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(Dimethyl)dioxomolybdenum(VI) complexes: syntheses and catalytic applications

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Abstract

Reaction of $MoO_2Br_2S_2$ complexes [S=THF, CH_3CN] with bidentate nitrogen donor ligands (L_2) leads to complexes of the type $MoO_2Br_2L_2$ in good yields, L_2=substituted bipyridylphenantroline, 1,4-R_2-diazabutadiene and bipyrimidine. Treatment of the latter complexes with Grignard reagents at low temperatures yields complexes of the general formula $MoO_2(CH_3)_2L_2$ and $MoO_2(C_2H_5)_2$(diphenylphenantroline). ^{1}H NMR and IR data are comparatively indifferent to the ligand changes. The ^{95}Mo NMR data of selected complexes reflect the donor capability of the organic ligands. Mass spectroscopy and temperature-dependent ^{95}Mo NMR spectroscopy show a significant stability of the Mo–N bond. The compound $MoO_2(CH_3)_2$(bipyrimidine) was additionally examined by single crystal X-ray analysis.

The catalytic activity of the $MoO_2R_2L_2$ complexes in olefin epoxidation with *t*-butyl hydroperoxide as oxidizing agent is strongly influenced by the nature of the ligand L and its steric bulk in the equatorial plane. The title complexes with a $Mo(CH_3)_2$ moiety are slightly less active in catalysis than the $MoBr_2$ precursor compounds. Increase of both reaction time and/or temperature lead to a significant increase in the product yield in all examined cases. At about 90°C catalyst decomposition hampers further product yield increase.

Keywords: Catalysis; Molybdenum; Nitrogen ligands; Olefine epoxidation; Oxide complexes

1. Introduction

Organometallic derivatives of transition metal oxides have been established as important species in many catalytic transformations, the most important of which are oxidation catalysis and olefin metathesis. Due to the developments achieved in the last decade, CH_3ReO_3 (MTO) [1–3] became the most prominent example of the capabilities of this type of oxo-alkyl compounds. The synthetic difficulties responsible for the comparatively late appearance of high-oxidation state organometallic chemistry have certainly hampered the progress of this field. In fact, although molecules like $CpVCl_2O$ [4], $[CpMoO]_2(\mu\text{-}O)$ [5] and a number of related derivatives are known since about 40 years, some of the most important oxo-complexes known to date, including Cp^*ReO_3 and MTO, were first obtained serendipitously by inadverted air oxidation of low oxidation state complexes [1,6–8]. It was only after the rational synthesis of MTO was accomplished that this particular complex opened up

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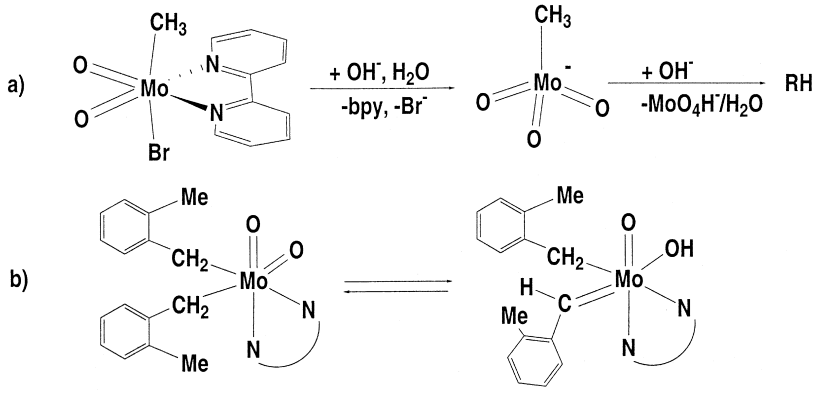
the way to a wealth of actual and potential catalytic applications [2].

Following the recognition of the importance of M-oxo-alkyl (M=Mo, W) complexes in olefin metathesis [9], and in contrast to the above mentioned serendipitous discoveries, the first examples of oxo-alkyls of molybdenum were prepared in a totally rational way by reaction of Grignard reagents with MoO_2Cl_2. Heyn and Hoffmann [10] first reported the synthesis of $MoO_2(Mesityl)_2$ some reactions of which were studied much later by Laï et al. [11]. This work was followed by that of the groups of Schrauzer, Arzoumanian and Teruel, who disclosed a variety of complexes of formula MoO_2R_2(bipy) (bipy=bipiridyl; R=Me, Et, Bu, CH_2Ph, etc.) [12–21] and some tungsten analogues [22,23]. Related studies by Kauffmann [24] on the alkylation of MoO_2Cl_2 and $MoOCl_4$ with lithium alkyls led to the formation of useful reagents for the in situ transformation of organic compounds, namely carbonyl containing functions. The high reactivity of these systems may be related to the absence of stabilizing ligands capable of playing the role of bipy in Schrauzer's complexes. This role, however, is not very well characterized and the chemistry of these Mo-oxo-alkyl complexes is hardly studied. The most important results reported concern the decomposition under basic conditions in aqueous solution to give $[RMoO_3]^-$ (not isolated) and the thermal decomposition of the benzyl derivative [19] both represented in Scheme 1.

