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Review

# Monomeric cyclopentadiene molybdenum oxides and their carbonyl precursors as epoxidation catalysts

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## Abstract

Monomeric cyclopentadiene molybdenum oxides were among the first synthesized high oxidation state organometallics. However, their syntheses and applications have long been overshadowed by their rhenium(VII) congeners, in particular by (pentamethylcyclopentadienyl)trioxorhenium(VII) and methyltrioxorhenium(VII). Only during the last decade a renaissance of the cyclopentadienyl molybdenum oxides is starting. Both with respect to synthetic access ways and to applications as oxidation catalysts in homogeneous and heterogeneous phase the interest in cyclopentadienyl molybdenum oxides and their tricarbonyl precursors is increasing. This results from the usually time-easy and straightforward synthetic procedures leading to these compounds and their easy heterogenizability, both on mesoporous materials and in ionic liquids. The catalytic performance, especially in olefin epoxidation with *tert*-butylhydroperoxide being the oxidant is very good and the derivatization to reach taylor made catalysts seems to be much easier than in the case of the organorhenium oxides. Another advantage in comparison to the latter complexes is the possible presence of two organic functionalities, which can be independently modified, e.g. for heterogenization of the complexes and for the enhancing of their catalytic activity at the same time.

*Keywords:* Catalysis; Molybdenum; Cyclopentadiene; Oxides; Carbonyles

## Contents

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## 1. Introduction

In the early days of organometallic chemistry the future importance of such compounds in catalysis was not foreseen. When the first high oxidation state organometallics were described about 45 years ago, they seemed to be mere curiosities. Accordingly, the first molybdenum (VI) cyclopentadienyl dioxo complex, $CpMoO_2Cl$, described by Cousins and Green [1] was not viewed as a potential catalyst. The quite difficult synthesis was only one of the obstacles on the way to possible applications. Major breakthroughs for the interest in and applicabilities of high oxidation state organometallics were marked by the finding of related organorhenium oxides by Beatty and Jones and by Herrmann et al. and the uncovering of their broad catalytic utilizability [2]. In the mean time, the synthetic approaches to monomeric cyclopentadiene molybdenum oxides are manifold, among them some very convenient ones. This also led to a growing interest in both their reaction behavior and their potential usefulness. This article intends to highlight the history of, and developments achieved on cyclopentadiene molybdenum dioxides and describes the applications they found up to now.

## 2. Synthesis of organomolybdenum (VI) complexes

In 1963 Cousins and Green reported on the first example of an organometallic molybdenum(VI) cyclopentadienyldioxo complex, $CpMoO_2Cl$ (Fig. 1) [1], being one of the first monomeric high oxidation state organometallic oxides ever obtained. This complex was synthesized in very low yields and adventitiously as the only isolable product from air oxidation of $CpMo(CO)_2(\pi\text{-}C_3H_5)$ in the presence of HCl. Green and co-workers later rationalized several synthetic methods of obtaining $CpMoO_2Cl$ [3–5] and its bromo derivative, $CpMoO_2Br$ (Fig. 1). Both derivatives were described as yellow solids, stable under nitrogen atmosphere, decomposing slowly under air and rapidly in solution.

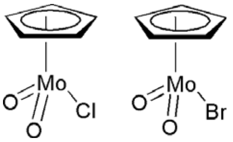

Fig. 1. Dioxo cyclopentadienyl halide complexes $CpMoO_2X$.

As mentioned before, the yields obtained via the synthetic procedures developed by Green et al. are generally low and the synthetic pathways are quite unspecific for obtaining $CpMoO_2Cl$, since several other species such as mono oxo and dimeric complexes are also formed. These difficulties are probably the cause for a gap between these early works and the next publications dealing with Cp dioxo molybdenum complexes.

In 1988, possibly inspired by the preparation and characterization of $Cp^*ReO_3$, synthesized independently nearly at the same time by Herrmann et al. and Sutton et al. [2,6–8], Faller and Ma reported the synthesis of $Cp^*MoO_2Cl$ ($Cp^*$ = pentamethyl cyclopentadienyl) [9,10]. $Cp^*MoO_2Cl$ was obtained 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 $PCl_5$ (Fig. 2). A substantial improvement in stability (the compound is thermally stable and can be handled easily in dry air), ease of preparation and ease of separation from other reaction products was observed in comparison to its Cp counterpart as described by Green et al. (see above). X-ray crystallography showed that $Cp^*MoO_2Cl$ presents the expected mononuclear piano-stool structure, but disorder between an oxygen and the chloride prevented the authors from obtaining accurate structural data.

Still in 1988, Legzdins et al. [11,12] reported a more general synthetic route to prepare complexes of the type $Cp'MoO_2R$ ($Cp' = Cp$, $Cp^*$; $R = CH_3$, $CH_2SiMe_3$). The synthetic procedure consists of the exposure of 16-electron dialkyl nitrosyl complexes $Cp'Mo(NO)R_2$ to water and molecular oxygen, converting them into the corresponding dioxo alkyl compounds in high yields (>80%) (Fig. 3). Interestingly, the yields obtained in the absence of water were ca. 15% lower, and no clear explanation could be given for this observation. The spectroscopic properties of the compounds reported by the research group of Legzdins are consistent with the familiar three-legged piano-stool molecular structures having mirror symmetry at the central metal atom. Treatment of the complexes of the type $Cp'MoO_2R$ with 30% aqueous $H_2O_2$ in $Et_2O$ results in their clean conversion to $Cp'MoO(\eta^2\text{-}O_2)R$ ($Cp' = Cp$, $Cp^*$; $R = Me, SiMe_3$).

While studying the reactivity of Cp-metal-nitrosyl complexes towards oxygen, Hubbard et al. found that $CpMo(NO)_2Cl$ and $Cp^*Mo(NO)_2Cl$ are transformed in the presence of oxygen into $Cp'MoO_2Cl$ [13]. The work also showed that treatment of $Cp'Mo(NO)_2CH_2X$ complexes with $O_2$ leads to the initial formation of $CH_2O$ together

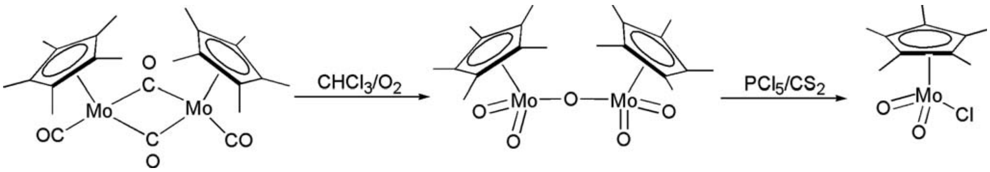

Fig. 2. Two-steps oxidation of the dimeric carbonyl precursor $[Cp^*Mo(CO)_2]_2$ to the dioxo cyclopentadienyl halide complex $Cp^*MoO_2Cl$.

