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Reactions of cyclopentadienylmolybdenum compounds with bismuth alkoxides

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Dedicated to Professor Dr Rolf Gleiter on the occasion of his 65th birthday

Abstract

The unique ability of bismuthmolybdate phases to act as heterogeneous catalysts for the oxidation of olefins stimulates research focussing on molecular Bi/Mo complexes, and in this context the behaviour of cyclopentadienyl molybdenum compounds in the presence of bismuth alkoxides has been investigated. While the reaction of [$CpMoCl_4$] with [$Bi(OEt)_3$]$_x$ did not yield a tractable product, its reaction with [$Bi\{OCH(CF_3)_2\}_3(THF)$]$_2$ (**6**), led to the isolation of [$CpMoCl\{OCH(CF_3)_2\}_3$] (**7**), formed in a halide/alkoxide exchange reaction. The crystal structure of **7** is discussed. A heterometallic Mo/Bi complex could be obtained via treatment of [Cp_2MoH_2] with **6**. Elimination of $HOCH(CF_3)_2$ provided [$Cp_2Mo(Bi\{OCH(CF_3)_2\}_2)_2$] (**8**), containing two Mo–Bi bonds as revealed by a single-crystal X-ray structure analysis. The oxidation of **8** with ^{t}BuOOH gave rise to the formation of the molybdocene alkoxide [$Cp_2Mo\{OCH(CF_3)_2\}_2$] in good yields, i.e. the Mo–Bi bonds were cleaved in a formal four-electron oxidation process — possibly via the intermediate formation of Mo–O–Bi moieties. To test for any intermediate and its in situ reactivity, the same reaction was also performed in the presence of an excess of *cis*-stilbene. It turned out that **8** behaved as an efficient catalyst for the epoxidation of this olefin. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkoxides; Epoxidations; Bismuth; Heterobimetallic; Molybdenum

1. Introduction

The unique property of $n MoO_3/Bi_2O_3$ phases to act as catalysts for the allylic oxidation of propene [1a] remains a subject of intense discussion [1b]. The results of recent investigations concerning heterogeneous oxidations on Mo/Bi oxide surfaces suggest that the oxygen atoms found in the organic oxidation products have their origin in previously *bridging* positions [1c], so that Bi(μ-O)Mo moieties are currently thought to be the active oxo-transfer sites also during the propene oxidation. This encourages research with the aim of preparing molecular species containing both Mo and Bi being linked by oxygen containing, or ideally 'pure' oxo ligands. In this context we have recently reported the first heterometallic Mo/Bi alkoxide complexes [2,3]. Their syntheses had been achieved starting from molybdenum organyls, where a part of the coordination sphere at Mo is shielded by tightly bound organic ligands: [Cp_2MoCl_2] had been chosen to be treated with in situ prepared [$Bi(OEt)_3$]$_x$ yielding [$Cp_2Mo(\mu\text{-}OEt)_2Bi(OEt)_2Cl$] (**1**), with a Mo and a Bi centre being bridged by two ethanolate ligands [2]. Reaction of [$((CH_3)C_3H_4)Mo(CO)_2(CH_3CN)_2Cl$] (**2**), with [$Bi(OEt)_3$]$_x$ had provided the heterotetranuclear complex [$((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}OEt)_3Bi(\mu\text{-}OEt)_2Bi(\mu\text{-}OEt)_3Mo(CO)_2((CH_3)C_3H_4)$] (**3**), in good yields [3], and treatment with [$Bi(OCH_2CH_2OCH_3)_3$]$_2$ a dinuclear chloro alkoxide [$((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}\kappa O, 2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}Cl)BiCl$] (**4**). Pretreatment of **2** with $AgBF_4$ and subsequent reaction with [$Bi(OCH_2CH_2OCH_3)_3$]$_2$ had further led to the chloride free complex [$((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}\kappa O, 2\kappa O'\text{-}OCH_2CH_2OCH_3)_3Bi(THF)$][$BF_4$] (**5**) [3].