In both cases, the bipy ligand is displaced from the Mo suggesting that the reactivity shown may be dependent on the stability of the Mo–bipy interaction. However, from a potentially large variety of $MoO_2R_2L_2$ complexes all known examples contain bipy or 4,4′-tBu$_2$bipy as the L_2 type ligand and only one mixed alkyl complex of type MoO_2RBr(bipy) was characterized. On the other hand, the poor solubility imparted by bipy to most of the MoO_2R_2(bipy) complexes has limited the number and scope of the spectroscopic studies on these complexes, namely those based on ^{95}Mo or ^{17}O NMR [21].

A few complexes of the related type Cp′MO_2R (M=Mo, W) have also been prepared and studied [25]. Trost and Bergman [26] reported on the epoxidation of olefins with alkylhydroperoxides catalyzed by Cp*MoO_2Cl. More recently, McCann and Beaumont [27] reported on the ring-olefin metathesis polymerization of norbornene catalyzed by MoO_2R_2(bipy) supported on montmorillonite K10.

In this context, and given our interest in the chemistry of organotransition metal oxides, we decided to prepare and study a number of dialkyl complexes of general formula $MoO_2R_2L_2$ where L_2 represents a variety of bidentate ligands of the type 1,4-diiminobutane (R-DAB), with different R groups, e.g. cyclohexyl, *p*-tolyl. Besides providing access to more soluble complexes which are better amenable to reactivity and spectroscopic characterization than the modestly soluble MoO_2R_2(bipy) derivatives, the different stereochemical and electronic characteristics of these ligands should impart distinct reactivities to the MoO_2R_2 core and provide access to a wider reactivity range, namely in oxidation reactions. In a recent study, we have shown that the activity in the epoxidation of cyclooctene with *t*-butylhydroperoxide



Scheme 1.

catalyzed by similar $MoO_2X_2L_2$ complexes is dependent both on the nature of X (Cl, Br) and L_2 (including R-DAB derivatives) [28–32].

In the present paper, we report the synthesis of several $MoO_2R_2L_2$ complexes, (R=CH_3, C_2H_5; L_2=R-DAB, etc.) and an examination of their catalytic activity in the epoxidation of cyclooctene with *t*-butylhydroperoxide, a field where the closely related alkylrhenium oxides have been so successful.

2. Results and discussion

2.1. Synthesis and spectroscopic studies

Eq. (1) shows the general synthesis of complexes $MoO_2R_2L_2$ from their parent bromides, $MoO_2Br_2L_2$ and Grignard reagents.

The bromides are readily prepared from $MoO_2Br_2S_2$ (S=THF, CH_3CN) and the corresponding L_2 ligand as described previously for all compounds **1a–11a** and in the experimental part for the newly prepared species **3a**, **5a**, **6a**, and **7a** (see Chart 1) [32]. In practise, the dibromides do not need to be isolated prior to Grignard reagent addition, and in some cases, this isolation has deleterious effects on the overall yield of the final Mo-dialkyl. Therefore, the whole process consists of dissolving $MoO_2Br_2(NCCH_3)_2$ in THF, treating it with the diimine ligand and react the in situ formed complex with the required amount of RMgCl at a temperature ranging between −40°C and −20°C. After warming to room temperature, the resulting solution is evaporated to dryness and the residue is treated with water under aerobic conditions. The resulting solution is extracted with dichloromethane in a separating funnel. The dichloromethane phase

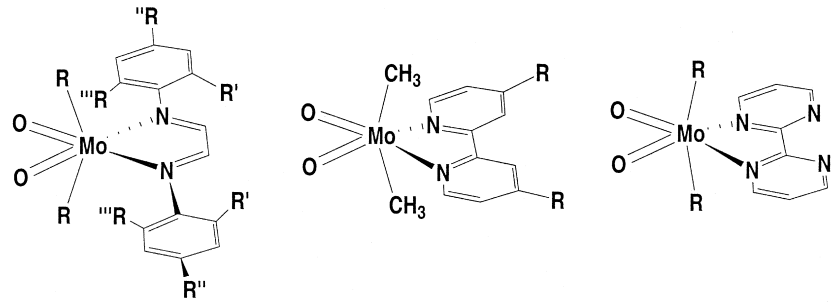
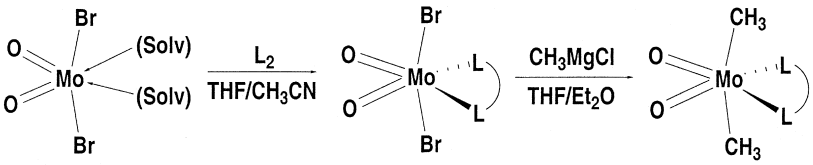


Chart 1.

is dried and the residue recrystallized to give the novel alkyl complexes $MoO_2R_2L_2$ (**1**–**11**, see Chart 1) in moderate to good yields. With the exception of the ethyl derivative **8**, all other examples are methyl derivatives. The organometallic complexes are in general more soluble than the corresponding dibromide precursors and do not precipitate from the reaction mixtures. The reaction is nearly quantitative with respect to the starting material, $MoO_2Br_2S_2$.