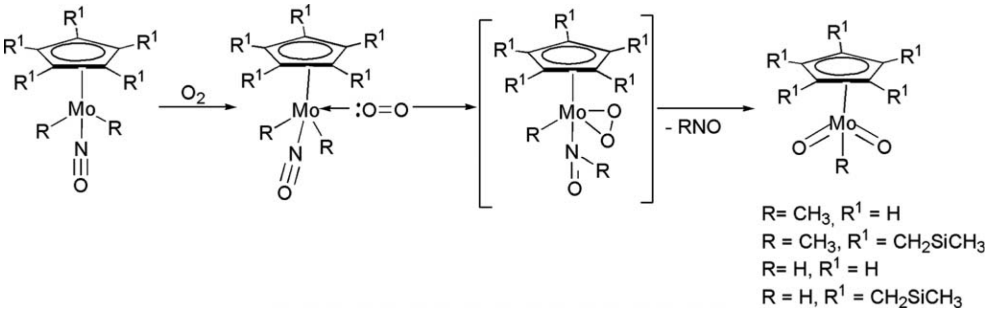

Fig. 3. Conversion of the dialkyl nitrosyl complexes $Cp'Mo(NO)R_2$ into the dioxo alkyl complexes $Cp'MoO_2R$ by exposure to $O_2$.

with the generation of $Cp'Mo(NO)_2Cl$. This demonstrates that the Mo–$CH_2$ moiety is more sensitive to oxidation than the Mo–NO moiety. In contrast to the $Cp'Mo(NO)_2CH_2X$ derivatives, alkyl complexes $CpMo(NO)_2R$ (R = Me, Et) and $Cp^*Mo(NO)_2R$ react with $O_2$ to originate $CpMoO_2R$ (R = Me, Et) and $Cp^*MoO_2Me$, showing that in this case the Mo–C bond is surprisingly resistant to oxidative attack, probably due to the absence of a labile α substituent.

Based on the synthetic methodology of Legzdins et al., the research group of P. Royo obtained $Cp^*MoO_2Br$ and its hydrolysis product $[Cp^*MoO_2]_2\mu$-O by exposing the complex $[Cp^*Mo(NO)MeBr]_2$ to air and light for one week [14].

Irradiation of $Cp^*Mo(CO)_3Cl$ in toluene under an oxygen purge for 2 h resulted in the formation of $Cp^*MoO_2Cl$ in ca. 60% yield [15] (Fig. 4). The use of the chloride carbonyl compound as precursor eliminated the need to conduct the reaction in chlorinated solvents.

$Cp^*MoCl_4$ was found to yield $Cp^*MoO_2Cl$ by reaction with aqueous NaOH in the presence of air [16]. Reaction times lower than 30 min lead to the formation of a mixture of $Cp^*MoO_2Cl$ and $Cp^*MoOCl_2$ (the logical intermediate to the dioxo complex) (Fig. 5), on the other hand, the use of excess base and longer reaction times lead to the formation of the μ-bridged oxo dimer $[Cp^*MoO_2]_2O$. This dimer is likely formed by hydrolysis of $Cp^*MoO_2Cl$ to generate $Cp^*MoO_2OH$, which then undergoes condensation via loss of $H_2O$. The base used in these reactions also has a strong influence on the products obtained. In fact, when $Cp^*MoCl_4$ is reacted with ${}^tBuNH_2$ in the presence of water and air an anionic trioxo complex $[Cp^*MoO_3]^-$ is formed that can be isolated as its $[{}^tBuNH_3]^+$ salt. The treatment of this complex with gaseous HCl gives a clean formation of $Cp^*MoO_2Cl$.

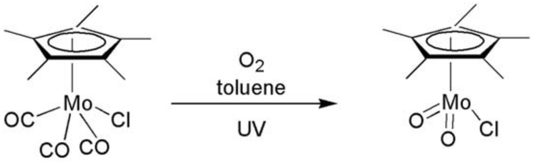

Fig. 4. Conversion of the carbonyl precursor $Cp^*Mo(CO)_3Cl$ to the dioxo complex $Cp^*MoO_2Cl$ by irradiation and oxygenation.

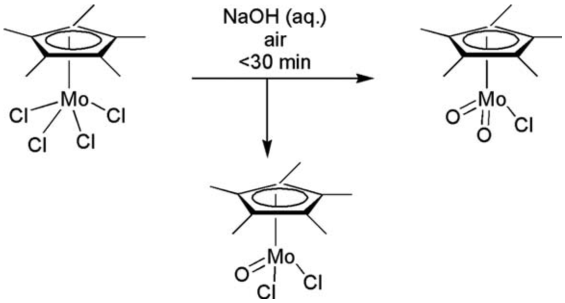

Fig. 5. Conversion of the tetrachloro complex $Cp^*MoCl_4$ to mono- and di-oxo complexes of formulae $Cp^*MoOCl_2$ and $Cp^*MoO_2Cl$, by exposure to NaOH and air.

In 1994 Bottomley et al. [17] reported the essentially quantitative (86% yield) synthesis of $Cp^*MoO_2Cl$ by oxidation of $[Cp^*Mo(CO)_2]_2$ with 30% aqueous $H_2O_2$ followed by immediate addition of HCl (Fig. 6). The decomposition of $Cp^*MoO_2Cl$ was found to be thermal, but accelerated by light and inhibited by dry oxygen. $Cp^*MoO_2CH_3$ could also be obtained by hydrolysis of $Cp^*Mo(N^tBu)_2CH_3$ with excess aqueous HCl in THF [18].

More than 20 years after the last synthesis presented by Green et al. for $CpMoO_2Cl$ [5], the readily available $(NH_4)_2Mo_2O_7$ was used as a starting material and reacted with $Me_3SiCl$ in 1,2-dimethoxyethane (DME) yielding

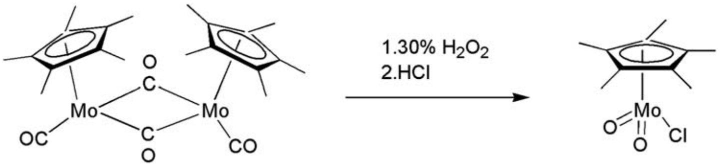

Fig. 6. Conversion of the dicarbonyl dimer $[Cp^*Mo(CO)_2]_2$ to the dioxo complex $Cp^*MoO_2Cl$ by treatment with $H_2O_2$ and subsequently with HCl.

$MoO_2Cl_2(DME)$, which reacts with TlCp to originate $CpMoO_2Cl$. However, the obtained yields were comparable to the ones previously reported [19]. $Cp(SiMe_3)MoO_2Cl$ and $Cp(SiMe_3)_2MoO_2Cl$ could also be obtained by reacting $MoO_2Cl_2(DME)$ with $NaCp(SiMe_3)$ and $NaCp(SiMe_3)_2$ [19]. Product yields are also moderate, even if the reaction is carried out at low temperature. Presence of the trimethylsilane group in the cyclopentadienyl ring is responsible for an enhancement of the complex solubility in supercritical $CO_2$ without significant modifications of the chemical properties of the metal [20].

A general and straightforward one-step synthesis of $(\eta^5\text{-}C_5R_5)MoO_2Cl$ ($R = H, CH_3, CH_2Ph$ (Bz)) complexes from their corresponding and readily available $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ precursors was reported by Romão, Kühn et al. [21]. The desired complexes could be obtained in yields up to 75% by stirring a solution of the carbonyl precursors in $CH_2Cl_2$ with excess of *tert*-butyl hydroperoxide (TBHP) for ca. 2 h (Fig. 7). Dimethyldioxirane is unable to oxidatively decarbonylate the $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ to $(\eta^5\text{-}C_5R_5)MoO_2Cl$ in contrast to the examples of $Cp^*ReO_3$ and $[TpMo(CO)_3]^-$ [22] (Tp = hydridotris(1-pyrazolyl)-borate).

