Synthesis of versatile organomolybdenum(II) complexes for the epoxidation of olefins, by Fritz E. Kühn et al., from TUM, Garching, Germany.

Title: Aryl-substituted organomolybdenum(II) complexes as olefin epoxidation catalysts

The synthesis of novel organomolybdenum(II) complexes, active in oxidation catalysis, is described. High turnover frequencies of over 15 000 h⁻¹ have been achieved with cis-cyclooctene as a model substrate. Furthermore, it was possible to epoxidise industrially relevant substrates with high yields and selectivities. Additionally, a density functional theory study was performed to contribute to a rational design for future epoxidation catalysts.

As featured in:
Aryl-substituted organomolybdenum(II) complexes as olefin epoxidation catalysts†

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The epoxidation of selected olefins with a benzyl-substituted organomolybdenum complex and its fluorinated counterpart is described. With hexafluorobenzene (HFB) as solvent, turnover frequencies (TOFs) of >15 500 h−1 are achieved in the epoxidation of cyclooctene with tert-butyl hydroperoxide (TBHP) as the oxidant. The fluorinated complex, [CpMo(CO)3BzF5], proved to be superior to the non-fluorinated derivative in activity and selectivity with a variety of substrates. This can be explained via X-ray crystallography analysis and with the help of density functional theory (DFT) calculations. Besides, both compounds were applied in two-phase catalytic reactions. Recycling for multiple catalytic runs is achieved without a significant loss of activity.

Introduction

Epoxides are important intermediates for a variety of chemical products, e.g. food additives, cosmetics, pharmaceuticals and polymers.1–3 The non-catalytic chlorohydrin process based on the process developed by Wurtz in 1859 and the more environmentally friendly, catalytic Halcon-ARCO process, established in the 1960s, are examples of large scale epoxide production methods.2,3 The Halcon-ARCO process utilizes organometallic compounds, such as [Mo(CO)6], as pre-catalysts that are, according to current textbook knowledge, oxidized to catalytically active oxo-perooxo species. Subsequently many homogeneous and heterogeneous molybdenum catalysts for the epoxidation of olefins have been synthesized and examined.4–13 Among other compound classes, molybdenum complexes featuring an η5-coordinated cyclopentadienyl (Cp) ligand have attracted interest as epoxidation catalysts.

Originally, high oxidation state compounds such as [[η5-C5R5]Mo=O2Cl] (R = H, Me, Bz) were targeted,14 but it turned out that the carbonyl precursor complexes of the type [[η5-C5R5]Mo(CO)3Cl] (R = H, Me, Bz) are usually more easily stored due to their higher stability. They also can be used as catalyst precursors for olefin epoxidation.14–19 As in the Halcon-ARCO process, tert-butyl hydroperoxide (TBHP) proved to be the oxidant of choice, readily oxidizing the carbonyl compounds to active catalyst species and, usually more slowly, olefins to epoxides catalysed by the organometallic species created before.

When alkyl groups R’ are attached to the molybdenum centre, a great variability of molecular catalysts is available, e.g. ansa-bridged complexes, which was found to be the benchmark system concerning the activity in the epoxidation of cyclooctene for some time.20,21 Very recently, the activity of the fluorinated organomolybdenum complex [CpMo(CO)3CF3] was compared to its non-fluorinated counterpart [CpMo(CO)3CH3].21,22 This examination revealed that the substitution of a methyl group in the tricarbonyl compound [CpMo(CO)3CH3] with a fluorinated methyl group leads to a distinct increase of Lewis acidity on the metal center. However, in this case the oxidation of the carbonyl precursor to the active species is very slow, so that only the application of an already oxidized catalyst showing a higher activity for olefin epoxidation was illustrated.22

To obtain a more profound insight into the influence of the electronic environment on the catalytic activity of MoCp compounds, two new aryl-substituted complexes, [CpMo(CO)3Bz] and [CpMo(CO)3BzF3], have been synthesized. DFT calculations...
were performed and their catalytic properties in olefin epoxidation were examined. The present work aims to compare and investigate the influence of fluorination on the Lewis acidity of the metal centre and the activity in catalysis.