In contrast to our experience with the synthesis of the prototype MoO_2Me_2(bipy) reported in the literature [13] the syntheses are reproducible. However, a fast work-up and a minimum amount of water are necessary conditions for a successful preparation. The need for the aerobic work-up seems essential for obtaining good yields.

The complexes **1**–**11** can be handled in air for brief periods of time. Obviously, the chelating dimeric ligands stabilize the otherwise extremely reactive $MoO_2(CH_3)_2$ [24] moiety to a very significant extent, in the same way as they stabilize MoO_2X_2 [28].



(1)

The characterization of the new halide complexes **3a**, **5a**, **6a**, and **7a** is straightforward and follows the same general lines described for many other similar derivatives, of the type $MoO_2Br_2L_2$ [28]. In compound **5a**, three instead of two ligand resonances can be observed by ^{1}H NMR due to the different chemical environment of the formerly equivalent protons of the free ligand. The signal sets do not change their appearance significantly by heating or cooling the solution, thus showing a kinetically stable ligand–Mo interaction.

The ^{1}H NMR spectra of the dialkyl complexes (**1**–**11**) show only small variations between the chemical shifts of the free and bonded ligands. The chemical shift of the Mo-bonded CH_3 substituents varies between ca. 0.4 and 0.9 ppm in agreement with the values reported in the literature [12–21]. Variable temperature ^{1}H NMR spectra remain invariant for all complexes tried, namely the complexes with the DAB substituents. The ^{95}Mo NMR spectra display their resonances in the region between ca. 420 and 520 ppm which is at lower field relative to both their bromo and chloro analogues (ca. 180 and 280 ppm) as well as $MoO_2Br_2(NCCH_3)_2$ ($\delta(^{95}Mo)$= 278 ppm).

These data show an inverse dependence of the chemical shift of the ^{95}Mo NMR spectra with the electronegativity of the R and X ligands since the signals of the bromo complexes (3a, 5a, 7a, 11a) are observed at higher field than those of the methyl derivatives **1**–**11** (Table 1, see also Ref. [33]). The $\delta(^{95}Mo)$ chemical shift difference between the CH_3 and the Br complexes is ca. 150–250 ppm. This kind of inverse dependence of the $\delta(^{95}Mo)$ chemical shift with the electronegativity of the ancillary ligands has been reported before for Mo(VI) complexes [32,33]. The ^{95}Mo NMR signals of the methyl complexes with the N-heterocyclic aromatic ligands, bipy (**4**) bipym, (**5**) and phen (**7**) are shifted to higher field

Table 1
^{95}Mo NMR shifts of MoR_2O_2L complexes (R=CH_3, Br)

Compound	$\delta(^{95}Mo)$ [ppm]	$\Delta\nu_{1/2}$ [Hz]
1	526	200
2	471	170
3a	291	110
4	432	170
5a	238	500
5	425	210
6	447	150
7	436	210
7a	177	110
8	370	200
9	469	130
11a	277	110
11	520	320

($\delta(^{95}Mo)$=ca. 420–450 ppm) relative to those of the complexes with substituted diimino-butane (R-DAB) ligands (1, 2, 9, 11) ($\delta(^{95}Mo)$=ca. 470–530 ppm). The main difference in the electronic characteristics of these two groups of diimine ligands is the higher π-acceptor capability of the R-DAB ligands over the bipy type ligands [34,35].

The IR data also support the view that all the complexes described in this work display a distorted octahedral C_{2v}-geometry (see X-ray section) with the oxygen atoms in *trans* position to the organic N-donor ligands in the equatorial plane and the methyl groups (or bromo atoms, resp.) in *trans* position to each other in the apical positions.

The mass spectra provide further evidence supporting the existence of comparatively strong Mo–N interactions. In contrast to the above mentioned $(CH_3)ReO_3L$ (L=Lewis base) the $MoO_2(CH_3)_2L_2$ complexes do not break-up readily in $MoO_2(CH_3)_2$ and L_2 fragments under CI-MS conditions. The fragmentation process is more complicated. This is in good agreement with the invariance of the VT ^1H NMR measurements mentioned above. In contrast, the RRe(VII)O_3 complexes, which also have been applied successfully as oxidation catalysts, undergo temperature-dependent ligand exchange processes [36–38].

2.2. X-ray crystallography

Compound **5** was further characterized by single crystal X-ray crystallography. Details of the X-ray experiment are given in Table 2. Key bond distances and angles are listed in Table 3. The bipyrimidine complex **5** (Fig. 1) is monomeric and belongs to the general family of compounds with a $TrX_2O_2N_2$ core geometry (Tr=transition metal) and is in accord with the IR and NMR results.

The Mo atom is off center and shifted away from the nitrogen atoms bisecting the oxygens. All observed distances and angles around the metal center are within or close to the known range for Mo=O double bonds (168.1–174.0 pm [13,39]), Mo–N distances, (226.5–235.3 pm [13,40]), Mo–C single bonds (218.9–225.6 pm [12,14]), and the angles O–Mo–O angles (108.2–113.1° [17,39]), N–Mo–N (68.4–70.0° [16,17]), C–Mo–C (145.5–155.8° [15,16]).