In comparison to the synthetic routes described previously, the oxidative decarbonylation of $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ provides a more general route comprising different substituents on the Cp ring. All three compounds originally described in the work of Romão, Kühn et al. can be handled in air for brief periods of time, but are somewhat moisture sensitive in solution. $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ is significantly more stable than its Cp and Cp* counterparts, probably due to the steric bulk of the Cp ligand. A noteworthy increase in stability, even in comparison to $Cp^*MoO_2Cl$ had been previously observed with the compound $(\eta^5\text{-}C_5Ph_4(2,5\text{-dimethoxyphenyl}))MoO_2Br$ [23]. Detailed spectroscopic examinations have shown that the carbonyl precursor show a stronger Mo-$(\eta^5\text{-}C_5R_5)$ interaction than their dioxo congeners. The mechanism of the oxidative decarbonylation has been addressed by Gonçalves et al. [24]. While CO liberation was observed, no $CO_2$ formation could be detected.

Another synthetic method for $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ was presented by Martins, Romão, Poli et al. [25]. Treatment of the $\eta^2$-acyl complex $(\eta^5\text{-}C_5Bz_5)MoCl_3(COCH_3)$ with excess TBHP in $CH_2Cl_2$ originated $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ (Fig. 8). The obtained yield is much higher than the yields previously reported for other cyclopentadienyl complexes.

An X-ray structure of $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ has also been obtained. However, attempts to alkylate $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ with allylmagnesiumbromide and $ZnMe_2$ failed.

While trying to obtain model compounds for transition metal complexes anchored on silica surfaces (see below), complexes of the type $Cp^*MoO_2OR$ ($R = SiBz_3$, $[(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]$) were obtained [26,27]. $Cp^*MoO_2OSiBz_3$ was received by the reaction of $[CpMoO_3]^-$ with $Bz_3SiCl$ [27]. This reaction also afforded as by-product $Cp^*MoO_2Cl$. Reaction of $Cp^*MoCl_4$ and $[(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]SiOH$ in the presence of triethylamine led to the isolation of $Cp^*MoORSi_2O_3(OH)_2$ ($R = [(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]$), which on the exposure to atmosphere is oxidized to $Cp^*MoO_2OR$ ($R = [(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]$) (Fig. 9) [28].

The previously mentioned $(\eta^5\text{-}C_5Ph_4(2,5\text{-dimethoxyphenyl}))MoO_2Br$ complex [23] was obtained by heating a toluene solution of $(\eta^5\text{-}C_5Ph_4(2,5\text{-dimethoxyphenyl}))Mo(CO)_3Br$ at reflux temperature under a dioxygen atmosphere until the carbonyl bands disappear completely from the infrared spectrum (yield >80%).

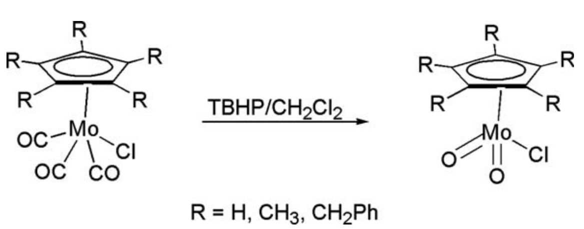

Fig. 7. Conversion of the carbonyl precursor $Cp'Mo(CO)_3Cl$ to the dioxo complex $Cp'MoO_2Cl$ by treatment with TBHP.

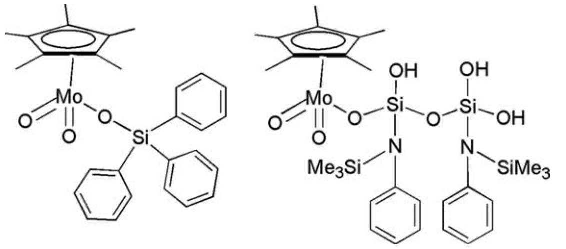

Fig. 9. Dioxo complexes of the type $Cp^*MoO_2OR$ ($R = SiBz_3$, $[(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]$).

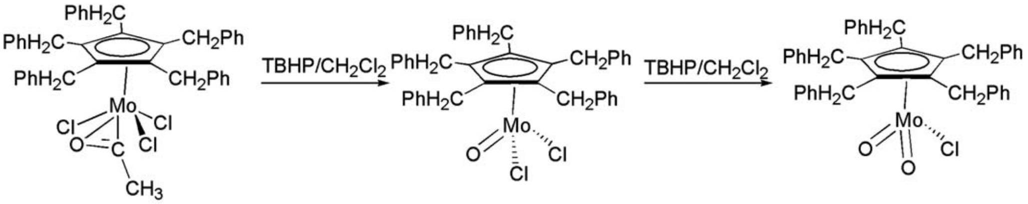

Fig. 8. Conversion of the $\eta^2$-acyl complex $(\eta^5\text{-}C_5Bz_5)MoCl_3(COCH_3)$ to the dioxo complex $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ by treatment with TBHP.

Other examples of complexes where the cyclopentadienyl ring shows a high degree of substitution are for instance $(C_5H(^iPr)_4)MoO_2Cl$, reported recently by Poli et al. [28]. The authors followed the same synthetic approach as Geoffrey et al. [16] for $Cp^*MoO_2Cl$ and reported also the X-ray crystal structure of $(C_5H(^iPr)_4)MoO_2Cl$. Following this work, Poli et al. also reported speciation studies of $Cp^*Mo$ complexes over the entire pH range in an essentially pure aqueous environment by stopped-flow kinetic analysis, on-line electrochemical flow-cell and electrospray mass spectroscopy [29–31], revealing the existence and stability of the complexes $Cp^*MoO_2OH$ and $[Cp^*MoO_2]^+$ as a function of pH. The authors also concluded that the inertness of the $Cp^*$–Mo bond, which resists hydrolysis down to pH zero, has as consequence the blocking of three coordination positions, rendering the $Cp^*Mo^{VI}$ species unable to form extended oligonuclear aggregates.

## 3. Epoxidation reactions under homogeneous conditions

The catalytic activity of dioxomolybdenum complexes containing cyclopentadienyl ligands was – until recently – solely examined for $Cp^*MoO_2Cl$ by Bergman and Trost [15]. $Cp^*MoO_2Cl$ was shown to act as a catalyst for the epoxidation of several olefins (such as cyclooctene, geraniol, 1,2,4,5-tetramethylcyclohexa-1,4-diene), as long as they do not include any electron-withdrawing groups. Apart from TBHP, other alkyl hydroperoxides such as cumene hydroperoxide and *n*-hexylhydroperoxide could be used as oxidants (Fig. 10a). However, both with $H_2O_2$ and $Ph_3COOH$ no catalytic reaction occurred (Fig. 10b) and $Cp^*Mo(O_2)OCl$ was formed.

