII) counterparts is that a wider variety of potentially applicable catalysts is already available. It is also possible to utilize more than one organic ligand, bound by a covalent Mo–C interaction. Accordingly, both immobilisation and the introduction of chirality would be possible via groups more strongly attached to the metal atom. Immobilisation has already been successfully achieved for several high oxidation state Mo organometallics and there seems to be no serious doubt that efficient chiral catalysts will follow soon. Besides additional synthetic work, theoretical examination will be needed to achieve optimal results.

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