Table 2
Crystallographic data for $MoO_2(CH_3)_2(C_8H_6N_4)$ (**5**)

Chemical formula	$C_{10}H_{12}MoN_4O_2$
fw	316.17
Color/shape	colorless/fragment
Crystal size (mm)	0.60×0.54×0.24
Crystal system	orthorhombic
Space group	P bca
a (pm)	1638.7(1)
b (pm)	1202.2(1)
c (pm)	1186.8(1)
$\alpha=\beta=\gamma$ (°)	90
V (10^6 pm^3)	2338.0(3)
Z	8
T (K)	193
ρ_{calcd} (g cm^{-3})	1.796
μ (mm^{-1})	1.117
F_{000}	1264
λ (pm)	71.073
Scan method	ω-scan
Θ-Range (°)	2.49 to 26.29
Data collected (*h*,*k*,*l*)	+20, +14, +14
No. of reflections collected	2612
No. of independent reflections	2285
No. of observed reflections	2285 (all data)
No. of parameters refined	202
R_{int}	–
$R1$[a]	0.0357
$wR2$[b]	0.0859
GOF[c]	1.025
Weights *a*/*b*[d]	0.0665/0.7870
$\Delta\rho_{max/min}$ (e Å^{-3})	+0.74, −0.92

[a] $R1=\sum(\|F_0|-|F_c\|)/\sum|F_0|$.
[b] $wR2=[\sum w(F_0{}^2-F_c{}^2)^2/\sum w(F_0{}^2)^2]^{1/2}$.
[c] $GOF=[\sum w(F_0{}^2-F_c{}^2)^2/(NO-NV)]^{1/2}$.
[d] $w=1/[\sigma^2(F_0{}^2)+(a*P)2+b*P]$ with P: [max(0 or $F_0{}^2$)+ $2F_c{}^2$]/3.

2.3. $MoO_2(CH_3)_2L_2$ complexes in olefin epoxidation catalysis

For comparison purposes with the parent $MoO_2X_2L_2$ complexes [28,32], the catalytic oxidation of cyclooctene with *t*-butylhydroperoxide is chosen. The *t*-butylhydroperoxide is used as a 5.5-M solution in decane. After its addition, homogeneous conditions are obtained. The applied temperature was 55°C. Further details are given in the experimental part. Fig. 2 displays an overview of the catalytic performance of the complexes examined. In general, the overall yield after 4 h is relatively low (between 5% and 60%). However, during 24 h reaction time, the yield increases and in some cases (complexes **2**, **4**) rises above 90%

Table 3
Selected interatomic distances (pm) and angles (°) for $MoO_2(CH_3)_2(C_8H_6N_4)$ (**5**)

Mo–C1	218.7(3)
Mo–C2	219.0(2)
Mo–O1	169.9(2)
Mo–O2	171.7(2)
Mo–N12	236.4(2)
Mo–N22	233.6(2)
C11–C21	148.5(3)
C1–Mo–C2	148.00(12)
C1–Mo–O1	101.33(10)
C1–Mo–O2	97.84(9)
C1–Mo–N12	79.75(9)
C1–Mo–N22	74.25(9)
C2–Mo–O1	99.47(10)
C2–Mo–O2	97.43(9)
C2–Mo–N12	76.89(9)
C2–Mo–N22	76.72(10)
O1–Mo–O2	110.26(9)
O1–Mo–N12	88.13(9)
O1–Mo–N22	155.52(9)
O2–Mo–N12	161.51(8)
O2–Mo–N22	94.23(8)
N12–Mo–N22	67.41(7)

showing that the stability of the catalyst under the reaction conditions is much higher than that observed for the related labile $MoO_2X_2(NCCH_3)_2$ [32].

2.4. Influence of the temperature

The influence of the temperature on the yield is depicted in Fig. 3 using the complexes **2**, **5**, and **9** as

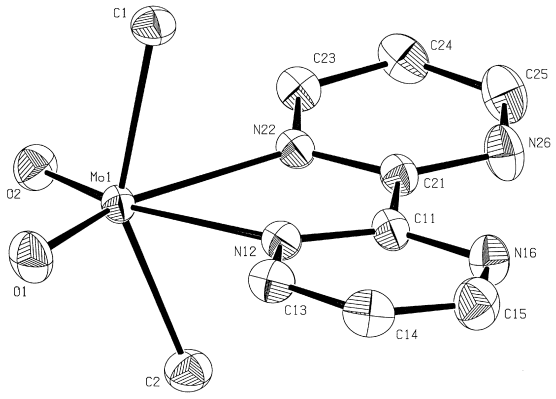


Fig. 1. ORTEP drawing of the molecular structure of $MoO_2(CH_3)_2(C_8H_6N_4)$ (**5**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

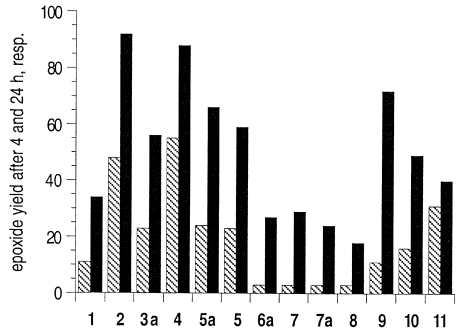


Fig. 2. Yield of cyclooctene epoxide in the presence of selected compounds as catalysts after 4 h reaction time. See text and experimental section for reaction details.