The authors found TBHP to react with $Cp^*MoO_2Cl$ (in the absence of olefins) originating a complex of the type $Cp^*Mo(O_2)OCl$ (Fig. 11). Curiously, catalytic reactions performed with the isolated $Cp^*Mo(O_2)OCl$ led to no olefination products, therefore this complex was considered to be a unwanted side product and it was concluded that the active species cannot be a $\eta^2$-coordinated peroxo complex. These results were later supported by Roesky et al. who received a X-ray crystal structure of $Cp^*Mo(O_2)OCl$. They also described this compound as being not active as olefin epoxidation catalyst in the presence of excess TBHP [32].

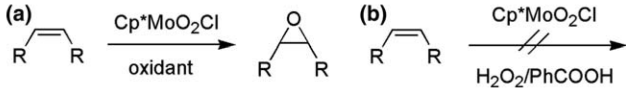

Fig. 10. Olefin epoxidation with $Cp^*MoO_2Cl$ as catalyst. (a) The reaction is achieved with TBHP or other alkylhydroperoxides as the oxidant. (b) The reaction does not occur when $H_2O_2$ or $Ph_3COOH$ is applied as the oxidant.

Throughout times other authors had also described the synthesis of cyclopentadienyl peroxo complexes, but without focusing on their potential catalytic activity. Faller and Ma were the pioneers in the synthesis of $Cp^*Mo(O_2)OCl$ [10]. Later, Royo et al. presented two other alternative synthetic pathways to obtain $Cp^*Mo(O_2)OCl$, which could also be applied to obtain $CpMo(O_2)OCl$ [33]. The molecular structure of $CpMo(O_2)OCl$ was determined by X-ray crystallography [34]. Prior to the synthesis of $Cp^*Mo(O_2)OCl$, Legzdins et al. obtained the complexes $Cp'Mo(O_2)OR$ ($Cp' = Cp$, $Cp^*$; $R = CH_3$, $CH_2SiMe_3$) [11,12].

Except for the formation of $Cp^*Mo(O_2)OCl$, the catalyst precursor $Cp^*MoO_2Cl$ seems to maintain its integrity during the catalytic reaction, showing no observable oxidation of the $Cp^*$ ligand (the catalytic reaction was performed in a deuterated solvent and monitored by $^1H$ NMR) [15]. The effect of the alkyl peroxide used on the relative rate of the epoxidation reaction was investigated and the obtained rates were consistent with the formation of an intermediate species in which the alkyl group of the peroxide moiety is intact. That is, the relative rates depend on the structure of the alkyl group of the alkyl peroxide. Catalyst loads of 2–5% were used depending on the substrate and the reaction temperatures spanned from RT (room temperature) to 60 °C.

Kühn, Romão et al. [21] have extended the study of the catalytic properties of $Cp'MoO_2Cl$ compounds. The complexes $(\eta^5\text{-}C_5R_5)MoO_2Cl$ (R = H, $CH_3$ (Me), $CH_2Ph$ (Bz)) were used as catalysts for the epoxidation of cyclooctene, styrene and 1-octene. The reactions were conducted at 55 °C using catalyst loadings of 1 mol%, with TBHP as oxidant. The influence of the ring substituents on the catalyst activity was studied in detail for cyclooctene. Both the complexes $(\eta^5\text{-}C_5H_5)MoO_2Cl$ and $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ show good activity, reaching a 100% conversion after 4 h reaction time. However, in a second and third catalytic run (by addition of new substrate) the complex $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ maintains most of its activity, while that of the Cp derivative declines strongly due to catalyst decomposition. $(\eta^5\text{-}C_5Me_5)MoO_2Cl$ reaches only about 60% of the activity of the other derivatives in the first run and shares the same decomposition problems observed for $(\eta^5\text{-}C_5H_5)MoO_2Cl$ under catalytic conditions. Due to

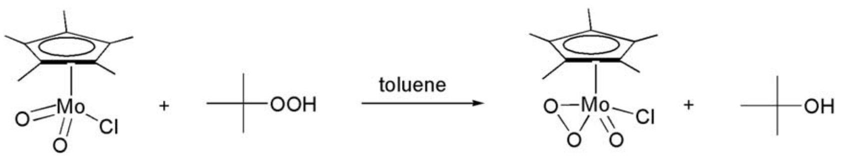

Fig. 11. TBHP reacts with $Cp^*MoO_2Cl$ to form a $\eta^2$-peroxo complex of formula $Cp^*Mo(O)_2OCl$.

its high stability and activity, catalytic runs were performed using a lower catalyst load of ($\eta^5$-$C_5Bz_5$)$MoO_2Cl$. Using a 0.1% catalyst load under the same reaction conditions, TOFs (turnover frequencies) of 4000 $h^{-1}$ were obtained, and lowering the Mo compound load to 0.01%, values of 20,000 $h^{-1}$ could be achieved. However, at these low catalyst loadings the residual amount of water present in the system gains increasing influence on the catalytic performance after some time and therefore, the catalytic activities trail off considerably after 1 h reaction time for the lowest catalyst amounts applied. The high activity of ($\eta^5$-$C_5Bz_5$)$MoO_2Cl$, despite its higher steric bulk, was ascribed both to its higher stability towards moisture and the lower electronic density at the Mo center, in comparison to the derivatives ($\eta^5$-$C_5Me_5$)$MoO_2Cl$ and ($\eta^5$-$C_5H_5$)$MoO_2Cl$, due to a weaker Mo-ring bond, as reflected in the $^{95}$Mo NMR and vibrational spectroscopy. Styrene and 1-octene could also be transformed to their respective epoxides with ($\eta^5$-$C_5H_5$)$MoO_2Cl$, ($\eta^5$-$C_5Me_5$)$MoO_2Cl$ and ($\eta^5$-$C_5Bz_5$)$MoO_2Cl$, the best results being again obtained with ($\eta^5$-$C_5Bz_5$)$MoO_2Cl$. Ring opening of the styrene epoxide to the diol is not significant under the conditions applied; 1-octene, being an un-activated, un-functionalized olefin reacts significantly slower than the other substrates.

The groups of Martins, Romão and Poli extended the study of the catalytic performance of the dioxomolybdenum complexes containing cyclopentadienyl ligands to the complex $C_5H(^iPr)_4MoO_2Cl$ and to several dinuclear complexes [25]. One of the aims of this study was to assess the activity dependence of $Cp'MoO_2Cl$ complexes by the nature of the ring substituents using TBHP as oxidant. The authors concluded that the nature of the substituents strongly influences the overall performance of the catalysts, both in terms of initial activity rates but, more importantly, in terms of their long-term performance at 24 h reaction time. The steric bulk was not considered the decisive parameter to control this dependence, but the authors state that the reactivity of the complexes can be explained in terms of the ability of the $Cp'MoO_2Cl$ complexes to undergo ring-slippage or distortion that might alleviate the steric pressure on the intermediates. The same study also showed that $Cp'MoO_2Cl$ complexes are catalytically active in aqueous solutions provided TBHP is used instead of $H_2O_2$. These results came not unexpectedly, since the authors had previously reported on the $Cp^*MoO_2$(VI) fragment surviving a wide range of pH conditions in aqueous solutions [31]. The mechanism of the reaction of $Cp'MoO_2Cl$-type complexes with TBHP, however, remains still to be clarified [32].

The carbonyl precursor compounds of the $Cp'MoO_2Cl$ complexes were also found to be active catalysts for the epoxidation reactions (Fig. 12) [21,31].

