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Catalytic olefin epoxidation with cyclopentadienyl–molybdenum complexes in room temperature ionic liquids

Fritz E. Kühn,[a,*] Jin Zhao,[a] Marta Abrantes,[a,b] Wei Sun,[a] Carlos A. M. Afonso,[c] Luis C. Branco,[c,d] Isabel S. Gonçalves,[e] Martyn Pillinger[e] and Carlos C. Romão[b,*]

[a] *Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany*

[b] *Instituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa, Quinta do Marquês, EAN, Apt. 127, 2781-901 Oeiras, Portugal*

[c] *CQFM, Department of Chemical Engineering, Instituto Superior Técnico, 1049-001 Lisboa, Portugal*

[d] *Requimte/CQFB, Department of Chemistry, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Monte da Caparica, 2829-516 Caparica, Portugal*

[e] *Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*

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

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1. Introduction

Molybdenum(VI) complexes are versatile catalysts for the oxidation of organic substrates.[1] It has been shown that compounds of the type Cp′$Mo(CO)_3Cl$ can be used as olefin epoxidation catalyst precursors being oxidized in situ to the Mo(VI) catalyst thereby presenting over the use of application of previously isolated but more sensitive Mo(VI) species of formula Cp′MoO_2Cl. The more stable carbonyl compounds can be stored easily for long periods of time.[2a] Furthermore, Cp′$Mo(CO)_3R$ (R = alkyl, or *ansa*-alkyl) complexes have also been described as homogeneous epoxidation catalyst precursors, showing a comparable catalytic activity to their chloro-analogues.[2b] This type of complexes is highly selective towards epoxide formation and surpasses most other Mo(VI)-dioxo complexes (e.g., of the composition $MoX_2O_2L_2$ (X = Cl, Br, Me; L = Lewis base)) significantly in catalytic activity and rivals even the highly active and well examined Re(VII) epoxidation catalyst methyltrioxorhenium (MTO).[3a–c] The by-product of the oxidation of olefins with TBHP (*tert*-butyl hydroperoxide) in the presence of Mo(VI) dioxo complexes, *t*-BuOH, however, hampers the catalytic reaction with increasing concentration.[3d–f] Heterogenization of the catalyst, or two-phase homogeneous catalysis, are therefore recommendable ways to avoid high amounts of *t*-BuOH in the same phase as the catalyst after several catalytic runs.[2c] Another even more important advantage of the application of heterogeneous catalysts is the easy catalyst/product separation, which causes considerable catalyst losses in purely homogeneous systems.

In the last decade room temperature ionic liquids (RTILs) have been attracting considerable attention as possible replacements for conventional molecular solvents due to their unique physical properties such as

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* Corresponding authors. Tel.: +49 (0)89 289 13108; fax: +49 (0)89 289 13473; e-mail: fritz.kuehn@ch.tum.de

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nonvolatility, nonflammability, thermal stability and high polarity. Additionally, they enable solubilization of inorganic complexes (catalysts), while being immiscible with most hydrocarbons. As such, they provide a nonaqueous alternative for two-phase catalysis, in which the catalyst is 'immobilized' in the ionic liquid and can be easily separated from the products and recycled.[4] RTILs have been used in several types of reactions such as hydrogenation, hydroformylation, oxidation, oligomerization of alkenes and aldehyde olefination.[4] With regard to epoxidation catalysis, however, the application of RTIL is just emerging. Song and Roh first reported a Mn(III) (salen) complex (Jacobsen's complex) catalyzing asymmetric epoxidation in an ionic liquid a few years ago.[5] Since then, RTILs have been successfully applied in the olefin epoxidation with Fe(III) porphyrin, Mn(III) porphyrin, or MTO as catalyst.[6] It was found that some ionic liquids show enhancement in reaction rates and selectivity. An investigation on the catalytic activity of $MoX_2O_2L_2$ (X = Cl, Me; L = Lewis base) complexes in RTIL was reported recently by Valente et al.,[7] in which a series of RTILs were tested as solvents in the catalytic epoxidation of *cis*-cyclooctene, using TBHP as oxidant. It shows that the use of RTILs for the recycling of dioxomolybdenum(VI) complexes is promising if the right RTIL is chosen for a certain catalyst. Additionally, catalyst recycling by removal of the by-product *t*-BuOH may become much easier.

Among the large variety of RTILs available in the literature, in this study we chose RTILs of the imidazolium salt type with different anions as solvents or 'immobilizing agents', due to their high oxidation stability as well as their easy accessibility in terms of synthesis.[8] The performance of cyclopentadienyl molybdenum carbonyl complexes of the general formula $Cp'Mo(CO)_3X$ (X = Cl, Me; Cp = C_5H_5, C_5Me_5) in the presence of RTILs is examined in this work.