examples. At 20°C, the product yield is very low in all cases (<10%). Catalytic runs at higher temperatures (55°C and 70°C) lead to significant growth of the product yield. A further increase from 70°C to 90°C does not lead to a further significant increase of the yield. In the case of compound **5**, the yield is exactly the same, in the case of complex **2**, the yield is even lower at 90°C. It is likely that at this temperature, a partial thermal decomposition of the catalysts takes place, reducing the amount of active species present in the reaction mixture. In fact, reacting the catalyst precursors with *t*-BuOOH at 90°C produces a considerable amount of CH_4 after 4 h, whereas at 55°C, only traces of CH_4 are formed (see below). Further evidence for the stability of the catalysts below 90°C arises from the fact that they can be used for a second catalytic run, with a new charge of substrate, leading to the same product yields within the experimental error range in most cases.

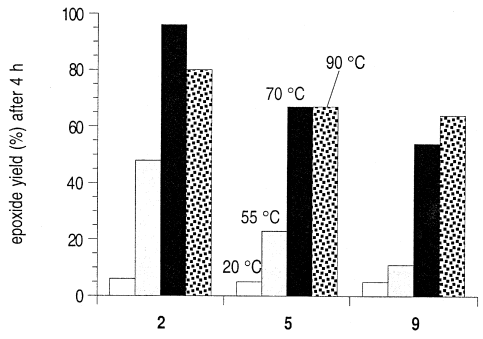


Fig. 3. Temperature dependence of the catalytic activity of selected $MoO_2(CH_3)_2L_2$ complexes.

2.5. Influence of the ligands X and L

The particular characteristics of the ancillary ligands X and L in the $MoO_2X_2L_2$ (X=Br, CH_3; L_2=diimine) complexes have a considerable influence on the product yield as can be seen in Fig. 2. In the first place, a comparison between the yields obtained for the bromo complexes **5a** and **7a** reveals that they are more active than their methyl analogues **5** and **7**. This trend means that the more electronegative substituents accelerate the epoxidation reaction. We have previously reported the epoxidation of cyclooctene with *t*-BuOOH catalyzed by chloro and bromo complexes $MoO_2X_2L_2$ (X=Br, Cl; L_2=R diimine) where the activity increases in the order Br<Cl [28] taking the complexes MoO_2X_2(*o*-phenyl-DAB) as an example (X=Cl, Br, CH_3) the yield of cyclooctene epoxide under the standard conditions decreases in the order Cl (89%)>Br (73%)>CH_3 (35%). Considering that the halides are more labile than the methyl substituent, they may create more coordinatively unsaturated intermediates responsible for the increase in activity. However, the higher reactivity of the less labile chloride in comparison to the bromide does not indicate this being the decisive factor. Anyway, we did not find any indication for a breaking of the Mo–X bond during the course of the catalysis [28,32]. The complexes containing the phenanthroline ligand (6a, 7, 7a, 8) display the lowest catalytic activity independently of the nature of X. On the contrary, considering only the methyl and ethyl complexes, the highest activities are observed for the compounds bearing *p*-MePhN=CHCH=NPh-Me-p (**2**) 4,4′-*t*Bu_2bipy (**4**) and CyN=CHCH=NCy (**9**) ligands in the order **2** > **4** > **9**. The other ligands produce intermediate yields between ca 35% for **1** and ca 60% for **5**. As mentioned above, the R-DAB type ligands are better π-acceptors than 2,2′-bipyridine and, of course, than 4,4′-*t*Bu_2bipy. The intermediate reactivity of **4** between **2** and **9** shows that the π-accepting capabilities do not play a significant role in this chemistry where the Mo is in a high oxidation state. However, the lower reactivity of **10** compared to **9** is compatible with the idea that the electronic deficiency at the metal favors the epoxidation reaction. In fact, it has been shown that the C-alkylated diazabutadiene ligands R-DAB ligands are substantially less electron attracting than their unsubstituted counterparts, R-DAB [34]. Steric effects might be responsible for the pronounced lowering of the activity of **1** relative to **2** and of **11** relative to **9**. On the other hand, the low activity of the phenanthroline (phen) derivatives suggests that the flexibility of the coordination sphere plays a very important role in the reaction. Indeed, the only pronounced difference between phen and all the other ligands used is the rigidity of the former. If at some stage of the reaction partial dissociation of one N–Mo bond is involved, phen will strongly disfavor this step comparatively to all other ligands under consideration (Chart 1). In all other cases, rotation along the C–C bond connecting the imines will assist such partial dissociation and/or coordination rearrangement around the Mo(VI) centre.

2.6. Catalyst stability

All catalytic reactions show the same time-dependent curve. A typical curve is presented in Fig. 4. After a quick increase of the yield within the first hour, the reaction velocity slows somewhat down. At lower temperatures (our standard temperature was 55°C) the initial increase is somewhat slower, at higher temperatures it is quicker. The appearance of these curves gives no indication for the transformation of the original catalyst in another species during the reaction time, e.g. by loss of the ligands R or L_2. The formation of the active catalyst therefore must occur very quickly and take place at the very beginning of the reaction, immediately after the addition of the peroxide.