Results and discussion

Synthesis, IR spectroscopy and X-ray crystallography

The reaction of Na[CpMo(CO)₃] with benzyl bromide and pentfluorobenzyl bromide, respectively, leads to air- and moisture-stable compounds 1 and 2 in yields of ca. 80% under ambient conditions (Scheme 1).

The formation of the new compounds was confirmed by ¹H-NMR with a shift of the Cp signals from 3.84 (THF-d₈) to 5.20 and 5.51 ppm [CDCl₃], respectively. In the ¹³C-NMR spectra of both compounds, only two carbonyl signals can be observed at 239.87 ppm and 228.27 ppm for complex 1 and at 238.98 ppm and 227.57 ppm for compound 2.

IR spectroscopic examinations were performed on both complexes, since the vibrational bands of the carbonyl ligand represent a sensitive tool for the determination of the electronic properties at the metal centre.

The infrared spectra of [CpMo(CO)₃R]-type complexes are well documented in literature. The frequencies of the cyclopentadienyl ligand are virtually independent of the ligand R bound to the metal centre. The CO stretching vibrations are, however, very sensitive to the changes of the ligand group R. The characteristic stretching bonds of 1 and 2 are summarized in Table 1. The C=O symmetric stretching frequency of the C=O bond of compound 2 is found to be 20 wavenumbers higher than that of compound 1.

The observed differences can be explained by the lower electron density at the metal centre in the case of compound 2, generating a weaker metal–ligand interaction. This induces strengthening of the C=O bond – reflected in shorter bond distances.

There is a slight difference in the Mo–R bond lengths (2.386(2) Å in 1 vs. 2.356(2) Å in 2), reflecting the changed electron density at the metal atom in the solid state. The Mo–R bond length is slightly longer for both compounds than that observed for the previously reported methyl derivative (2.326(3) Å). The fluorination of the benzyl moiety does not lead to such a pronounced change of the Mo–R bond distance as observed in the cases of the methyl and the CF₃ derivative (2.234(3) Å). This can be considered as an indication of a more similar reactivity of compounds 1 and 2 with respect to decarbonylation.

Furthermore, the bond distances between Mo and the carbonyl ligands are very similar for both compounds (see Fig. 1 and 2 and ESI†).

DFT examinations

To gain more insight into the electronic properties at the metal centre, DFT calculations of compounds [CpMo(CO)₃CH₃] (1) and [CpMo(CO)₃BF₅] (2) were performed. They reveal that the Lewis acidity of compound 2 at Mo is higher than that of compound 1 (for further details see ESI† S1.1). As ⁹⁵Mo-NMR is also an indicator of electron deficiency, the shifts of 1 (~1588 ppm) and 2 (~1513 ppm) indicate that the metal centre of compound 2 is indeed more electron deficient. It had been possible to ascribe the slower decarbonylation, higher stability and shorter Mo–R bond length of the fluorinated compound [CpMo(CO)₃BF₅] in comparison with those of [CpMo(CO)₃CH₃] to the differences of the highest occupied molecular orbitals (HOMOs). These differences are not observed for compounds 1 and 2 (Fig. 3). Especially, both HOMOs show an Mo–CH₃R overlap, which explains the observed similar Mo–R bond lengths for 1 and 2.
Therefore a similar oxidative decarbonylation rate is to be expected. This is supported by the reaction of compounds 1 and 2 with excess TBHP. After the addition of TBHP, the formation of a dioxo and an oxo-peroxo species (correlating with complete decarbonylation) occurs within 13 min for 1 and 5 min for 2.29 The oxidative decarbonylation was monitored via $^1$H NMR spectroscopy. These observations are in accord with several computational and experimental studies which deal with the formation of dioxo and oxo-peroxo species with TBHP as the oxidant. After decarbonylation the dioxo species forms, which can be transformed to the oxo-peroxo species with an excess of oxidant. Both species can take part in the catalytic epoxidation of olefins with TBHP as the oxidant of choice. Detailed mechanistic studies to further examine the active species are under way.29

This difference in the rate of decarbonylation is quite small in comparison with the methyl (20 min) and trifluoromethyl derivatives (>60 min).22

### Epoxidation catalysis

Both complexes are well soluble in dichloromethane (DCM), acetonitrile (CH$_3$CN), chloroform (CHCl$_3$), toluene and benzene. For all kinetic experiments and for all applied substrates, one homogeneous phase was obtained.