2. Experimental part

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately (THF) or kept over 4Å molecular sieves. Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets. ^1H, ^{13}C NMR spectra were obtained using a 400MHz Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett-Packard integration unit HP 3396 Series II. GC–MS spectra were obtained on a Hewlett-Packard 6890 Series GC System and Hewlett-Packard 5973 Series Mass Selective Detector.

2.1. Synthesis and characterization

The RTILs $[BMIM]PF_6$, $[C_8MIM]PF_6$, $[BMIM]NTf_2$ and $[BMIM]BF_4$ were prepared and purified as described in the literature.[8] $CpMo(CO)_3Me$ (**1**), $Cp^*Mo(CO)_3Me$ (**2**), $CpMo(CO)_3Cl$ (**3**), $Cp^*Mo(CO)_3Cl$ (**4**) and $CpMoO_2Cl$ (**5**) were prepared according to literature procedures.[2,9] Their spectroscopic data are in accordance with the data reported previously.

2.2. Catalytic reactions with compounds 1–4 as catalysts

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

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

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

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

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

3. Results and discussion

Compounds of the type $Cp'Mo(CO)_3Me$ ($Cp = C_5H_5$ (**1**), C_5Me_5 (**2**)) and $CpMo(CO)_3Cl$ (**3**) were tested in epoxidation catalysis at 55 °C, using *cis*-cyclooctene as substrate, TBHP as oxidant and a RTIL as co-solvent. The catalytic reactions were initially performed in air (laboratory atmosphere) in order to test the performance of the system under the easiest possible reaction conditions. The ionic liquids were equilibrated in air prior to use in these reactions.

Compounds **1**–**3** (Chart 1) dissolve easily in the RTILs $[BMIM]NTf_2$, $[BMIM]PF_6$ and $[BMIM]BF_4$ (Chart 1), originating clear solutions. After the addition of TBHP and stirring for 10 min, in the case of $[BMIM]NTf_2$, the reaction solution changes from yellow (for compounds **1** and **2**) or red (for compound **3**) to a pale yellow suspension. In the case of $[BMIM]PF_6$, a clear yellow solution forms, while in the case of $[BMIM]BF_4$, a colourless solution with a small amount of bluish-white suspended solid is obtained. After the addition of the substrate and the internal standard, all the systems are biphasic because the RTIL and the substrate are not miscible. At the end of the 1st run all the systems maintain their initial appearance.

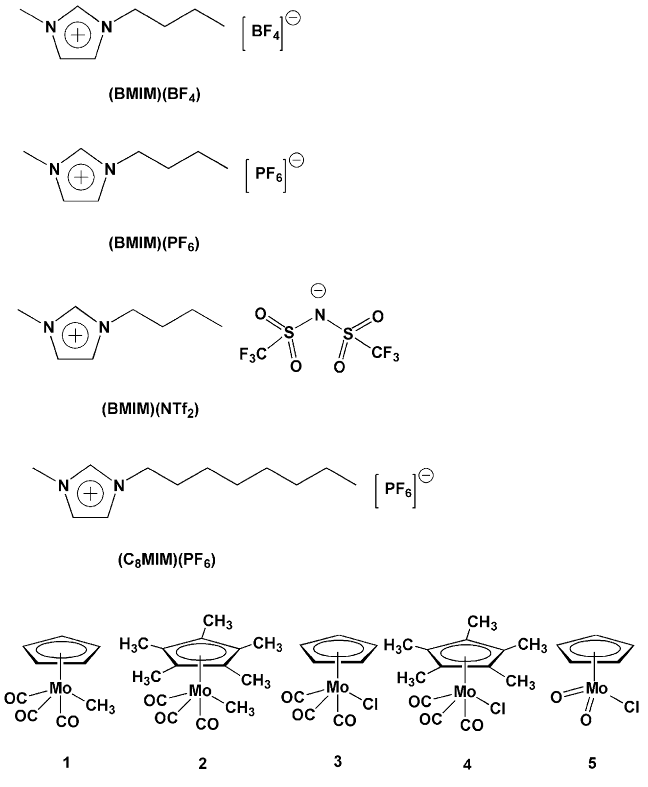

Chart 1.