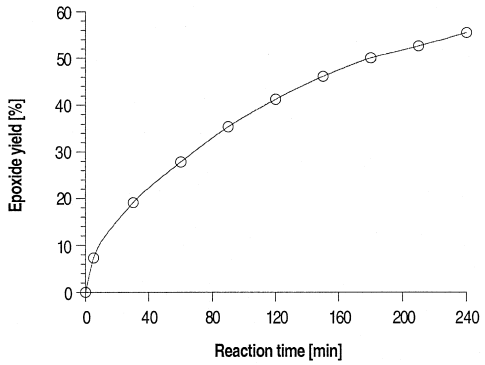


Fig. 4. Time dependence of the conversion of cyclooctene to cyclooctene epoxide with *t*-butylhydroperoxid in the presence of compound **3** as the catalyst.

The liberation of methane, ethane as well as the formation of methanol after the addition of the peroxide were monitored by gas phase GC and GC-MS examinations at the standard temperature of our catalytic studies (55°C). Four complexes, namely **1**, **4**, **7**, and **9** were chosen as examples. Compound **9** provided the only case where methane formation was above the experimental error (12% after 4 h, 14% after 24 h; the % values refer to the possible-CH_3 loss, both CH_3-groups per molecule would be 100%). In all other cases significantly less then 1% methane evolved within 24 h. Ethane and methanol were only formed in insignificant amounts in all examined cases.

The chemical stability of the Mo–CH_3 bonds in the presence of peroxides and alcohols (the byproducts in catalysis, e.g. *t*-butanol with *t*-butylhydroperoxide) was also tested using complex **4** as an example. Addition of excess *t*-butanol, H_2O_2, or acetic acid, does not change the ^{1}H and ^{95}Mo chemical shifts of complex **4** at 55°C, indicating that no reaction is taking place to any detectable extent. On the other hand, addition of excess *t*-BuOOH to **4** shifts the signal from$\delta(^{95}\text{Mo})$=432 ppm to $\delta(^{95}\text{Mo})$=442 ppm and the Mo–CH_3 resonance from $\delta(^1\text{H})$=0.55 ppm to $\delta(^1\text{H})$=0.88 ppm. This clearly indicates that there is an interaction between *t*-BuOOH and **4** but that the Mo–CH_3 bond remains.

2.7. Influence of the peroxides and substrates

In order to establish the influence of the nature of the peroxide on the catalytic epoxidation of cyclooctene, we compared *t*-butylhydroperoxide with three other peroxides using compound **4** as catalyst under the standard reaction conditions (55°C; see above and experimental part). With H_2O_2 and Ph_3COOH no significant product formation was observed. With *t*-BuOOH 55% cyclooctene epoxide was formed within 4 h, with *m*-ClPhC(O)OOH, the product yield reached 75% after 4 h. The latter peracid, however, is so reactive itself that a comparable product yield is reached even without the presence of a Mo(VI) catalyst.

The role of the olefin in the reaction was studied using the compounds **1**, **3**, **4**, and **9** in the epoxidation of cyclohexene and styrene. The results are summarized in Fig. 5. The best yield is reached in all cases with cyclohexene as substrate, the yields with styrene, which is not so easy to oxidize and more sensitive to diol formation, are considerably lower. While in the case of cyclooctene, the product yields vary significantly, they are more uniform in the case of the generally very reactive cyclohexene and of styrene as substrates. The latter substrate is usually very sensitive to diol formation and significantly less reactive to the epoxide.

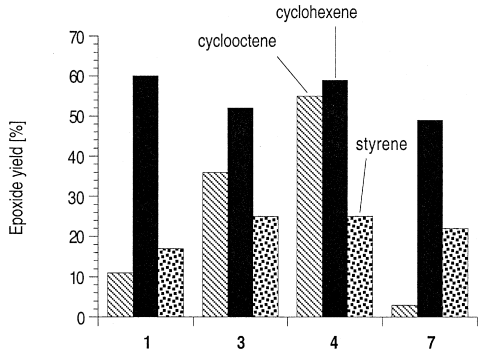


Fig. 5. Product yield after 4 h reaction time with selected $MoO_2(CH_3)_2L_2$ compounds as catalysts with cyclohexane, cyclooctane, and styrene, resp., as substrates.

3. Conclusions

The organometallic oxo-Molybdenum derivatives, $MoO_2(CH_3)_2L_2$ with diimine ligands are able to catalyze the olefin epoxidation reaction with *t*BuOOH but not with H_2O_2. The soluble homogeneous catalysts operate best at ca. 55–70°C under which conditions they are stable and only marginal Mo–CH_3 bond breaking seems to take place. In this regard, they obviously resemble the very resistant CH_3ReO_3 epoxidation catalyst precursor and highlight the catalytic potential of organometallic oxide compounds of which, to our knowledge, they are only the third example after CH_3ReO_3 and Cp*MoO_2Cl. The ancillary diimine ligands have a direct influence on the reaction yields. The combined stereochemical influence of the L_2 and the R ligands may open interesting possibilities for the stereochemical control of the reaction. Work to clearify the mechanism of the oxidation with the $MoO_2(CH_3)_2L_2$/*t*BuOOH system, including theoretical calculations and the attempted synthesis of possible methyl-oxo-peroxo or *t*-butylhydroperoxo intermediates, is currently under way in our laboratories.