This follows directly from the chemistry involved in the synthesis of the dioxo complexes, since in the catalysis TBHP is present in large excess and oxidizes readily the carbonyl compounds. The carbonyl complexes are more stable than the dioxo complexes, and therefore can be used directly as easily storable forms of catalyst precursors. In fact, the carbonyl compounds reach (within the measurement error) the same TOFs as do the oxides when used as epoxidation catalysts in the presence of TBHP [21]. However, in the case of $(C_5Bz_5)Mo(CO)_3Me$ conversion to the epoxide was also reported to stagnate after 30 min of reaction [25].

Based on the finding that the carbonyl precursor compounds of the $Cp'MoO_2Cl$ complexes were also active catalysts for the epoxidation reactions, several carbonyl compounds of formula $Cp'Mo(CO)_3R$ (R = alkyl) were synthesized and applied directly as epoxidation catalysts in the presence of excess TBHP (Fig. 13) [34].

The formation of the respective dioxo complexes was confirmed by in situ IR spectroscopy. The authors showed that the carbonyl complexes can be applied as active (TOFs up to ca. 6000 $h^{-1}$; TON > 500) and selective epoxidation catalysts. The study also showed that increasing the alkyl substitution of the Cp ligand lowers the catalytic activity, and that ansa-bridged derivatives, being more difficult to synthesize than their non-bridged congeners, seem to show no significant advantage when applied in catalysis. The original idea behind the synthesis of ansa-bridged compounds was to hinder Cp-loss after possible intermediate ring slippage. Ansa-bridged derivatives have been used to introduce chirality in the system by transforming the bridging C-atoms into chiral centers. However, it turned out that ansa-bridges with only two carbon atoms in the bridge are not sufficiently stable, due to considerable ring strains under oxidative conditions [35]. Introducing chirality with a chiral substituent on the Cp-ring has also been attempted.

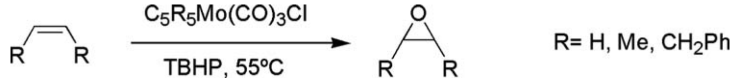

Fig. 12. Olefin epoxidation applying carbonyl compounds of composition $Cp'Mo(CO)_3Cl$ and excess of TBHP.

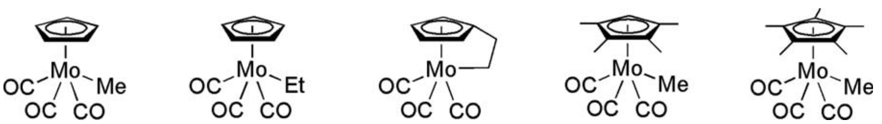

Fig. 13. Examples for synthesized carbonyl precursors of the $Cp'MoO_2R$ compounds.

Such an approach leads to stable but low enantiomeric excesses (ca. 20% ee) due to the free rotation of the Cp-ring [36]. As it seems, the combination of both a longer chain bridge and the introduction of chirality either on the bridge, close to the Mo atom or on the – then fixed – Cp ring could lead to a useful chiral catalyst, leading to high ees.

Recently, monomeric molybdenum(VI) tricarbonyl complexes bearing 1,4,7-triazacyclononane and 1,1,1-tris(aminomethyl) ethane ligands have been synthesized. From a structural point of view they are closely related to the title complexes. As in the case of the Cp complexes, they are assumed to be oxidized in situ to oxo-complexes and can be applied as epoxidation catalysts, however, with a somewhat lower activity and an induction period for the carbonyl-oxo transformation, preceding the catalytic reaction [37].

The catalytic activity of $Cp(SiMe_3)MoO_2Cl$ [19,20] and $Cp(SiMe_3)_2MoO_2Cl$ [20] in oxidation reactions was also reported. Montilla et al. have studied the catalytic properties of $Cp(SiMe_3)MoO_2Cl$ in the oxidation of $PPh_3$ by molecular oxygen and the epoxidation of cyclohexene by TBHP in different media [20]. Epoxidation of cyclohexene was first attempted with $O_2$ and $H_2O_2$ as oxidant but failed under various conditions. However (and also not unexpectedly), $Cp(SiMe_3)MoO_2Cl$ was shown to catalyze the epoxidation of cyclohexene with TBHP in supercritical $CO_2$, under a variety of temperatures (from 40–70 °C) and with 1.4 mol% of catalyst [20]. Less satisfactory values than those obtained by using $Cp'MoO_2Cl$ in conventional solvents [15] were attributed to technical problems during the depressurization process.

## 4. Heterogenization and heterogeneous catalytic applications

Immobilization of organomolybdenum (VI) catalysts has received considerable attention in recent years, since immobilizing defined catalysts or catalyst precursors may combine the most advantageous properties of both homogeneous and heterogeneous systems: easier product/catalyst separation, high activity and selectivity. Many efforts have been dedicated to enhance the activity of such heterogenized complexes, being usually lower than under homogeneous conditions, due to low loadings and problems concerning the accessibility of the catalytic sites. The latter point may be, however, an advantage, if considered from a selectivity point of view. Quite often the selectivity observed is indeed better with heterogenized catalysts than with homogeneous catalysts. Since in some cases leaching occurs (sometimes very severely), a part of the activity may in fact result from a homogeneous catalyst. The recyclability is of utmost interest for industrial applications, but often not trivial to obtain. Different supports have been investigated in the case of $CpMo(CO)_3X$-systems, largely mesoporous sieves and ionic liquids.

### 4.1. Heterogenization on mesoporous sieves

The mesoporous silicates, designated as MCM-41 and MCM-48 by Mobil scientists [38] (Mobil Catalytic Material), are among the best studied inorganic supporting materials. They provide high surface areas ($1000\ m^2\ g^{-1}$), high pore volumes ($1\ cm^3\ g^{-1}$), very narrow pore size distributions, large numbers of inner surface silanol groups and high chemical and thermal stability. Various ways of immobilization have been developed, from direct grafting [39–42] to tethering via a functionalized spacer ligand, introduced either on the complex or on the support. The modified mesoporous materials are characterized by elemental analysis (EA), which indicates in particular the metal loading, by powder X-ray diffraction, $N_2$ adsorption, magic angle spinning (MAS) NMR spectroscopy ($^{13}C$, $^{29}Si$), IR spectroscopy, and in some cases EXAFS (extended X-ray absorption fine structure) spectroscopy. The catalytic behavior of the resulting heterogenized complexes is evaluated mainly in olefin epoxidation, in terms of activity, selectivity and recyclability.

Exchanging a ligand of the complex with a silanol group of a zeolite leads to a direct bonding between metal and support (direct grafting). $CpMo(CO)_3Cl$ has been successfully directly grafted on protonated MCM-41 and MCM-48 [39], zeolite-Y, zeolite-β [40] and SBA-15 [41,42] through the reaction of the chloro ligand with the hydroxyl groups of the carrier materials (with concomitant HCl elimination) without significant loss of ordering of the carrier material (Fig. 14).