The turnover frequencies (TOFs) obtained in these reactions are all considerably lower than the TOFs of the reactions performed without solvent (Table 1). This slower catalytic reaction may be due to dilution effects, phase transfer problems between the viscous RTIL and the other components of the reaction system (e.g., the olefin) may at least in part result from a certain amount of decomposition of the catalysts in the RTIL, due to the water content of the RTILs. Notably, all examined catalysts perform worse in the presence of the RTIL with the highest water content ($[BMIM]BF_4$ is miscible with water),[8a] both in terms of TOFs and conversions after 4 and 24 h. This is as expected considering the water sensitivity of the Mo(VI) species,[2] which act as active catalysts. As can be concluded directly from the initial colour changes, the catalysts decompose directly after their formation due to the high water content of $[BMIM]BF_4$ (bluish colour originates from molybdenum oxide hydrates, EA-evidence). The lowest equilibrated water content is present in $[BMIM]NTf_2$. Accordingly, the epoxide yields after 4 and 24 h are the best of all RTIL-containing systems. However, the TOFs observed in the $[BMIM]NTf_2$-containing system are considerably lower than in the $[BMIM]PF_6$-containing system. This at first glance is a strange outcome, however, also explainable. As suggested by the formation of a suspension, the Mo(VI) species are not so easily soluble in this RTIL, therefore leading to a much lower efficient catalyst concentration. Examination of the solubility of compound **5** in the RTILs confirms this statement.

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

This additional factor is spotted when considering the RTILs not as necessarily 'innocent' solvents.[10] While the epoxide content increases in the $[BMIM]PF_6$-containing systems during the early stages of the reaction, its eventual disappearance becomes obvious as the reaction progresses. Analysis of the reaction mixture shows the concomitant formation of diol. This diol formation cannot, however, be only or mainly due to the presence of water. With a large excess of water the catalyst would decompose to a significant degree. Furthermore, in the $[BMIM]BF_4$-containing system no significant diol formation is observed. Additionally, the $Cp'Mo(CO)_3X$-derived catalyst systems are known to display generally a high selectivity towards epoxide formation, due to their comparatively low Lewis acidity. Both MoO_2X_2 and MTO containing epoxidation catalyst systems require the presence of Lewis bases to avoid epoxide ring opening reactions.[3,11] In the $[BMIM]PF_6$-containing systems, however, the formation of HF can be observed (^{19}F NMR evidence) due to slow degradation of the RTIL under the applied conditions. HF, being a

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

Solvent	TOF[a] (mol/mol*h)[a]			Epoxide yield (%) after 4h			Epoxide yield (%) after 24h		
	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)	CpMe (**1**)	CpCl (**3**)	Cp*Me (**2**)
No solvent	820	960	270	100	100	68	100	100	100
[BMIM]PF$_6$	316	528	144	20	5.6	27	0	0	0
[BMIM]NTf$_2$	33	46	24	43	58	28	100	100	83
[BMIM]BF$_4$	14	15	10	8	7	6	38	31	27

[a] Determined after 5min of reaction.

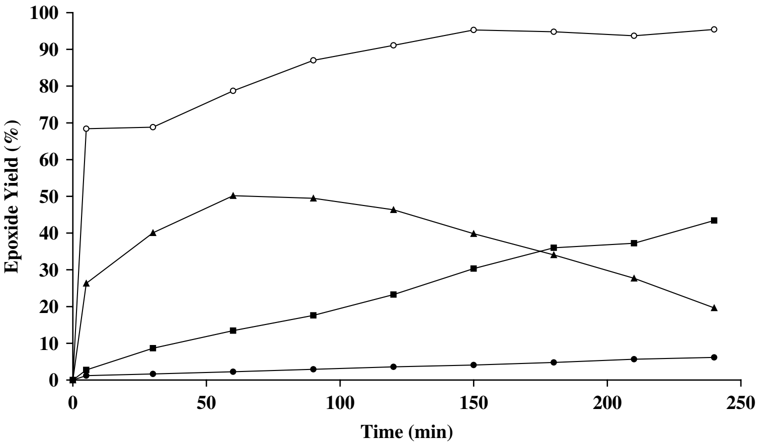

Figure 1. Kinetics of cyclooctene epoxidation in the presence of the complex CpMo(CO)$_3$Me (**1**) without solvent (○), or using [BMIM]NTf$_2$ (■), [BMIM]PF$_6$ (▲) or [BMIM]BF$_4$ (●) as solvent (laboratory atmosphere, water equilibrated RTILs).

Lewis acid, promotes the epoxide ring opening in the presence of water. In order to confirm the influence of HF, formed from the PF$_6^-$ counter ion, another RTIL containing this anion was applied, namely [C$_8$MIM]PF$_6$. The formation of diols from the epoxide was again observed during the course of the reaction. Due to the (generally) lower water content of this solvent,[8a] the initial catalytic activity is somewhat higher than that observed in the [BMIM]PF$_6$-containing system.