4. Experimental

All preparations and manipulations were performed with standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone ketyl; CH_2Cl_2 and CH_3CN over CaH_2), distilled under argon and kept over 4 Å molecular sieves (3 Å for CH_3CN).

Microanalyses were performed at the ITQB and in the Mikroanalytisches Laboratorium der TU München (M. Barth). Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer, isobuten was used as a CI-gas.

NMR spectra were measured on a Bruker CXP 300 and Bruker Avance DPX-400. ^{1}H NMR spectra were recorded at 300 or 400 MHz, resp., ^{95}Mo NMR spectra at 26.07 MHz. The IR spectra were measured on a Unican Mattson Mod 7000 FTIR spectrometer. *o*-Tolyl-DAB [41], 2,6-Me-phenyl-DAB [42], MoO_2Br_2 [41], MoO_2Cl_2 [41] $MoO_2Br_2(NCMe)_2$ [32,42], $MoO_2X_2L_2$ (L=*p*-tolyl-DAB, *t*Bu-Bipy, CYDAB, Me-CYDAB, *t*Bu-DAB, X=Br or Cl) [28] H_2Biim [43], MoO_2Br_2(bipyrimidine) (**5a**) [32], were prepared as published or with minor changes. $MoO_2X_2\cdot 2$(THF) and $MoO_2X_2\cdot 2(CH_3CN)$ were prepared as described in Ref. [33].

4.1. Preparation of $MoO_2(CH_3)_2$(*o*-tolyl-DAB) (**1**)

A solution of $MoO_2Br_2(NCCH_3)_2$ (0.80 g, 2.16 mmol) in THF (15 ml), was treated with *o*-tolyl-DAB (0.51 g, 2.16 mmol). The colour of the solution changed immediately to yellow and the reaction was stirred for further 30 min. To this solution at −20°C isopropanol bath, 2.1 equivalents of CH_3MgBr, were slowly added. The reaction was allowed to warm-up to room temperature and was stirred for 2 h. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness in a rotative evaporator and the residue was recrystallised from CH_2Cl_2/Et_2O/hexane. Yield, 82%. Anal. Calcd for $C_{18}H_{22}MoO_2N_2$ (394.33): C, 54.83; H, 5.62; N, 7.10. Found: C, 54.73; H, 5.48; N, 6.96. IR (KBr, ν cm^{-1}): 3028 m, 2965 m, 2915 m, 1626 s, 1588 s, 1505 vs, 1458 s, 1400 m, 1248 m, 1043 m, 939, 907, vs., ν(Mo=O), 748 s, 713 m, 662 m, 613 m, 542 m. CI-MS (98Mo), [*m*/*z*, rel. int.%]: 266 ([M+–C_9H_8N], 5), 235 ([L–H]+, 38), 221 ([L–CH_3]+, 51), 132 ([$C_9H_{11}N$]+, 60), 118 ([L/2]+, 53), 107 ([C_7H_9N]+, 100). ^{1}H NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 8.24 (s, 2H), 7.90 (d, 2H), 7.47 (d, 2H), 7.07 (m, 2H), 6.70 (m, 2H), 2.22 (s, 6H), 0.86 (s, 6H).

4.2. Preparation of $MoO_2(CH_3)_2$(*p*-tolyl-DAB) (**2**)

To a suspension of MoO_2X_2(*p*-tolyl-DAB) (X=Cl, Br), in diethyl ether or THF at −20°C (isopropanol bath), 2.1 equivalents of CH_3MgX, (X=Cl, Br), were slowly added. The reaction was allowed to warm up to room temperature and was stirred for 90 min. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness in a rotative evaporator and the residue was recrystallised from CH_2Cl_2/*n*-hexane. Yield, 60%. Anal. Calc. for $C_{18}H_{22}N_2O_2Mo$ (394.33): C 54.84; H 5.62; N 7.10. Found: C 54.89; H 5.69; N 6.61. IR (KBr, ν cm^{-1}): 3023 m, 2910 m, 1505 vs, 1375 m, 1221 m, 1111 m, 936, 905, vs, ν(Mo=O), 853 m, 818 s. CI-MS (98Mo), [*m*/*z*, rel. int. %]: 396 ([M]+, 14), 382 ([M–CH_2]+, 31), 368 ([M–C_2H_4]+, 8), 152 ([$MoN_2C_2H_2$]+, 25), 135 ([MoC_3H]+, 41), 106 ([C_8H_{10}]+, 100). ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., δ ppm): 8.28 (s, 2H), 7.53 (d, 4H), 7.00 (d, 4H), 2.42 (s, 6H), 0.87 (s, 6H).

