

# Molybdenum and tungsten complexes of composition $(\eta^5\text{-C}_5\text{R}_5)\text{MR}'(\text{CO})_3$ and their use as olefin epoxidation catalyst precursors

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## Abstract

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

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**Keywords:** Homogeneous catalysis; Molybdenum; Olefin epoxidation

## 1. Introduction

Carbonyl complexes of transition metals have been applied as oxidation catalysts since more than 30 years [1]. The characterization and successful catalytic application of high oxidation state congeners such as oxides and peroxides during the last two decades, however, shifted the attention in oxidation catalysis to these latter complexes [2]. Nevertheless, it also turned out that carbonyl complexes bearing other ligands, such as Cp derivatives are in several cases—with or without catalysts—oxidizable to oxide and peroxide complexes without losing their Cp ligands [3].

Based on the successful catalytic application of organorhenium oxides of formula  $\text{RReO}_3$ , such as methyltrioxorhenium (VII) (MTO) in oxidation catalysis [4] we started to examine molybdenum and tungsten compounds of the composition  $\text{MX}_2\text{O}_2\text{L}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{Me}$ ;  $\text{L} = \text{Lewis base}$ ) [5] and  $\text{Cp}'\text{MO}_2\text{Cl}$  ( $\text{Cp}' = \text{Cp} (\text{C}_5\text{H}_5)$ ,  $\text{Cp}^* (\text{C}_5\text{Me}_5)$ ,  $\text{BzCp} (\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5)$ ) [6] as oxidation catalysts. Some com-

pounds of formula  $\text{Cp}'\text{MO}_2\text{X}$  surpass the  $\text{MX}_2\text{O}_2\text{L}_2$  derivatives in catalytic activity in the olefin epoxidation and rival the most active  $\text{RReO}_3$  complex, MTO, in its epoxidation activity. There are, however, some important differences between the Mo, W and Re complexes mentioned above. In the presence of the  $\text{RReO}_3$  catalysts  $\text{H}_2\text{O}_2$  can be used as oxidizing agent while the Mo and W compounds of formulae  $\text{MX}_2\text{O}_2\text{L}_2$  and  $\text{Cp}'\text{MO}_2\text{Cl}$  need TBHP as oxidant. Furthermore, while  $\text{Cp}'\text{MO}_2\text{X}$  compounds are quite active catalysts,  $\text{Cp}'\text{ReO}_3$  derivatives do not catalyze the olefin epoxidation at all [4,7].

Recently we have shown that  $\text{Cp}'\text{MoO}_2\text{Cl}$  complexes can be easily obtained from carbonyl precursors by oxidation with TBHP in yields up to 75%. Applying  $\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$  as oxidation catalyst in the presence of TBHP, however, leads to similar results as the application of  $\text{Cp}'\text{MoO}_2\text{Cl}$ . The carbonyl precursor is oxidized to the oxide and catalyzes the olefin epoxidation with the same oxidizing agent, which was previously applied for its own oxidation. During this oxidation process the ligands  $\text{Cp}'$  and Cl remain attached to the metal. The carbonyl complexes are even more stable than the oxides and therefore ideal storage forms of the catalyst, which

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can be generated in situ from the carbonyl precursor [6]. In this work we use this concept for the catalytic application of several compounds of formula  $Cp^*M(CO)_3R$  ( $M = Mo, W$ ;  $R = alkyl$ ) as oxidation catalysts and compare their catalytic activity with respect to variations in the ligands  $R$  and  $Cp^*$ .

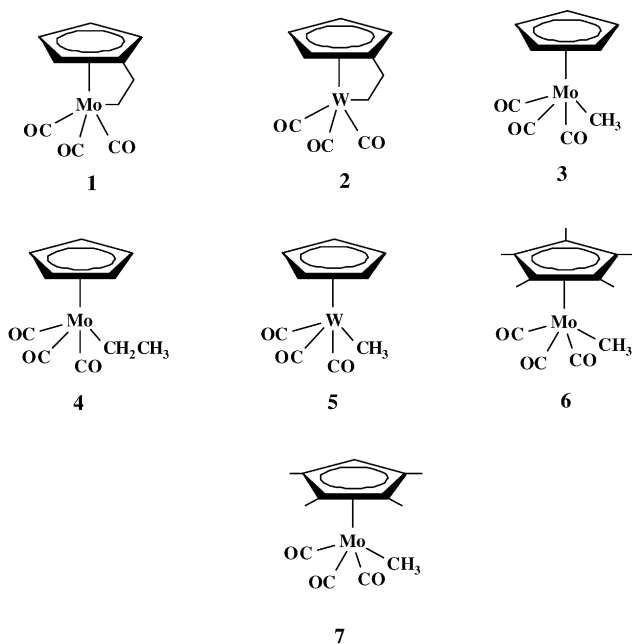


Chart 1.