It is obvious that the next step towards molecular Mo/Bi/O systems has to consist of the formal substitu-

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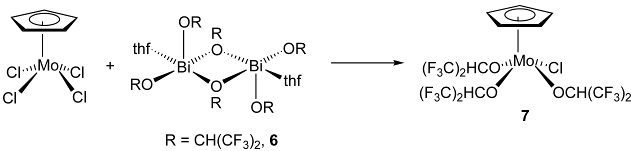
tion of the alkoxo by oxo ligands. Bearing this target in mind, we have recently pursued two possible strategies:

1. Alkoxides containing metals in their highest oxidation states are known to often eliminate ethers thereby generating oxo ligands [4]. Hence, we have performed reactions aimed at producing Mo(V)/Bi alkoxides [5], from which oxo compounds should potentially become accessible via ether elimination.
2. Compounds containing Mo–Bi bonds were prepared and subsequently treated with oxo-transferring reagents, in order to insert O atoms into the metal–metal bonds.

Here we report the results obtained in these investigations.



R = $CH(CF_3)_2$, **6**

7

+ 1/x $[Bi_2(OR)_3Cl_3]_x$

Scheme 1.

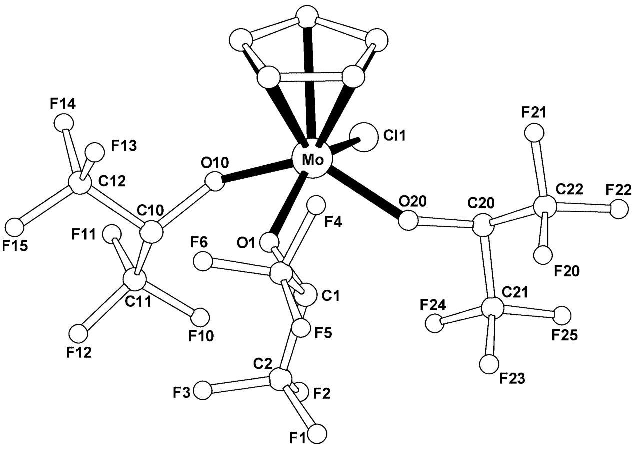


Fig. 1. Molecular structure of **7** with partial atom labelling scheme.

Table 1
Selected bond lengths (Å) and bond angles (°) for **7**

Bond lengths		*Bond angles*	
Mo–O(20)	1.941(2)	O(20)–Mo–O(10)	131.24(8)
Mo–O(10)	1.956(2)	O(20)–Mo–O(1)	80.48(7)
Mo–O(1)	1.969(2)	O(10)–Mo–O(1)	81.29(7)
Mo–Cl(1)	2.3705(8)	O(20)–Mo–Cl(1)	84.63(5)
O(1)–C(1)	1.388(3)	O(10)–Mo–Cl(1)	82.40(5)
O(10)–C(10)	1.395(3)	O(1)–Mo–Cl(1)	141.55(6)
O(20)–C(20)	1.392(3)		

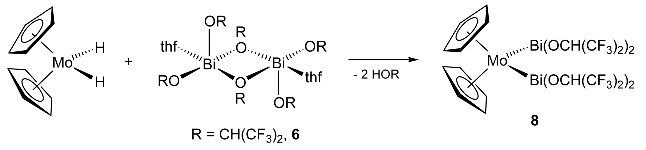
2. Results and discussion

Following the first strategy $[CpMoCl_4]$ was chosen as the organomolybdenum(V) source to be reacted with $[Bi(OEt)_3]_x$ analogous to $[Cp_2MoCl_2]$, whose reaction had given rise to the isolation of **1**. After suspending $[CpMoCl_4]$ in CH_2Cl_2 and treating it with $[Bi(OEt)_3]_x$ a red–brown solution was obtained, from which a reddish solid was isolated. This, however, showed a very high sensitivity prohibiting reliable mass-spectrometric analyses and due to its paramagnetism NMR spectroscopic investigations could neither be performed. Moreover, all attempts to crystallise the compound failed, so its identity is still unknown.

The replacement of the alkoxide $[Bi(OEt)_3]_x$ by $[Bi\{OCH(CF_3)_2\}_3(THF)]_2$ (**6**), in such experiments again led to a red–brown solution, but simultaneously a brown solid precipitated. After filtering, the solvent was removed and recrystallisation from toluene yielded red–brown crystals. Single-crystal X-ray analysis identified the corresponding compound as $[CpMoCl\{OCH(CF_3)_2\}_3]$ (**7**) (Scheme 1) and its molecular structure is shown in Fig. 1 (selected bond distances and angles are listed in Table 1). While there is evidence for compounds of the type $[CpMoCl_2(OR)_2]$ with R = Me and Et (on the basis of elemental analyses and IR spectroscopy [6]), there is no complex of the general formula $CpMoCl(OR)_3$ like **7** existent in the literature. The molecular geometry of **7** can be described as a four-legged piano-stool, where O(1), O(10), Cl(1) and O(20) are located roughly in a plane forming a distorted square. The CpMo unit is capping this square, the largest angle being the one characterising the O(20)–Mo–Cl(1) unit [84.63(5)°], while the smallest angle is found within the O(20)–Mo–O(1) moiety [80.48(7)°]). The Mo–O distances are all of a similar size (ca. 1.95 Å) and there are no structural peculiarities.