The monomeric complexes 1 and 2 were applied as catalysts for the epoxidation of selected terminal and internal alkenes using tert-butyl hydroperoxide (TBHP, 5.5 M solution in n-decane) as oxidant. To determine the optimal reaction conditions concerning the solvent, temperature, catalyst and oxidant loading, cyclooctene was chosen as substrate. The results obtained for the temperature and solvent screening are summarized in Table 2.

A comparison of the two compounds in the catalytic cyclooctene epoxidation reveals the superiority of the fluorinated complex 2. This behaviour is in accord with the more pronounced Lewis acidity of this compound.36,37 Both compounds show the best activity in hexafluorobenzene (HFB) as solvent (Table 2, entry 6). This is in accord with the recent observations for related catalytic systems where the activity of the organomolybdenum complex [CpMo(CO)$_2$CF$_3$]$_2$ was found to be superior when a solvent able to activate the oxidant, like hexafluoroisopropanol (HFIP), is used.22

To further investigate the difference in activity, all following investigations concerning the catalyst loading were performed in benzene and HFB.

Based on the results summarised in Table 3, it can be stated that catalyst 2 is roughly 20% more active than 1. Furthermore HFB positively influences the catalytic activity of both compounds. When examining a variety of substrates (see Table 4), it can be observed that open chain alkenes such as styrene and 1-octene are epoxidised with good to moderate efficiency. Compared to known MoCp systems,

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent$^a$</th>
<th>Yield$^b$ [%] after 4 h/24 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r.t.</td>
<td>55 °C</td>
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<tr>
<td>1</td>
<td>DCM</td>
<td>74/100</td>
</tr>
<tr>
<td>2</td>
<td>CHCl$_3$</td>
<td>66/100</td>
</tr>
<tr>
<td>3</td>
<td>Benzene</td>
<td>75/100</td>
</tr>
<tr>
<td>4</td>
<td>Hexane</td>
<td>72/100</td>
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<tr>
<td>5</td>
<td>MeOH$^c$</td>
<td>&lt;10/&lt;10</td>
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<tr>
<td>6</td>
<td>HFB$^d$</td>
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<tr>
<td>7</td>
<td>[C$<em>8$H$</em>{15}$][NTf$_2$]</td>
<td>72/100</td>
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<td>8</td>
<td>[C$<em>8$H$</em>{15}$][NTf$_2$]</td>
<td>74/100</td>
</tr>
</tbody>
</table>

| $^a$ Reaction conditions: reactions were carried out using a molar ratio of catalyst:substrate:oxidant of 1:100:200 in 0.5 mL of solvent. $^b$ Yield determined by GC-MS. $^c$ MeOH: methanol, HFB: hexafluorobenzene. |
Table 3  Activity of the pre-catalyst in terms of the catalyst loadinga

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Cat. conc. [mol %]</th>
<th>Benzene TOF [h⁻¹]</th>
<th>HFB TOF [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>1</td>
<td>2960</td>
<td>4250</td>
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<td>3</td>
<td>1</td>
<td>0.05</td>
<td>10 430</td>
<td>11 580</td>
</tr>
<tr>
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<td>1</td>
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<td>6370</td>
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<tr>
<td>5</td>
<td>2</td>
<td>0.1</td>
<td>12 220</td>
<td>13 470</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0.05</td>
<td>15 540</td>
<td>17 820</td>
</tr>
</tbody>
</table>

a Reaction conditions: 55 °C, 0.5 mL of solvent, molar ratio cyclooctene : TBHP of 1 : 2.