## 2. Experimental

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

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

Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra of isolated compounds were measured on a Bio-

Rad FTS 525 spectrometer using KBr pellets, in situ spectra were recorded in KBr cells in methylene chloride as the solvent (cat.:oxidant 1:5–1:10). Far-IR measurements were performed on a Bio-Rad FTS 525 system as Nujol mulls or polyethylene pellets using a  $6 \mu m$  Mylar beam splitter.  $^1H$ -NMR,  $^{95}Mo$ - and  $^{13}C$ -NMR spectra were obtained using a 400 MHz Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer; catalytic runs were monitored by 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.

### 2.1. Crystallography

Crystal structure analysis of compound **7** [10]:  $C_{13}H_{16}MoO_3$ ,  $M_r = 316.20$ , pale yellow fragment ( $0.10 \text{ mm} \times 0.20 \text{ mm} \times 0.30 \text{ mm}$ ), monoclinic,  $P2_1/n$  (No.: 14),  $a = 13.5372(2) \text{ \AA}$ ,  $b = 14.3485(2) \text{ \AA}$ ,  $c = 14.0502(2) \text{ \AA}$ ,  $\beta = 94.6173(7)^\circ$ ,  $V = 2720.23(7) \text{ \AA}^3$ ,  $Z = 8$ ,  $d_{calc} = 1.544 \text{ g cm}^{-3}$ ,  $F_{000} = 1280$ ,  $\mu = 0.958 \text{ mm}^{-1}$ . Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems device at the window of a rotating anode (NONIUS FR591) with graphite monochromated  $Mo K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collection was performed at 123 K within the  $\theta$  range of  $2.01^\circ < \theta < 25.36^\circ$ . A total of 63,252 reflections were integrated, corrected for Lorentz, polarization, and, arising from the scaling procedure, corrected for latent decay and absorption effects. After merging ( $R_{int} = 0.051$ ), 4990 [ $3742: I_o > 2\sigma(I_o)$ ] independent reflections remained and all were used to refine 435 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  and converged with  $R_1 = 0.0249$  [ $I_o > 2\sigma(I_o)$ ],  $wR_2 = 0.0559$  [all data], GOF = 1.039, and shift/error <0.002. The final difference-Fourier map shows no striking features ( $\Delta e_{min/max} = +0.31/-0.34 \text{ e \AA}^{-3}$ ). The unit cell contains two crystallographical independent molecules A and B. They differ in the orientation of the methyl group bound to molybdenum with respect to the Cp-ring. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-249731 (7). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223 336 033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

$C_5Me_4HMo(CO)_3CH_3$  (**7**). Yield (80%). Anal. Calcd. for  $C_{13}H_{16}O_3Mo$  (316.20): C, 49.38; H, 5.10. Found: C, 49.56; H, 5.27. IR (KBr  $\nu \text{ cm}^{-1}$ ): 3063 w, (CH of Cp),

2005 vs, 1923 vs, (CO).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, rt.,  $\delta$  ppm): 0.51 (s, 3H,  $\text{C}_5(\text{CH}_3)_4\text{HMoCH}_3(\text{CO})_3$ ), 1.82 and 1.86 (12H,  $\text{C}_5(\text{CH}_3)_4\text{HMoCH}_3(\text{CO})_3$ ), 4.96 (s, 1H,  $\text{C}_5(\text{CH}_3)_4\text{HMoCH}_3(\text{CO})_3$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100.28 MHz, rt.,  $\delta$  ppm):  $-13.0$  ( $\text{C}_5(\text{CH}_3)_4\text{HMoCH}_3(\text{CO})_3$ ), 10.6, 12.2 ( $\text{C}_5(\text{CH}_3)_4\text{HMoCH}_3(\text{CO})_3$ ), 88.9, 103.9, 106.8 ( $\text{C}_5(\text{CH}_3)_4\text{HMoCH}_3(\text{CO})_3$ ), 163.9 (CO).  $^{95}\text{Mo-NMR}$  ( $\text{CDCl}_3$ , 26.07 MHz, rt.,  $\delta$  ppm):  $-1685$ . FAB-MS (NBA as FAB-matrix)  $m/z$  (%);  $\text{M}^+ = 316$  (17).