It can be recorded at this stage that the reaction of $[CpMoCl_4]$ with a $[Bi(OR)_3]$ compound containing an *electron rich* residue R (i.e. ethyl) did not yield a tractable product, while in the case of an *electron poor* residue R (i.e. hexafluoroisopropyl) Cl/OR exchanges took place (the alkoxide ligands obviously not being capable of bridging both Mo and Bi). We therefore continued with the experiments following the second strategy (vide supra).

As mentioned above, the aim of the second concept was the insertion of oxo atoms into Mo–Bi bonds. O atom insertions into metal–metal bonds [e.g. into those of $In_4\{C(SiMe_3)_3\}_4$ [7]] have been successfully achieved in the past with the aid of oxo-transfer reagents such as *p*-nitrosyl toluene. Starting materials, $L_xM–M'L'_y$, suitable to be employed in this type of reaction thus have to be composed of complex metal fragments (L_xM and $M'L'_y$), whose M–L and M′–L′ bonds are stable under



Scheme 2.

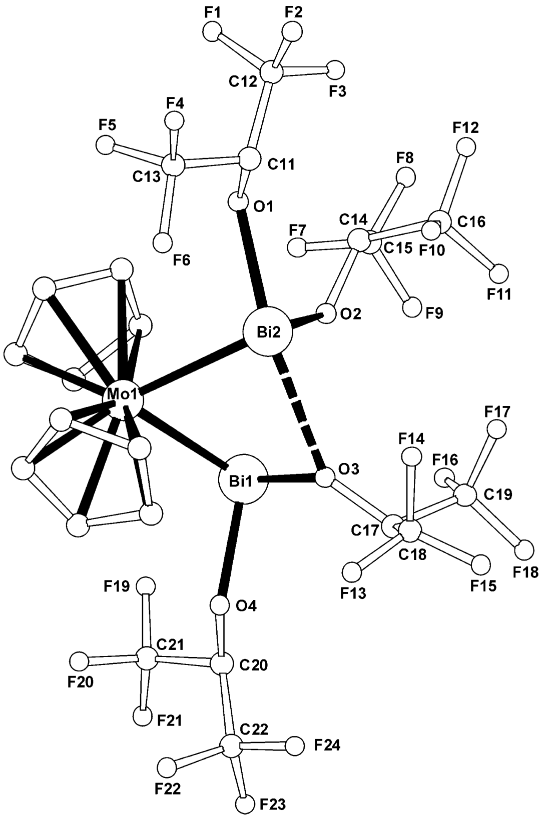


Fig. 2. Molecular structure of **8** with partial atom labelling scheme.

Table 2
Selected bond lengths (Å) and bond angles (°) for **8**

Bond lengths		*Bond angles*	
Mo(1)–Bi(1)	2.788(2)	Bi(2)–Mo(1)–Bi(1)	76.72(3)
Mo(1)–Bi(2)	2.8478(9)	Mo(1)–Bi(2)–O(1)	101.50(8)
Bi(1)–O(4)	2.189(3)	Mo(1)–Bi(2)–O(2)	96.14(9)
Bi(2)–O(1)	2.214(3)	O(1)–Bi(2)–O(2)	87.0(2)
Bi(1)–O(3)	2.199(3)	Mo(1)–Bi(1)–O(4)	101.15(9)
Bi(2)–O(2)	2.176(3)	Mo(1)–Bi(1)–O(3)	91.43(8)
		O(3)–Bi(1)–O(4)	86.5(2)

oxidising conditions. There are some compounds containing Mo–Bi bonds known (e.g. $[ClBi\{Mo(CO)_3Cp\}_2]$ [8] and $[Mo_2(CO)_4(MeCp)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ [9] as well as certain others [10]), but none of them meets this requirement of oxidative stability, as they all contain carbonyl ligands, which are very prone to attack by oxo-transfer reagents. We therefore decided to prepare novel Mo–Bi compounds with Mo centres in comparatively high oxidation states (wearing inert ligands) and Bi centres in alkoxidic coordination spheres.