Higher molybdenum loadings are observed when greater amounts of aluminium are contained in the material. For example loading reaches 2.8 wt% with zeolite-Y, where Si/Al is 2.5, whereas a loading of only 1.3 wt% results with

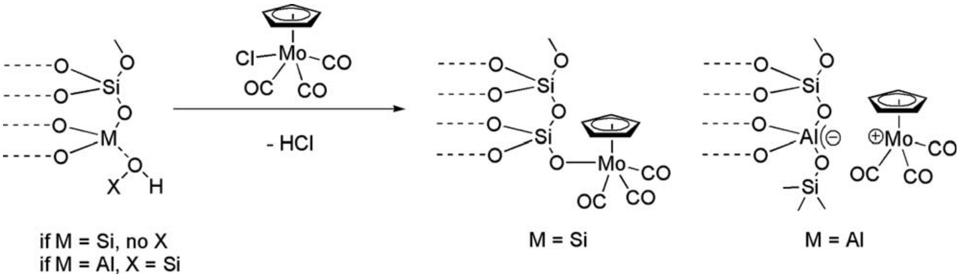

Fig. 14. Immobilization of $CpMo(CO)_3Cl$ on carrier materials by direct grafting.

zeolite-β where Si/Al is 12.5 [40]. Aluminium containing MCM-41/48-carrier systems show a higher molybdenum content (1.3–1.6 wt%) than siliceous MCM-41/48 (0.8–0.9 wt%) [39]. The presence of aluminium enhances the ionic character of the H–OSi bonds, which favours a higher molybdenum loading.

The successfully anchored molybdenum (II) complexes are oxidatively transformed in situ to the respective molybdenum (VI) oxide with TBHP as described above.

Another useful strategy for the confinement of metal centers in molecular sieves is the covalent attachment of coordination complexes via a spacer ligand (tethering). $CpMo(CO)_3Cl$ [43] has also been successfully anchored on mesoporous sieves by an ester functionality introduced on the cyclopentadienyl ring, whereas the chloro ligand remains [42] (Fig. 15 a). Turning the methoxycarbonyl into an amide moiety leads to the complex $[(EtO)_3Si–(CH_2)_3–N(H)C(O)]–CpMo(CO)_3Cl$, which is immobilized on MCM by the siloxane arm [43] (Fig. 15 b).

Loadings are comparatively low in the case of the methoxycarbonyl functionality (ca. 0.3 wt% for $MCM-41-O–C(O)-Cp-Mo(CO)_3Cl$), and much higher when applying a longer siloxane amide arm (ca. 13 wt% for $MCM-41-Si(OEt)–(CH_2)_3–N(H)–C(O)-Cp-Mo(CO)_3Cl$). As probable explanations both steric and electronic effects have been given [43,44].

A series of cyclopentadienylmolybdenum complexes containing a siloxane functional group, either directly attached to the metal center ($MCM-Si(OR)–(CH_2)_n-MoCp(CO)_3$) or to the cyclopentadienyl moiety ($MCM-Si(OMe)–(CH_2)_3-Cp-Mo(CO)_3Me$), has been synthesized, and tested under homogeneous conditions [45]. These complexes have then been successfully grafted on MCM-41 and MCM-48 [45–47] (Fig. 16a and b).

The siloxane group has also been fixed first on the mesoporous framework instead of attaching it to the complex prior to the reaction with the surface [48] (Fig. 16c). When the functionalized complex is grafted on the non-functionalized MCM the loading is strongly dependent on the length of the siloxane bridge. The grafting process is made easier with longer spacers: 1.7 wt% Mo is achieved for $MCM-41-Si(OMe)–(CH_2)_3-MoCp(CO)_3$, and only 0.3 wt% for the

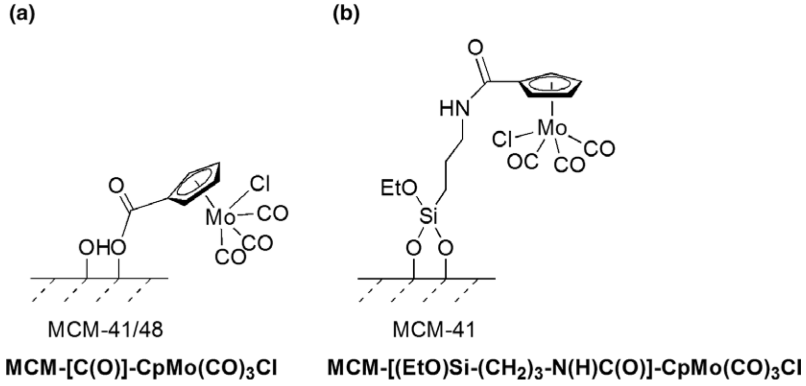

Fig. 15. Immobilization of $Cp'Mo(CO)_3Cl$ on carrier materials by tethering.

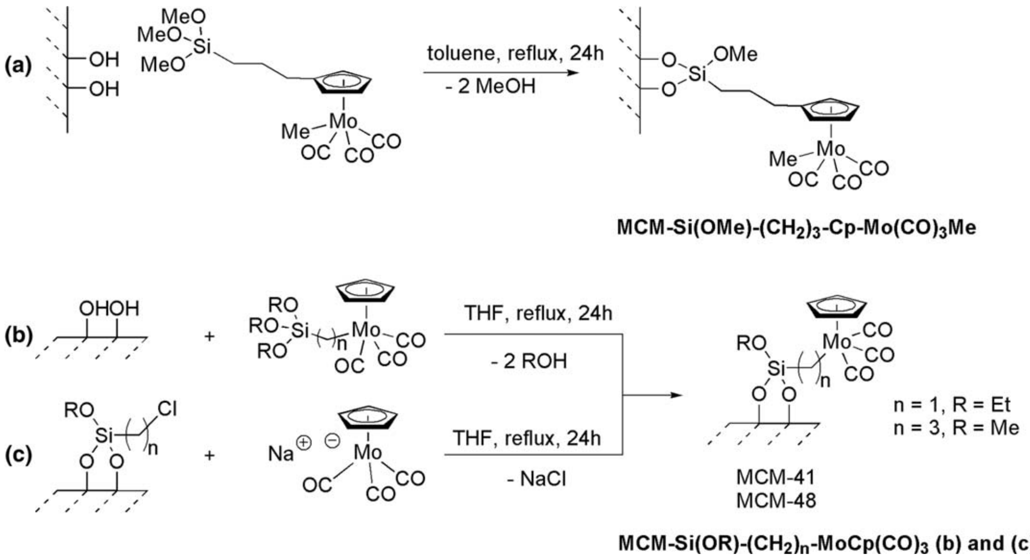

Fig. 16. Tethering of tricarbonyl complexes $Cp'Mo(CO)_3R$ on carrier materials via a siloxane spacer. (a) The siloxane functionality is attached to the Cp ligand. (b) The siloxane functionality is directly attached to the metal. (c) The siloxane functionality is attached to the supporting material.

analogue MCM-41-Si(OEt)–($CH_2$)-MoCp$(CO)_3$CpMo$(CO)_3$. By contrast, the loading is quite equivalent for the same product materials obtained from the reaction between the functionalized mesoporous material and [CpMo(CO)]$_3$Na (Fig. 16c): 1.0 and 0.9 wt% are observed for MCM-41-Si(OMe)–$(CH_2)_3$-MoCp$(CO)_3$ and MCM-41-Si(OEt)–($CH_2$)-MoCp$(CO)_3$, respectively. The CpMo$(CO)_3$ moiety has also been grafted on mesoporous materials MCM-41/-48 [49], SBA-15 [41] previously modified by the use of *p*-(iodomethyl)phenyltrimethoxysilane, affording materials with molybdenum contents of 6.4, 8.3 and 4.9 wt% for MCM-41, MCM-48 and SBA-15, respectively (Fig. 17).