## 2.2. Catalytic reactions with compounds 1–7 as catalysts

- Method A: Cis-cyclooctene (800 mg, 7.3 mmol), 1.00 g mesitylene (internal standard), 1 mol% (73  $\mu\text{mol}$ ) of compounds 1–7 as catalyst.
- Method B: Styrene (250 mg, 2.39 mmol), 100 mg mesitylene (internal standard), 1 mol% (24  $\mu\text{mol}$ ) of compounds 1 and 3 as catalyst.
- Method C: 1-octene (800 mg, 7.12 mmol), 1.00 g mesitylene (internal standard), 1 mol% (71  $\mu\text{mol}$ ) of compounds 1 and 3 as catalyst.

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

The course of the reaction was monitored by quantitative GC-analysis. Samples were taken after 5 and 10 min and then every 30 min diluted with chloroform and chilled in an ice bath. For the destruction of hydroperoxide and removal of water a catalytic amount of manganese dioxide and magnesium sulphate was added. The resulting slurry was filtered over a filter equipped Pasteur pipette and the filtrate injected in the GC column.

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

## 3. Results and discussion

### 3.1. Syntheses and characterization

Compounds 1–7 (Chart 1) were synthesised according to literature procedures or to modified literature procedures as described in the experimental part. The compounds are stable at room temperature and can be handled in laboratory atmosphere for several hours. Spectroscopic data, particularly IR

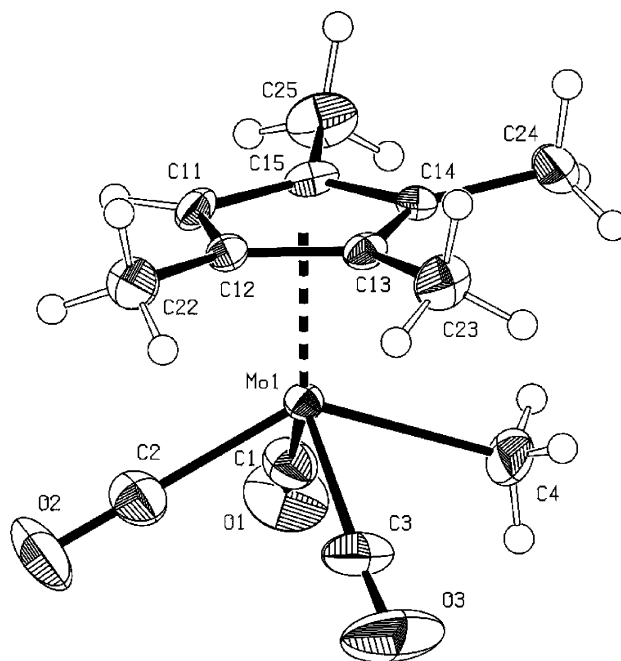


Fig. 1. ORTEP style plot of molecule A in the solid state of compound 7. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ]: Mo1–C1 1.983(3), Mo1–C2 1.979(3), Mo1–C3 1.981(3), Mo1–C4 2.311(4), Mo1–Cg 2.006; C1–Mo1–C2 79.8(1), C1–Mo1–C3 106.1(1), C1–Mo1–C4 72.3(1), C1–Mo1–Cg 128.2, C2–Mo1–C3 79.5(1), C2–Mo1–C4 133.2(1), C2–Mo1–Cg 117.0, C3–Mo1–C4 73.4(1), C3–Mo1–Cg 124.5, C4–Mo1–Cg 109.8. Cg denotes the centre of gravity in the Cp\* ring.

vibrations,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR shifts have already been presented in the literature and will not be further discussed here. The X-ray crystal structure of compound 7 has been determined (see Fig. 1). The bond distances and bond angles are, as expected, similar to their congeners described elsewhere [11].