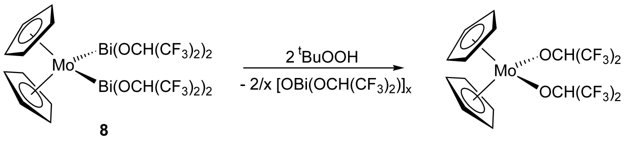
Principally, Mo–Bi compounds could be imagined to become accessible via formal Brønstedt acid–base reactions. $[Cp_2MoH_2]$ contains Mo–H bonds, that can be cleaved in various ways [11], and the lone pair at molybdenum in contact with $[Bi(OR)_3]$ compounds should allow the formation of a precursor complex being capable of eliminating alcohol under generation of Mo–Bi bonds. Molybdocene dihydride was therefore treated with **6** in toluene. From the resulting reaction mixture a red–brown solid was isolated, which could be recrystallised from CH_2Cl_2. The corresponding compound was identified as $[Cp_2Mo(Bi\{OCH(CF_3)_2\}_2)_2]$ (**8**) by means of NMR and IR spectroscopic elemental analysis as well as by a single-crystal X-ray diffraction analysis (Scheme 2). The molecular structure of **8** is depicted in Fig. 2 and selected bond distances and angles are listed in Table 2. As can be seen, **8** possesses two Mo–Bi bonds whose lengths [Mo(1)–Bi(1): 2.788(2) Å and Mo(1)–Bi(2): 2.8478(9) Å] are comparable to those found in the known MoBi compounds [8–10]. The Bi–Mo–Bi angle 76.72° is not much larger than the H–Mo–H angle in $[Cp_2MoH_2]$ (75.5°) [12] which means that there cannot be significant repulsive forces between the two $Bi(OR)_2$ moieties at the Mo centre. The question whether or not there is an *attractive* interaction between the two Bi atoms is difficult to answer solely on the basis of the molecular geometry, but certainly the Bi–Bi distance of 3.498(2) Å is too long to be interpreted in terms of a Bi–Bi bond, such bonds usually have lengths around 3.0 Å {e.g. 3.035(3) Å in $[Bi_2(SiMe_3)_4]$ and 2.990(2) Å in Bi_2Ph_4 [13]. Comparing the Bi–O distances of the terminal alkoxide ligands in $[Bi\{OCH(CF_3)_2\}_3THF]_2$ (**6**), (2.176-2.214 Å) [14] with those in **8**, it is found that — not surprisingly — they are all quite similar. It has to be noted though that the distance between the O(3) and the Bi(2) atom in **8** is with 2.693(3) Å only slightly longer than some of the Bi–O bond distances belonging to the *bridging* alkoxide functions in **6** (2.688 Å). This seems to suggest that the corresponding alkoxide ligand in **8** bridges the two Bi centres unsymmetrically (as indicated by the dotted line in Fig. 2), which would explain the small Bi–Mo–Bi angle. Such an interaction of O(3) with Bi(2) is also in line with the fact that the Bi(2)–O(1) bond — being located in *trans* position to Bi(2)–O(3) [the angle O(1)–Bi(2)–O(3) amounts to 161°] — is the longest one among the terminal Bi–O bonds in **8**. Compound **8** is fluxional in solution though, only one set of alkoxide signals can be observed in the ^1H- and ^{13}C-NMR spectra, respectively.

The reaction of $[Cp_2MoH_2]$ with $[Bi(O^tBu)_3]$ leads to a red–brown, crystalline solid too, whose NMR spectra can be interpreted analogously to those of **8**, so that an assignment to a corresponding product $[Cp_2Mo$-

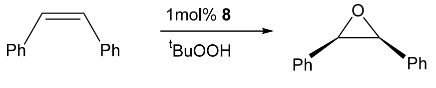
$\{Bi(O^tBu)_2\}_2]$ **9**, seems reasonable. However, the compound proved to be far more sensitive than **8** (possibly, as for steric reasons stabilisation by alkoxid bridging cannot be achieved) so that neither an elemental analysis nor a single-crystal X-ray analysis could be performed.