Table 4  Substrate scope of the catalytic system

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrateα</th>
<th>Catalyst</th>
<th>Conv. [%]</th>
<th>Sel. [%]</th>
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<td>1-Octene</td>
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<td>2</td>
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<td>99</td>
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<tr>
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<td>2</td>
<td>54</td>
<td>99</td>
<td></td>
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<td>Cis-stilbene</td>
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<td>76</td>
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<tr>
<td>8</td>
<td>2</td>
<td>57</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Trans-stilbene</td>
<td>1</td>
<td>47</td>
<td>86</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>55</td>
<td>94</td>
<td></td>
</tr>
</tbody>
</table>

α Reaction conditions: 1 mmol of substrate, 2 mmol of TBHP in decane, 0.5 mol% catalyst, 55 °C, 0.5 mL of benzene, 24 h. b Conversion and selectivity were determined via ¹H-NMR.

They are active and selective catalysts for the epoxidation of olefins using TBHP as an oxidant. Both compounds were examined by DFT calculations, leading to the result that they are much more similar to each other with respect to the HOMOs than the related CH₃ and CF₃ derivatives. Accordingly, the oxidation of the carbonyls to the active species is more similar. The somewhat enhanced Lewis acidity of 2 explains its higher catalytic activity. This is in accord with the obtained crystal structures and previous studies concerning the influence of Lewis acidity on epoxidation activities. Catalytic results show no formation of diol, underlining the high selectivity of the utilized compounds for standard substrates. Both compounds are highly soluble in common organic solvents in contrast to many previously reported related complexes.

With benzene and hexafluorobenzene as solvents, TOFs of up to ca. 18 000 h⁻¹ can be achieved in the epoxidation of cyclooctene. Moreover, both compounds are able to epoxidize more demanding substrates such as styrene and stilbenes in acceptable yields applying a 0.5 mol% catalyst. When the precatalysts are dissolved in imidazolium-based ionic liquids, the product phase can be easily separated from the reaction medium and the molecular catalysts can be reused for (at least) 8 consecutive cycles with very low losses of activity.

Experimental section

Material and methods

All experimental synthetic work was carried out using standard Schlenk techniques under argon. Catalytic reactions were performed under laboratory atmosphere. Solvents were dried by standard procedures and stored under argon over molecular sieves. Commercially available chemicals were used as received, unless stated otherwise. High-resolution NMR spectra were measured with a Bruker Avance DPX-400 spectrometer (1H: 400.0 MHz; ¹C: 100.6 MHz; ¹F: 376.5 MHz; ⁹⁵Mo: 26.1 MHz). The signals were referenced to the
solvent residual signal (C₆D₆; 1H: 7.16 ppm; ¹³C: 128.06 ppm) or external standards in a capillary (¹⁹⁵Mo: Mo(CO)₆) in C₆D₆ at −1856 ppm). IR spectra were recorded on a Varian ATR-FTIR instrument. Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a saturated solution of 1 and 2, respectively, in hexane.

**Synthesis of the complexes**

The organomolybdenum complexes [CpMo(CO)₃Bz] (1) and [CpMo(CO)₃BzF₅] (2) were synthesised according to literature procedures.22,35,38

(1) [CpMo(CO)₃Bz] ¹H-NMR (CDCl₃, 298 K, 400 MHz): 7.24–7.00 (m, 5H, Bz), 5.20 (s, 5H, Cp), 2.93 (s, 2H, CH₂Bz). ¹³C-NMR (CDCl₃, 298 K, 101 MHz): 239.90 (CO), 228.28 (CO), 151.2, 128.05, 127.61, 123.76 (Bz), 94.05 (Cp), 4.98 (CH₂Bz).

(2) [CpMo(CO)₃BzF₅] ¹H-NMR (CDCl₃, 298 K, 400 MHz): 5.51 (s, 5H, Cp), 2.48 (s, 2H, CH₂BzF₅). ¹³C-NMR (CDCl₃, 298 K, 101 MHz): 239.02 (CO), 227.62 (CO), 144.9, 142.59, 138.76, 136.30, 151.34, 19 F-NMR (CDCl₃, 298 K, 376 MHz): −142.34, −163.40, −164.44. IR: ν = 2001.6 cm⁻¹ (vs), 1901.3 cm⁻¹ (s) (84% yield).