The  $^{95}\text{Mo}$  chemical shift is not an appropriate tool to distinguish between complexes in different oxidation states, however, it is highly sensitive to structural and electronic variations within a series of closely related mononuclear compounds [12], allowing insight into the electronic situation of the molybdenum centre. The present series of compounds exhibits highly shielded chemical shifts, which can be in general associated with low formal oxidation states.  $^{95}\text{Mo-NMR}$  data was only available for compound 3 [13] ( $\delta = -1736$  ppm in  $\text{C}_6\text{D}_6$  and  $-1729$  ppm in  $\text{CDCl}_3$ ), compounds 1, 4, 6 and 7 display their  $^{95}\text{Mo-NMR}$  signal in  $\text{CDCl}_3$  at  $-1708$ ,  $-1685$ ,  $-1596$  and  $-1628$  ppm, respectively. It is observed that increasing the ring methyl substitution, which is expected to increase the electron density in the Cp ring and presumably also around the metal, leads in fact to a shift to low field. This, at a first glance strange observation had already been made for the series of compounds (*mes*)Mo(CO) $_3$ , (*p*-xyl)Mo(CO) $_3$  and (tol)Mo(CO) $_3$  [14]. The authors explain these results based on thermodynamic data showing that there is an increase of the molybdenum–arene bond strength with increasing ring

methyl substitution, however, no quantitative interpretation was possible due to incomplete understanding of the complexity and relative importance of the several terms in the Ramsey equation.

### 3.2. Catalysis

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

The details concerning the catalytic reaction are given in the experimental part. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst. The catalysts were first stirred with TBHP until a color change from orange to yellow occurred, indicating the oxidation of the carbonyl complexes to the corresponding dioxo Mo(VI) compounds. For cyclooctene and 1-octene no significant formation of by-products (e.g. diol) was observed. For styrene, affording the epoxide more prone to ring opening reactions detectable amounts of diol as well as benzaldehyde and benzoic acid as by-products were found. The time dependent curves for compounds **1–7** are shown for cyclooctene in Fig. 2 and the TOFs in Table 1.

The curves show a similar evolution, having a quick increase of the yield during the first reaction hour and then slowing down (first order kinetics). From these curves it can be observed that there is a strong increase in activity on going from tungsten to molybdenum. This had already been observed before [5m,15] but in this case the difference is particularly pronounced. Increasing the reaction temperature increases the activity of the tungsten complexes, for instance for complexes **2** and **5** the yield rises from 10 to 41% and 15 to 61% after 4 h when the reaction is performed at 90 °C, instead of 55 °C, furthermore, at 90 °C the yields obtained after 24 h are almost quantitative (90, 100%).

Compounds **1** and **3** show a similar catalytic behaviour indicating that the replacement of a (CH<sub>2</sub>)<sub>2</sub> *ansa*-bridge by

a methyl group does not influence much the electronic situation on the metal centre and therefore also not the catalytic performance, on the other hand, the replacement of the methyl by a more electron-withdrawing group such as Cl leads to better catalytic results if applied in a 0.01:1:2 (cat.:substrate:oxidant) ratio [6]. The replacement of Cp by a more electron donating ligand like Cp\* causes a decrease on the catalytic activity, on rendering the molybdenum centre more electron-rich, this phenomena has also been observed in the related compounds Cp'Mo(CO)<sub>3</sub>Cl, which have been previously studied [6]. The application of compound **7** allows a clearer insight into this phenomena, in fact, the absence of one methyl group in the methylated cyclopentadienyl ring already increases the activity on going from **6** to **7** (68–75% after 4 h). These results additionally support the conclusion drawn from spectroscopic results (see also [6] with respect to Cp'Mo(CO)<sub>3</sub>Cl complexes) that the precursor compounds Cp'M(CO)<sub>3</sub>L are not transformed to an uniform catalyst species, e.g. a simple Mo(O<sub>2</sub>)<sub>2</sub>O<sub>2</sub>-type complex, after losing their organic ligands. On the contrary, the different organic ligands have significant influence on the catalyst performance, as it was observed in the case of RReO<sub>3</sub> compounds, which also do not lose their organic ligand R under catalytic conditions [2,4] and this influence is maintained in repeated catalytic runs. No indications for a loss of the Cp' and the R/L-ligand are found in the case of the complexes examined in this work.