In the next step **8** was treated with O-atom donors. Neither the reaction with O_2 nor the one with PhNO yielded a tractable soluble product. If, however, **8** is treated with two equivalents of ^{t}BuOOH, a suspension of a white solid in a brown solution forms overnight. From the solution $[Cp_2Mo\{OCH(CF_3)_2\}_2]$ [2] can be isolated in 58% yield (Scheme 3), i.e. in the course of the reaction the Mo–Bi bonds are oxidatively cleaved yielding a Mo^{IV} compound as well as (most likely) a Bi^{III} oxo alkoxide. The conversion therefore formally corresponds to a four-electron oxidation and it could indeed have proceeded via insertion of two O atoms (whose source is the ^{t}BuOOH) into the two Mo–Bi bonds in the primary step. The resulting intermediate $[Cp_2Mo(OBi\{OCH(CF_3)_2\}_2)_2]$ (**I**), could then be imagined to decompose yielding $[Cp_2Mo\{OCH(CF_3)_2\}_2]$ and $[OBi\{OCH(CF_3)_2\}]_x$ in the course of intramolecular alkoxide ligand migrations — a process which had already been observed previously [2] as part of the reaction between $[Cp_2Mo{=}O]$ and $[Bi\{OCH(CF_3)_2\}_3\text{-}THF]_2$, and also led to the formation of $[Cp_2Mo\{OCH(CF_3)_2\}_2]$. Naturally, the question occurred whether the primary product (may it be **I** or a different species) has a sufficient life time and oxo-transfer capability to show in situ reactivity and we therefore decided to perform the reaction outlined in Scheme 3 in the presence of an olefin.

cis-Stilbene was heated (65 °C) together with one equivalent of ^{t}BuOOH in the presence of 1 mol% of **8** for 63 h. A ^{1}H-NMR spectrum of the reaction mixture later showed that 18% of the stilbene had been converted to give *cis*-stilbene oxide and 1% to give *trans*-stilbene oxide (^{t}BuOH is formed as the byproduct). Furthermore, the precipitation of a white solid (vide supra) was *not* observed in the presence of the olefin, probably because the intermediate epoxidises before it has time to decompose under elimination of $[OBi\{OCH(CF_3)_2)]_x$. Compound **8** thus represents an active catalyst for the epoxidation of stilbene. It is interesting to note that neither $[Cp_2Mo\{OCH(CF_3)_2\}_2]$ nor $[Bi\{OCH(CF_3)_2\}_3THF]_2$ (**6**), showed any activity in analogous reactions; hence the Bi–Mo units are essential.



Scheme 3.



Scheme 4.

Current research focuses on the preparation of $[Cp_2Mo\{Bi(OR)_2\}_2]$ compounds with residues R that will enable the subsequent isolation of the corresponding intermediates formed after treatment with HOO^tBu as well as on the reactions of organomolybdenum(VI) compounds with bismuth alkoxides (Scheme 4).

3. Experimental

3.1. General procedures

All manipulations were carried out with a vacuum line (at a background pressure $< 10^{-3}$ mbar) or else, in a glove-box, or by means of Schlenk-type techniques involving the use of a dry Ar atmosphere. Microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg using a CHN-Analyser Heraeus. Samples were prepared in a glove box. The deuteriated solvents had been condensed into the NMR tubes before the tubes were flame-sealed. All NMR spectra were recorded using Bruker Avance-DPX 200 (^{1}H: 200,132 MHz; ^{13}C: 50.323 MHz) spectrometer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets using a Bruker FT-IR spectrometer IFS-66.

The melting/decomposition points were recorded in a sealed glass tube using Gallenkamp type melting point apparatus MFB 595010.

3.2. Materials

Tetrahydrofuran (THF) and hexane were distilled from potassium, toluene from sodium metal under Ar. Petroleum ether (40:60) was distilled from P_4O_{10} and CH_2Cl_2 from CaH_2 under an Ar atmosphere.

$[Cp_2MoH_2]$ [15], $[Bi(OEt)_3]_x$ [16], $[Bi\{OCH(CF_3)_2\}_3\text{-}THF]_2$ [14] and $[Bi\{OC(CH_3)_3\}_3]$ [16] were prepared by published procedures. $CpMoCl_4$ was purchased from Stream.