In order to reduce the influence of water, compound **3**, being overall the most active of the examined catalysts, and its Cp* derivative **4** were examined in dried [BMIM]NTf$_2$. This RTIL does not display the HF-formation problem.[10] Interestingly, the dried [BMIM]NTf$_2$ seems to enhance the catalyst solubility, since a clear yellow solution is obtained. The initial TOF is considerably higher than in the system with a higher water content and a lower catalyst solubility (Table 2). Even the generally considerably less active catalyst[2a] derived from compound **4** shows a good catalytic performance in a dryer RTIL (Table 2). The reactions performed with compound **3** were repeated with its isolated reaction product with TBHP, CpMoO$_2$Cl (**5**), leading to the same results within the measurement errors.

In summary, for all the examined catalysts in this study, the best results for olefin epoxidation were achieved using the RTIL [BMIM]NTf$_2$ as co-solvent, which is in accordance with the previous results obtained by Valente et al. using the isoelectronic complexes MoX$_2$O$_2$L$_2$ (X = Cl, Me; L = Lewis base) in RTILs for olefin epoxidation.[7] These results prompted us to perform some recycling experiments. The systems containing [BMIM]NTf$_2$ can be reused in further catalytic cycles. However, some catalytic activity is lost between the 1st and 2nd runs, probably due to loss of catalyst during the recycling process (see Experimental part and Fig. 2). This is common for both the water equilibrated and the dried systems.

In order to optimize our systems under the easiest possible conditions (not dried RTIL, laboratory atmosphere), we tried to combine the advantages of the [BMIM]PF$_6$ and [BMIM]NTf$_2$ systems. Although [BMIM]PF$_6$ promotes ring opening, it was hoped that its presence in small amounts would improve the solubility of the catalysts. Using complex **1** in a 4:1 volume ratio of [BMIM]NTf$_2$ and [BMIM]PF$_6$, the reaction proceeds with comparable epoxide yields after 4 and 24h to that obtained in pure [BMIM]NTf$_2$ during the first run, thus maintaining the selectivity to the epoxide. The catalyst in the ionic liquid phase can be recovered without significant mass loss and can be reused three times *without any loss of activity*. This result additionally rules out the possibility that the lower catalytic activity of the catalysts in not dried [BMIM]NTf$_2$-containing systems results from catalyst decomposition. When a mixture of [BMIM]NTf$_2$ and [BMIM]PF$_6$ with a volume ratio of 3:2 is used as co-solvent, the epoxide yield reaches 53% with 100% selectivity after 4h reaction. However, after 24h, the epoxide yield decreases to 28%. In mixtures containing higher amounts of [BMIM]PF$_6$, the epoxide ring-opening reaction is again

Table 2. Catalytic results for compounds **3** and **4** with [BMIM]NTf_2-containing systems under nitrogen with dry [BMIM]NTf_2

Solvent	TOF[a] (mol/mol*h)[a]		Epoxide yield (%) after 4 h		Epoxide yield (%) after 24 h	
	CpCl (**3**)	Cp^*Cl (**4**)	CpCl (**3**)	Cp^*Cl (**4**)	CpCl (**3**)	Cp^*Cl (**4**)
[BMIM]NTf_2	500	415	100	72	100	100

[a] Determined after 5 min of reaction.

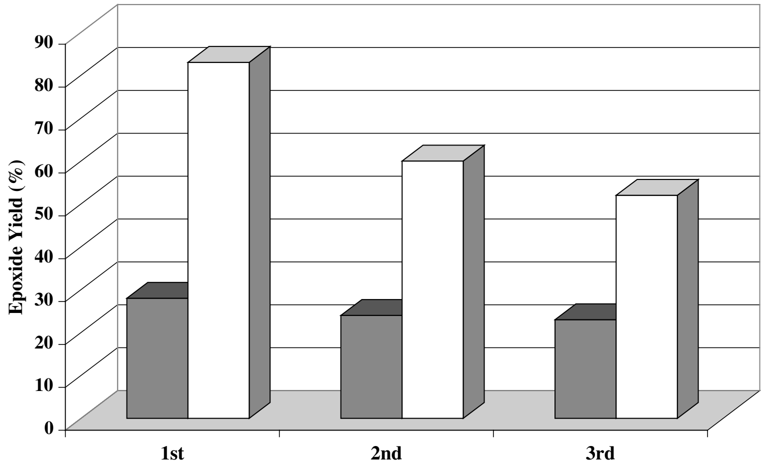

Figure 2. Epoxide yield for the first, second and third runs after 4 h (grey) and 24 h (white) reaction time in the presence of $Cp^*Mo(CO)_3Me$ (**2**) and using [BMIM]NTf_2 as solvent (laboratory atmosphere with water equilibrated RTIL).

preferred, probably due to the higher HF concentration. In this context it should be pointed out that desirable properties of RTILs can be obtained by simple mixing of different ionic liquids. This opens up many possibilities to modify their behaviour and applications.

4. Conclusion

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

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