A lower catalyst loading than 1 mol% was examined for compound **3** (0.1 mol%), increasing the TOF to ca. 6000 h<sup>-1</sup>. Under the same conditions Cp'Mo(O<sub>2</sub>)Cl-catalysed oxidations reach maximum TOFs of ca. 4000 h<sup>-1</sup> [6]. The latter catalyst is easily obtained from Cp'Mo(CO)<sub>3</sub>Cl in isolated yields up to 75%. We have already shown that Cp'Mo(CO)<sub>3</sub>Cl can also be successfully applied as catalyst (precursor) in situ [6]. The direct application of the carbonyl complexes leads to equal activities as the application of the isolated oxides but the latter procedure requires an additional synthesis step, causing a loss of at least 25% of the desired complex. These facts suggested the direct application of the carbonyl complexes also in the case of the compounds described in this work.

Some of the expected oxide and peroxide products of general formulae Cp'MoO<sub>2</sub>R and Cp'Mo(O<sub>2</sub>)OR, in this work generated in situ from the carbonyl precursors **1–7** have been obtained previously by other routes and were isolated and thoroughly characterized [11c,16]. We exemplarily isolated the reaction products of excess TBHP with compound **3** and compared the received <sup>1</sup>H-, <sup>13</sup>C-NMR and IR data with the available literature data [16c]. The obtained data are identical (within the error range of the experimental methods applied) with the published data of CpMoO(O<sub>2</sub>)(CH<sub>3</sub>). In situ recorded vibrational spectra suggest intermediary formation of CpMoO<sub>2</sub>(CH<sub>3</sub>), but this compound could not be obtained without the concomitant formation of CpMoO(O<sub>2</sub>)(CH<sub>3</sub>), even when stoichiometric amounts of TBHP are applied. CpMoO(O<sub>2</sub>)(CH<sub>3</sub>), isolated from the oxidation of CpMo(CO)<sub>3</sub>(CH<sub>3</sub>) (**3**) with ex-

Table 1

Cyclooctene epoxide yields reached with Cp'Mo(CO)<sub>3</sub>R-derived catalysts at a given time when applied at 55 °C with a catalyst:cyclooctene:TBHP-ratio of 1:100:200

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

<sup>a</sup> At 90 °C.

<sup>b</sup> At 75 °C.

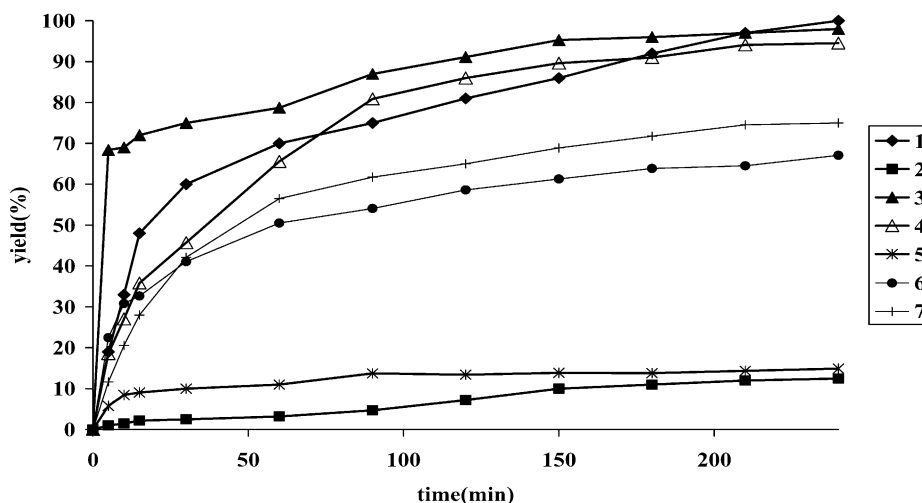


Fig. 2. Catalytic activity of compounds 1–7 in the presence of TBHP in the catalytic epoxidation of cyclooctene.

cess TBHP as sole product in nearly quantitative yields, was additionally applied in the oxidation of cyclooctene with TBHP. Freshly prepared, it catalyzes the reaction as does the in situ generated species under the same reaction conditions. Based on these results it seems justified to assume that  $\text{Cp}'\text{MoO}(\text{O}_2)\text{R}$  type complexes act as catalytically active species in the cases examined in this work.