3.3. $[CpMoCl\{OCH(CF_3)_2\}_3]$ (7)

To a suspension of 0.30 g (1.0 mmol) $[CpMoCl_4]$ in 20 ml CH_2Cl_2 a solution of 1.56 g (1.0 mmol) $[Bi\{OCH(CF_3)_2\}_3THF]_2$ dissolved in CH_2Cl_2 is added via cannula. After stirring a red–brown solution is obtained as well as a brown solid which is filtered off. The volatiles are removed and the residue is extracted with toluene (20 ml). After cooling to − 65 °C for 2

Table 3
Crystal data and refinement structure parameters for compounds **7** and **8**

	7	**8**
Empirical formula	$C_{14}H_8ClF_{18}O_3Mo$	$C_{22}H_{14}Bi_2F_{24}O_4Mo$
Formula weight	697.54	1312.21
Crystal colour	Red–brown	Red–brown
Crystal system	Orthorhombic	Triclinic
Lattice type	Primitive	Primitive
Unit cell dimensions		
a (Å)	14.014(3)	10.090(2)
b (Å)	17.545(4)	12.203(2)
c (Å)	17.928(4)	13.748(3)
α (°)	90	82.54(3)
β (°)	90	73.66(3)
γ (°)	90	77.09(3)
V (Å^3)	4408.1(15)	1579.3(5)
Space group	*Pbca*	$P\bar{1}$
Z	10	2
D_{calc} (g cm^{-3})	2.102	2.760
F_{000}	2696	1204
Temperature (K)	200	200
μ (Mo–K$_\alpha$) (mm^{-1})	0.10422	
Diffractometer	Nonius Kappa CCD	
Radiation	Mo–K$_\alpha$, graphite monochromated ($\lambda = 0.71073$ Å)	
Detector position (mm)	34	34
Scan type	ω (1° per frame)	
$2\Theta_{max}$ (°)	55.0	52.1
Number of reflections measured		
Total	9531	70 547
Unique	5042	6180
R_{int}	0.0342	0.0601
Corrections	Lorentz–polarisation factor	
Structure solution	Direct method (SHELXS-97, SHELXL-97)	
Refinement	Full-matrix least-squares	
Number of observations ($I > 2\sigma(I)$)	3843	4808
Number of variables	362	480
Reflections/parameters ratio	13.93	12.88
Residuals		
R	0.0324	0.0280
R_w	0.0854	0.0490
R (all)	0.0494	0.0467
Goodness-of-fit	1.010	0.965
Final difference map		
Maximum peak (e Å^{-3})	0.418	1.211
Minimum peak (e Å^{-3})	−0.514	−0894

days red–brown crystals are obtained, which are suitable for X-ray diffraction (isolated yield: 0.11 g, 16%). Melting point (m.p.) (dec.): 130–140 °C IR (KBr, cm^{-1}): 3539 (w); 3140 (w); 2930 (w); 1375 (m); 1284 (s); 1181 (s); 1100 (s); 858 (s); 801 (m); 749 (s); 523 (m).

3.4. *[$Cp_2Mo(Bi\{OCH(CF_3)_2\}_2)_2$]* (*8*)

A yellow solution of 0.40 g (1.75 mmol) [Cp_2MoH_2] in 30 ml of toluene is added to a solution of 5.47 g (3.50 mmol) [$Bi\{OCH(CF_3)_2\}_3THF]_2$ in 50 ml of toluene via cannula. The colour changes to red and small amounts of a black solid precipitate which is filtered off. All volatiles are removed under vacuum leaving an oily red solid behind which is washed with petroleum ether (40:60). The resulting red powder is dissolved in 40 ml CH_2Cl_2 and after cooling to −70 °C red crystals of **8** are obtained within 3 days (yield: 1.87 g (1.43 mmol) 82%). M.p. (dec.): 105–110 °C. ^{1}H-NMR (CD_2Cl_2): $\delta_H = 5.58$ (s, 10H, Cp_H), 5.15 (sept., 4H, $^3J_{HF} = 6.49$ Hz, CH). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): $\delta = 125.0$ (q, 4 C, $^1J_{CF} = 284.95$ Hz, CF_3), 85.02 (s, Cp_C), 73.15 (sept., $^3J_{CF} = 31.25$ Hz, CH). ^{19}F-NMR (THF-d_8): $\delta_H = 76.3$ (s, CF_3). IR (KBr, cm^{-1}): 3129 (w); 2890 (w, br); 1370 (m); 1285 (s); 1261 (m); 1180 (s); 1122 (s); 1090 (s); 889 (m); 852 (m); 740 (m); 687 (m); 636 (s); 516 (m); 407 (m). Anal. Calc. for $C_{22}H_{14}Bi_2F_{24}O_4Mo$ (1312.21): C, 20.14; H, 1.08. Found: C, 19.70; H, 1.09%.