**Catalytic reactions**

All catalytic reactions were performed under laboratory atmosphere in a reaction vessel equipped with a magnetic stirrer.

**Cis-cyclooctene**

The substrate (1.30 mL, 1 mmol) and catalyst dissolved in 0.5 mL of solvent were added to the reaction vessel and heated to the investigated temperature. The reaction was initiated by the addition of TBHP (3.6 mL, 5.5 molar in decane).

**Analysis:** the course of the reaction was monitored by quantitative GC analysis. Samples taken were treated with MnO₂ and MgSO₄ to destroy excess peroxide and remove water from the sample. After filtration, the sample was diluted with dichloromethane and an external standard (mixture of 4 mg per 100 mL of p-xylol and 4 mg per 100 mL of indene in isopropanol) was added. The sample was then injected into a GC column and the conversion of cis-cyclooctene to cyclooctene epoxide was calculated from the calibration curves (R² > 0.999) recorded prior to the start of the reaction.

**1-Octene**

The substrate (800 mg, 7.3 mmol), dichlorothane (7.3 mmol, internal standard) and the catalyst (0.5 mol%, 36.5 μmol) were added to the reaction vessel and diluted in benzene (0.5 mL). Afterwards, the reaction was initiated by adding TBHP (2.65 mL, 5.5 molar in n-decane).

**cis-stilbene**

The substrate (0.291 g, 1.6 mmol), dichloroethane (1.6 mmol, internal standard), and the catalyst (0.5 mol%, 8 μmol) were added to the reaction vessel and diluted in benzene (0.5 mL). The reaction was initiated with the addition of TBHP (0.6 mL, 5.5 molar in n-decane).

**Trans-β-methylstyrene**

The substrate (0.118 g, 1.0 mmol), dichloroethane (1.0 mmol, internal standard) and the catalyst (0.5 mol%, 0.05 mmol) were added to the reaction vessel and diluted in benzene (0.5 mL). The reaction was initiated by adding TBHP (3.6 mL, 5.5 molar in n-decane).

Analysis: in the case of 1-octene, trans-β-methylstyrene and cis-stilbene, the course of the reaction was monitored by ¹H NMR analysis. Samples taken were treated with MgSO₄ and MnO₂ to remove water and destroy excess peroxide. Afterwards, the sample was diluted with CDCl₃, and the resulting slurry was filtered and the filtrate was analysed.

**Recycling experiments**

After the catalytic reaction, the upper phase was removed from the reaction vessel by addition of 5 mL of n-hexane after cooling down to room temperature. The upper phase was removed by means of cannulation. The samples were treated with MgSO₄ and MnO₂ to remove water and destroy excess peroxide. Afterwards, the sample was diluted with CH₂Cl₂ and the resulting slurry was filtered. A mixture of 4 mg mL⁻¹ indane and p-xylene in isopropanol (used as external standard) and the filtrate was injected into a GC column. Additionally, oil pump vacuum for 2.5 h at 55 °C allowed the removal of ¹BuOH from the remaining RTIL (room temperature ionic liquid) phase before further cyclooctene (0.800 g, 7.3 mmol) and TBHP (2.65 mL, 5.5 molar in n-decane) were added.

**X-ray single crystal structure determination**

Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a saturated solution of 1 and 2, respectively, in hexane.

**Computational details**

All calculations have been performed with Gaussian03.39 The level of theory contains the hybrid DFT functional B3LYP40,41 and the double zeta 6-31+G**42 basis set for all atoms excluding Mo and the Stuttgart 1997 ECP for molybdenum.43 All
obtained geometries have been identified via the number of negative frequencies as minima (\(N_{\text{imag}} = 0\)). Free energy differences have been calculated for the gas phase at 298.15 K and 1.0 atm.

**Acknowledgements**

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**Notes and references**