The observation that the  $\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$  derived catalysts are of higher activity at higher catalyst concentration (1 mol%), but of lower activity at lower catalyst concentration (0.1 mol%) than the  $\text{Cp}'\text{Mo}(\text{CO})_3\text{R}$  derived catalysts may be due to the more pronounced moisture sensitivity of the chlorine derived systems. At lower catalyst concentration the relative amount of water in the system is higher and catalyst decomposition by reaction with water is more likely and faster. Much stronger effects of the same type, supporting this explanation, have been reported with respect to  $\text{Re}(\text{VII})$  catalysts of composition  $\text{XReO}_3$  and  $\text{MeReO}_3$  [4b]. While the latter system is very stable in the presence of water, the highly reactive  $\text{ClReO}_3$  decomposes immediately in the presence of moisture under the formation of  $\text{HCl}$  and perhenic acid (“ $\text{HOREO}_3$ ”) [4b], the latter being catalytically inactive under the applied conditions. The overall (absolute) yield however, is generally lower with  $\text{Cp}'\text{Mo}(\text{CO})_3\text{L}$  ( $\text{L} = \text{Cl}$ , alkyl) derived catalysts at lower catalyst concentrations than that obtained with a higher catalyst concentration at a given time. At all concentrations catalyst decomposition due to the presence of water takes place to a certain, but minor degree according to in situ obtained spectroscopic data (NMR, IR-evidence). At lower catalyst concentrations the relative amount of residual water is higher, thus having a more pronounced effect. Nevertheless, with a catalytic load of 1 mol% compounds 1 and 3 could be recycled five times without significant loss of activity, for instance for 3 100% yield was obtained with five new substrate charges each time after ca. 4 h, in the sixth charge 60% was obtained after 4 h and on the seventh there was a major activity decrease to 10% yield after

24 h. This decrease in activity, however, is not mainly due to catalyst decomposition. The increasing amount of  $t$ -BuOH, also able to coordinate to the catalyst competes, due to its excessive amount increasingly successful with the substrate, thus slowing down the velocity of the catalysed reaction. Addition of excess  $t$ -BuOH to a catalytic reaction has exactly the same effect. Theoretical calculations as well as older examinations on other Mo-based catalysts support this explanation [1,51]. These observations also shed additional light on the earlier catalyst deactivation at lower catalyst concentrations described above. Due to the originally higher substrate concentration relative to the catalyst more  $t$ -BuOH forms in a given time. This also contributes to the reduction of the catalyst activity during the course of one (or more) catalytic runs depending on the catalyst: $t$ -BuOH relationship.

Compounds 1 and 3, being the most active derivatives, were also tested with styrene and 1-octene as substrates. The behaviour of the compounds is similar and with styrene after 24 h epoxide yields of about 50% could be obtained, with 1-octene, a linear non-activated olefin, the results can also be considered as quite good, since after 24 h conversion of ca. 60% and epoxide yields of ca. 45% can be reached. It should be noted that with the closely related and very active complex  $(\eta^5\text{-C}_5\text{Bz}_5)\text{Mo}(\text{CO})_3\text{Cl}$  after 24 h and under the same catalytic conditions a yield of only ca. 20% was reached, the results found in the literature for other active catalysts are also not higher than this latter value [17].

#### 4. Conclusions

The carbonyl compounds of composition  $\text{Cp}'\text{Mo}(\text{CO})_3\text{R}$  ( $\text{R} = \text{alkyl}$ ) have proven to be efficient catalyst precursors. The isolation of the more sensitive oxo and peroxy compounds prior to application in catalysis is not necessary, avoiding also material losses: the carbonyl complexes can be oxidized in situ and directly be used as catalysts. This

oxidation, however, does not include the loss of the Cp' and the R ligand, comparable to the situation observed for Cp'/Mo(CO)<sub>3</sub>Cl complexes. The activity and selectivity of the catalysts is high and they can be reused several times without significant decomposition. The by-product of the oxidation, *t*-BuOH hampers the catalytic reaction with increasing concentration, as it is known for other Mo(VI) oxidation catalysts. Heterogenization of the catalyst or two phase homogeneous catalysis might be promising ways to avoid high amounts of *t*-BuOH in the same phase as the catalyst after several catalytic runs and are accordingly under examination in our laboratories.

Furthermore, the synthetic pathway used for the preparation of compounds **1** and **4** should allow the easy introduction of a chiral ligand instead of methyl group. The presence of a chiral group in the immediate surrounding of the metal centre might lead to much higher enantiomeric excesses as have been reached in the past with related complexes, where the chirality centre was usually quite far away from the metal.

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