3.5. *[$Cp_2Mo(Bi\{OC(CH_3)_3\}_2)_2$]* (*9*)

The synthesis was performed in close analogy to the one described for **8** reacting 0.50 (2.19 mmol) of [$CpMoH_2$] in 20 ml of toluene with 1.87 g (4.38 mmol) of [$Bi(O^tBu)_3$] in 30 ml of toluene. Recrystallisation was performed from hexane yielding red crystals of **9**, which are thermally very sensitive (yield: 1.22 g (1.31 mmol) 60%).

^{1}H-NMR (toluene-d_8): $\delta_H = 4.79$ (s, 10H, Cp_H), 1.37 (s, 36 H, $OC(CH_3)_3$). $^{13}C\{^1H\}$-NMR (toluene-d_8): $\delta =$ 83.49 (s, Cp), 70.78 (s, $OC(CH_3)_3$), 35.37 (s, $OCH(CH_3)_3$). IR (KBr, cm^{-1}): 3421 (w, br); 3076 (w); 2959 (vs); 2854 (m); 1448 (s); 1375 (m); 1353 (s); 1258 (2w); 1180 (vs); 1106 (m); 1012 (m); 930 (s); 833 (m); 803 (m); 752 (m); 542 (m); 450 (w); 407 (m).

3.6. *Epoxidation reactions*

In a Glove-Box 0.005 g (0.003 mmol) of **8** are filled into an NMR tube. CD_2Cl_2 (0.5 ml) is cocondensed in a high vacuum line, and in a stream of Ar 0.05 ml (0.277 mmol) of *trans*-stilbene are added via a syringe. After addition of 0.075 ml of a 4.14 M ^{t}BuOOH solution in toluene (0.277 mmol) the colour changes from red to pale orange. The NMR tube is now flame-sealed and heated to 65 °C for 63 h. A colourless solution is obtained. The conversion can be determined via a ^{1}H-NMR spectrum.

3.7. *Crystal structure determinations*

The crystals were preselected in a glove box and immersed in fluorocarbon oil there. Individuals were then mounted on top of a fibre and quickly frozen to −70 °C. Centred reflections were refined by least-squares calculations to indicate the unit cells. Unit cell and collection parameters for the complexes are listed in Table 3. Diffraction data were collected in the appropriate hemispheres and under the conditions specified also in Table 3. The structures were solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculated idealised positions and refined isotropically. The listings of X-ray structural data for all complexes are available with the author on request.

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References

[1] (a) R.K. Grasselli, J.D. Burrington, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 394;
(b) J. Belgacem, J. Kress, J.A. Osborn, J. Mol. Catal. 86 (1994) 267;
(c) T. Ono, H. Numata, N. Ogata, J. Mol. Catal. 105 (1996) 3;
(d) M. Kinne, A. Heidenreich, K. Rademann, Angew. Chem. 110 (1998) 2637; Angew. Chem. Int. Ed. Engl. 37 (1998) 2509;
(e) A.B. Anderson, D.W. Ewing, Y. Kim, R.K. Grasselli, J.D. Burrington, J.F. Brazdil, J. Catal. 96 (1985) 222;
(f) G.W. Keulks, L.D. Krenzke, T.M. Notermann, Adv. Catal. 27 (1978) 183;
(g) R.K. Grasselli, J.D. Burrington, Adv. Catal. 30 (1981) 133.

[2] M. Hunger, C. Limberg, P. Kircher, Angew. Chem. 111 (1999) 1171; Angew. Chem. Int. Ed. Engl. 38 (1999) 1105.

[3] M. Hunger, C. Limberg, P. Kircher, Organometallics 19 (2000) 1044.

[4] (a) B.A. Vaartstra, W.E. Streib, K.G. Caulton, J. Am. Chem. Soc. 112 (1990) 8593;
(b) D.C. Bradley, H. Chudzynska, D.M. Frigo, M.E. Hammond, M.B. Hursthouse, M.A. Mazid, Polyhedron 9 (1990) 719;
(c) N.Y. Turova, V.G. Kessler, S.I. Kucheiko, Polyhedron 10 (1991) 2617;
(d) C. Limberg, S. Parson, A.J. Downs, D.J. Watkin, J. Chem. Soc. Dalton Trans. (1994) 1169.

[5] So far the oxidation states of the Mo centres in the known Mo/Bi alkoxides [2,3] do not exceed +IV.

[6] R.K. Multani, J. Nucl. Chem. 36 (1974) 1413.

[7] W. Uhl, M. Pohlmann, Chem. Commun. (1998) 451.