The heterogenized catalysts were tested mainly for olefin epoxidation with TBHP. In a typical run, utilizing cyclooctene as the substrate, the reaction is conducted at 55 °C, with two equivalents of TBHP. The immobilized carbonyl catalysts are oxidized in situ.

All the grafted samples are active (from 50% to 100% conversion) and highly selective catalysts for cyclooctene epoxidation with TBHP. Almost identical initial rates and activities are observed for the grafted tricarbonylcyclopentadienyl complex MCM-41-Si(OEt)–$(CH_2)_3$–N(H)–C(O)-CpMo$(CO)_3$Cl, and the corresponding dioxocyclopentadienyl complex MCM-41-Si(OEt)–$(CH_2)_3$–N(H)–C(O)-CpMo$(O)_2$Cl, prepared from the reaction of the former with an excess of TBHP [43]. This suggests that the in situ oxidative carbonylation is fast and very likely gives rise to the same type of active metal species as the homogeneously applied dioxocyclopentadienyl complexes under catalytic conditions.

Generally, the activity of the grafted catalysts is comparable to those of the corresponding homogeneous catalysts, of an equal order of magnitude or one order of magnitude lower. For example TOF values are 130 $h^{-1}$ for MCM-48-Si(OMe)–Ph–$CH_2$-MoCp$(CO)_3$, 1300 $h^{-1}$ for CpMo$(CO)_3$Cl and 820 $h^{-1}$ for CpMo$(CO)_3$Me with a ratio catalyst/TBHP/cyclooctene of ca. 0.01/2/1 [42]. It has been assumed that the lower activity of the heterogenized catalysts may be due to problems of accessibility of the active sites. In the case of $(RO)_3$Si-$(CH_2)_n$-MoCp$(CO)_3$ complexes ((*n*, R) = (3, Me) or (1, Et)) heterogenized on MCM, higher conversions and selectivities are again observed for the materials which present longer hydrocarbon bridges between the molybdenum atoms and the surface Si–O groups of the support: 100% conversion with 100% selectivity can be reached after 24 h reaction time with MCM-48-Si(OMe)–$(CH_2)_3$-MoCp$(CO)_3$ (synthesized according to path b, Fig. 16), whereas only 46% conversion with 78% selectivity are achieved with the corresponding MCM-48-Si(OEt)–($CH_2$)-MoCp$(CO)_3$ under the same conditions. The reduction of both the influence of the electron donor abilities of the surface on the Lewis acidity of the catalytic center, and of the steric bulk may explain these differences [46].

The structure of the mesoporous material is of utmost importance. For example the TOFs are lower with zeolites-Y and -β as supporting material for CpMo$(CO)_3$Cl (ca. 300–400 $h^{-1}$) [40] than with MCM-41/48 (>4000 $h^{-1}$) [39]. The catalytic activity is also better with a higher amount of aluminium in the framework, due to an enhanced resulting Lewis acidity of the molybdenum, and the supplementary activation of TBHP by the aluminium sites [39,40]. Under the same conditions the heterogenized catalyst of the formula [Cp*Mo$(CO)_3$] shows 100% conversion with 100% selectivity when supported by zeolite-Y (Si/Al = 2.5) and 98% conversion with 79% selectivity when supported by zeolite-β (Si/Al = 12.5) [40]. MCM-48-O–C(O)-Cp–Mo$(CO)_3$Cl provides higher catalytic efficiency (64% conversion with 100% selectivity) than the MCM-41 analogue [44] (58% conversion with 97% selectivity under the same conditions), probably due to the three dimensional pore openings of MCM-48, compared to the one dimensional pore openings of MCM-41.

In all cases the velocity of the catalytic transformation slows down during the course of the reaction. Such a behavior has been assigned to the interaction of the catalyst with the by-product *tert*-butanol.

According to the literature the way of heterogenization is also very important for the resulting catalytic performance. For example MCM-41-Si(OMe)–$(CH_2)_3$-MoCp$(CO)_3$ synthesized according to path b, Fig. 16, shows 95% conversion with 87% selectivity after 24 h reaction time, whereas the heterogenized complex of the same formula but obtained via path c, Fig. 16, leads to the epoxide with 68% conversion and 100% selectivity.

Control experiments show that in most cases activity does not come from leaching (and thus from a homogeneous catalysis) to a significant degree. In a typical test, the solid catalyst is removed from the solution phase at the reaction temperature after 50% conversion is reached, and the further conversion of the filtrate within an additional 24 h reaction time is recorded. Only in the case of [CpMo$(CO)_3$] directly grafted on SBA-15 a significant leaching is observed, as illustrated both by the activity of

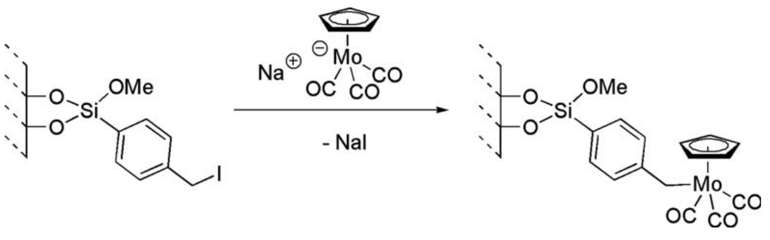

Fig. 17. [Mo$(CO)_3$]Na tethering on a *p*-(iodomethyl)phenyltrimethoxysilane functionalized supporting material.

the filtrate (20% further conversion) and by the decrease in the Mo content of the material (from 1.5 to 1.1 wt%) after reaction. By contrast, the tethering on SBA-15-Si(OMe)-Ph-$CH_2$-I leads to a much more stable material, since further conversion of only 3% is observed with the filtrate, and the Mo content changes from 4.9 before, to 4.7 wt% after the reaction.

However, the oxidative carbonylation of the heterogenized complex MCM-41-Si(OEt)–$CH_2$-N(H)-C(O)-Cp-Mo$(CO)_3$Cl appears to be accompanied with some metal leaching, as evidenced by a decrease in the molybdenum content from 13 to 9 wt% [43]. This leaching leads to an inactive Mo species after loosing the attachment to the surface.

Different recyclabilities are observed for the grafted catalysts. In the worst cases the activity drops between the first run and the second run to the half. Directly grafted MCM- and SBA-15-MoCp$(CO)_3$ exhibit such a behavior [39,41]. By contrast, zeolite-Y/-β-MoCp$(CO)_3$ can be reused with only a slight decrease in activity, but with a significant alteration of the selectivity [40]. The stability of the supported catalysts is improved when a grafted benzyl spacer ligand – Si(OMe)–Ph–$CH_2$– is applied on MCM [42] and SBA-15 [41]. The latter material shows for example 57%, 56% and 49% conversion with 100%, 84% and 95% selectivity, respectively for runs 1, 2 and 3. An amide functionality appears to be favourable to the stability as well, since the immobilized MCM-41-(Si(OEt)–$CH_2$)–N(H)–C(O)-Cp]-Mo$(CO)_3$Cl shows only a slight decrease in activity after three runs. However, a significant decrease in the catalytic properties is observed with siloxane spacer ligands, whatever the grafting process [46]. Only when low loadings are applied the grafted catalysts can be reused without clearly detectable loss of activity and selectivity [47] (Fig. 18).

The complexes anchored by an ester functionality on MCM materials (MCM-[O–C(O)–Cp]-Mo$(CO)_3$Cl) were shown to be very good for recycling, for example the MCM-48 anchored material leads to 64%, 60% and 56% conversion with 100%, 100% and 96% selectivity, respectively for runs 1, 2 and 3 (Fig. 19).

### 4.2. Heterogenization in ionic liquids

In the last decade room temperature ionic liquids (RTILs) have been attracting considerable attention as alternatives to conventional molecular solvents, due to their unique physical properties, such as non-volatility, non-flammability, thermal stability and high polarity. They additionally enable solubilization of inorganic complexes, while being immiscible with most hydrocarbons. They provide therefore a non-aqueous alternative for two-phases catalysis, in which the catalyst is "immobilized" in the ionic liquid and then separated from the products (i.e. recycled). RTILs have been used for several types of reactions, but are just emerging with regard to epoxidation catalysis. A manganese (II) salen complex catalysing asymmetric epoxidation in an ionic liquid was reported a few years ago [48]. Since then, RTILs have been successfully applied in the olefin epoxidation with manganese(III) porphyrins [49,50]. A series of imidazolium-based RTILs have been tested as solvents for the catalytic cyclooctene epoxidation with TBHP as oxidizing agent and (cyclopentadienyl)tricarbonyl molybdenum complexes CpMo$(CO)_3$R as the catalysts [51].

As recycling is conducted via an extraction operation with an organic solvent, the recovering of the catalyst is linked to the affinity of the latter for the RTIL on one side and for the extracting organic solvent on the other side. Complete recycling of the catalyst CpMo$(CO)_3$Me is achieved if a mixture of [BMIM]$NTf_2$ and [BMIM]$PF_6$ in a volume ratio 4/1 is used as RTIL. Increasing the applied amount of [BMIM]$PF_6$, however, pushes the reaction towards diol formation, which is the only reaction product in systems containing pure [BMIM]$PF_6$ as the RTIL (in spite of a very high TOF).

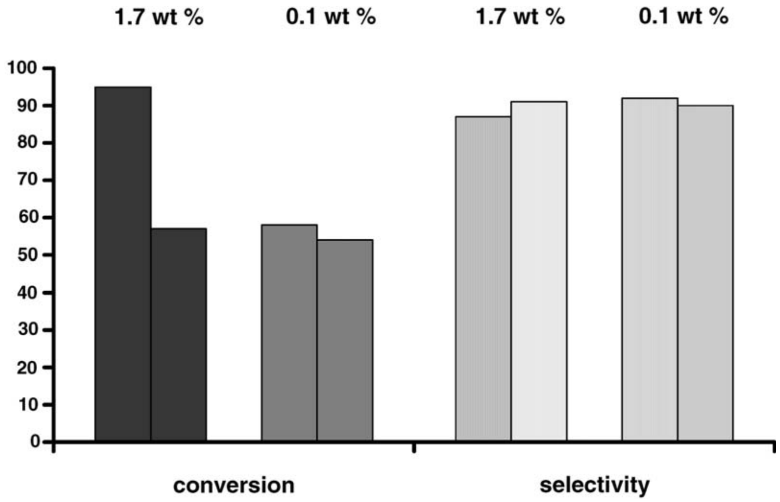

Fig. 18. Influence of the loading on both conversion and selectivity during recycling.

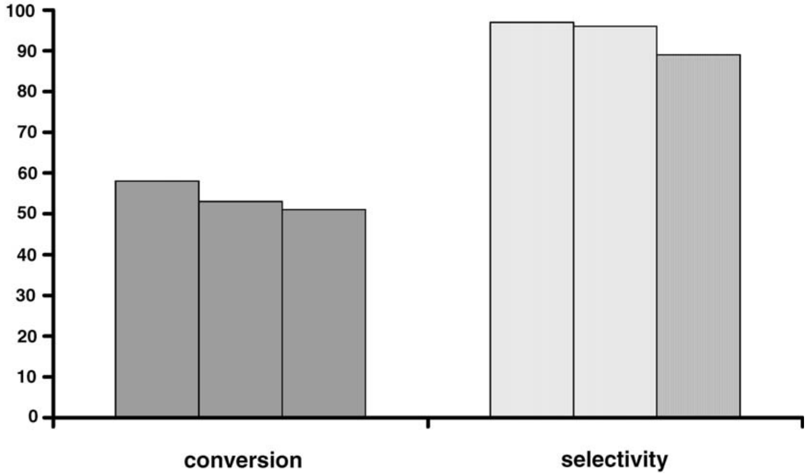

Fig. 19. Recyclability of MCM–[O–C(O)–Cp]Mo(CO)$_3$Cl.

### 4.3. Inclusion in cyclodextrins

Cyclodextrins are water-soluble cyclic oligosaccharides that are capable of forming inclusion compounds with a wide range of organic molecules, inorganic ions and organometallic species. Encapsulated organometallic complexes often exhibit markedly different physical and chemical characteristics compared to the bulk material, particularly when applied in catalysis. CpMo(CO)$_3$Cl, a precursor of the dioxo complexes of formula CpMoO$_2$Cl (see above) has been immobilized in plain β-cyclodextrin and permethylated β-cyclodextrin. Products with a 1:1 host/guest stoichiometry were obtained and fully characterized [52]. Additionally the complex CpMo(CO)$_3$CH$_2$-CONH$_2$ was immobilized in plain β-cyclodextrin and permethylated β-cyclodextrin and the products were also fully characterized. Both compounds were additionally tested as olefin epoxidation catalysts with TBHP as the oxidizing agent. While the material obtained with permethylated β-cyclodextrin is fully soluble (without additional co-solvent) in the reaction mixture and displays a catalytic activity similar to homogeneous CpMo(CO)$_3$CH$_2$CONH$_2$, the β-cyclodextrin inclusion compound is insoluble, leading to a considerably lower catalytic activity. Dependent of the nature of the host and the co-solvent (if any), the catalyst systems can either be heterogeneous, homogeneous or liquid–liquid biphasic. While the β-cyclodextrine inclusion compound has, according to the authors, potential to be used in heterogeneous solid–liquid systems, the permethylated β-cyclodextrin inclusion compound seems to be more suited to homogeneous or liquid–liquid biphasic systems [53].

## 5. Conclusion

The synthetic availability of the title complexes was increased considerable during recent years, due to the efforts of several research groups, a necessity to pave the way for their growing importance as catalysts. Cyclopentadienyl molybdenum dioxides and their carbonyl precursors can now be utilized as efficient olefin epoxidation catalysts, both in homogeneous and heterogeneous phase. As has been pointed out previously, they are, on average, more active in epoxidation catalysis than the related MoO$_2$X$_2$L$_2$ (X = Cl, Br, Me; L = Lewis base) [54,55] compounds and they are also fairly easy to modify. The tuning ability of both the cyclopentadienyl ligand and the remaining non-oxo ligand will probably soon allow the access to stable chiral derivatives, which then would be potential catalysts for chiral reactions. There is no serious doubt that the importance of this class of organometallic complexes will further broaden in the coming years and several novel applications will emerge.

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