[8] W. Clegg, N.A. Compton, R.J. Errington, N.C. Norman, A.J. Tucker, M.J. Winter, J. Chem. Soc. Dalton. Trans (1988) 2941.

[9] W. Clegg, N.A. Compton, R.J. Errington, N.C. Norman, Polyhedron 7 (1988) 2239.

[10] (a) T. Groeer, M. Scheer, Organometallics 19 (2000) 3683;
(b) C.J. Carmalt, L.J. Louis, N.C. Norman, J. Chem. Soc. Dalton Trans. (1996) 455;
(c) W. Clegg, M.R.J. Elsegood, L.J. Farrugia, F.J. Lawlor, N.C. Norman, A.J. Scott, J. Chem. Soc. Dalton Trans. (1995) 2129;
(d) R.E. Bachman, K.H. Whitmire, Inorg. Chem. 34 (1995) 1542;
(e) R.J. Errington, G.A. Fisher, N.C. Norman, A.G. Orpen, S.E. Stratfort, Z. Anorg. Allg. Chem. 620 (1994) 457;
(f) A. Crispini, R.J. Errington, G.A. Fisher, F.J. Funke, N.C. Norman, A.G. Orpen, S.E. Stratfort, O. Struve, J. Chem. Soc. Dalton Trans. (1994) 1327;
(g) R.J. Errington, L.J. Farrugia, G.A. Fisher, Niklaus Anja, N.C. Norman, J. Chem. Soc. Dalton Trans. (1993) 1201;
(h) W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, D.C.R. Hockless, N.C. Norman, A.G. Orpen, S.E. Stratford, J. Chem. Soc. Dalton Trans. (1992) 3515;
(i) W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, D.C.R. Hockless, N.C. Norman, A.G. Orpen, S.E. Stratford, Polyhedron 10 (1991) 123;
(j) K. Merzweiler, L. Brands, Z. Naturforsch. B 47 (1992) 978;
(k) F. Calderazzo, A. Juris, R. Poli, F. Ungari, Inorg. Chem 31 (1992) 340;
(l) F. Calderazzo, A. Juris, R. Poli, F. Ungari, Inorg. Chem 30 (1991) 1274;
(m) W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, D.C.R. Hockless, N.A.L. Williams, S.E. Stratford, S.J. Stephen, J. Chem. Soc. Dalton Trans. (1992) 193;
(n) W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, N.C. Norman, T.B. Marder, J. Chem. Soc. Dalton Trans. (1991) 2887;
(o) W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, N.C. Norman, N. Wishart, J. Organomet. Chem. 399 (1990) C21;
(p) A.M. Caminade, M. Veith, V. Huch, W. Malisch, Organometallics 9 (1990) 1798;
(q) W. Clegg, N.A. Compton, R.J. Errington, N.C. Norman, J. Organomet. Chem. 335 (1987) C1;
(r) D. Greissinger, W. Malisch, H.-A. Kaul, J. Organomet. Chem. 252 (1983) C23;
(s) P. Panster, W. Malisch, J. Organomet. Chem. 134 (1977) C32.

[11] (a) Organomolybdenum Compounds Part 12, Gmelin Handbook of Inorganic and Organometallic Chemistry, 8th ed., Springer, Berlin, 1994;
(b) B.C. Bursten, M.G. Gatter, Organometallics 3 (1984) 895.

[12] A.J. Schultz, K.L. Stearley, J.M. Williams, R. Mink, G.D. Stucky, Inorg. Chem. 16 (1977) 3303.

[13] W. Frank, V. Reiland, G.J. Reiß, Angew. Chem. 110 (1998) 3154; Angew. Chem. Int. Ed. Engl. 37 (1998) 2984.

[14] C.M. Jones, M.D. Burkart, R.E. Bachman, D.L. Serra, S.J. Hwu, K.H. Whitmire, Inorg. Chem. 32 (1993) 5136.

[15] (a) A.R. Dias, M.L.H. Green, J. Chem. Soc. D (1969) 962;
(b) A.R. Dias, M.L.H. Green, J. Chem. Soc. A (1971) 2807;
(c) L. Lugo, G. Lanza, I.L. Fragala, C.L. Stern, T.J. Marks, J. Am. Chem. Soc 120 (1998) 3111.

[16] M. Massiani, R. Papiernik, L.G. Hubert-Pfalzgraf, J.C. Daran, Polyhedron 10 (1991) 437.