4.3. Preparation of $MoO_2(CH_3)_2$(2,6-Me-phenyl-DAB) (**3**)

A solution of $MoO_2Br_2(NCCH_3)_2$ (1.00 g, 2.70 mmol) in THF (15 ml), was treated with 2,6-Me-phenyl-DAB (0.70 g, 2.70 mmol). The colour of the solution changed immediately to yellow and the reaction was stirred for further 30 min. To this solution at −40°C (isopropanol bath), 2.1 equivalents of CH_3MgBr, were slowly added. The reaction was allowed to warm-up to room temperature and was stirred for 3 h. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was

taken to dryness and the residue was recrystallised from CH_2Cl_2/pentane. Yield, 60%. Anal. Calcd for $C_{20}H_{26}MoO_2N_2$ (422.38): C, 56.87; H, 6.20; N, 6.63. Found: C, 57.01; H, 6.18; N, 6.74. IR (KBr, ν cm^{-1}): 3021 m, 2955 m, 2918 m, 1618 vs, 1593 vs, 1474 s, 1443 m, 1375 m, 1186 s, 1094 m, 962 m, 945 s, 912, vs, ν(Mo=O), 820 m, 760 s, 677 m, 515 m. ^{1}H NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 8.05 (s, 2H), 7.49 (b, 4H), 7.13 (b, 2H), 2.68 (s, 6H), 2.23 (s, 6H), 0.87 (s, 6H).

4.4. Preparation of MoO_2Br_2(2,6-Me-phenyl-DAB) (**3*a***)

A solution of $MoO_2Br_2(NCCH_3)_2$ (0.30 g, 0.81 mmol) in THF (10 ml), was treated with 2,6-Me-phenyl-DAB (0.21 g, 0.81 mmol). The colour of the solution changed immediately to yellow and the reaction was stirred for further 1 h. After concentration to ca. 3 ml, an orange solid was precipitated by addition of diethyl ether. The product was washed with diethyl eher and dried under vacuum. Yield, 95%. Anal. Calcd for $C_{18}H_{20}MoBr_2O_2N_2$ (552.12): C, 39.16; H, 5.65; N, 5.07. Found: C, 38.98; H, 5.76; N, 4.97. IR (KBr, ν cm^{-1}): 3144 m, 2976 m, 2876 m, 1499 s, 1474 vs, 1261 m, 1223 m, 1168 m, 1094 m, 1031 m, 955 s, 916 vs, 912, vs, ν(Mo=O), 864 m, 775 s, 567 m. CI-MS (98Mo, 79Br), [*m*/*z*, %]: 393 ([M–2Br]+, 3), 312([M–2Br–C_6H_{10}]+, 4), 288 ([MoO_2Br_2]+, 8), 209 ([MoO_2Br]+, 5), 149 ([$C_{10}NH_{15}$]+, 41), 120 ([C_9H_{12}]+, 100), 106 ([C_6H_{10}]+, 82). ^{1}H NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 8.17 (s, 2H), 7.45 (b, 4H), 7.12 (b, 2H), 2.66 (s, 6H), 2,20 (s, 6H).

4.5. Preparation of $MoO_2(CH_3)_2$(*t*BuBipy) (**4**)

To a suspension of MoO_2X_2(*t*BuBipy) (X=Cl, Br), in diethyl ether at −20°C (isopropanol bath), 2.1 equivalents of CH_3MgCl were slowly added. The reaction was alowed to warm-up to room temperature and was stirred for 90 min. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness and the yellow residue was recrystallised from CH_2Cl_2/diethyl ether. Yield, 60%. Anal. Calc. for $C_{20}H_{30}N_2O_2Mo$ (426.41): C 56.34; H 7.09; N 6.57. Found: C 56.06; H 7.14; N 6.54. IR (KBr, ν cm^{-1}): 3044 m, 2963 vs, 2905 vs, 2868 s, 1611 vs, 1547 s, 1479 s, 1408 vs, 1368 s, 1302 m, 1252 s, 1202 m, 1140 m, 1017 m, 928, 903, vs, ν(Mo=O), 887 vs, 868 vs, 849 vs, 750 s, 608 s. CI-MS (98Mo), [*m*/*z*, %]: 299 ([M–2*t*Bu–CH_3]+, 3), 268 ([L]+, 34), 253 ([L–CH_3]+, 100), 237 ([L–CH_3–CH_4]+, 12), 223 ([L–3×CH_3]+, 5), 237([L–C_4H_8]+, 18). ^{1}H NMR ($CDCl_3$, 300 MHz, r.t., δ ppm): 9.41 (d, 2H), 8.14 (d, 22H), 7.49 (dd, 2H), 1.44 (s, 18H), 0.55 (s, 6H).

4.6. Preparation of $MoO_2(CH_3)_2$(bipyrimidine) (**5**)

A solution of $MoO_2Br_2(NCCH_3)_2$ (1.17 g, 3.16 mmol) in THF (30 ml), was treated with bipyrimidine (0.50 g, 3.16 mmol) and the reaction was vigorously stirred for 1 h. The resulting yellow mixture was cooled in a isopropanol bath (−20°C), 2.1 equivalents of CH_3MgBr, were slowly added. The reaction was allowed to warm-up to room temperature and was stirred for 4 h. The orange suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane/chloroform and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness and the residue was recrystallised from CH_2Cl_2/diethyl ether. Yield, 80%. Anal. Calcd for $C_{10}H_{12}MoO_2N_4$ (316.17): C, 37.99; H, 3.83; N, 17.72. Found: C, 38.12; H, 3.95; N, 17.64. IR (KBr, ν cm^{-1}): 3073 m, 2972 m, 2905 m, 1572 vs, 1551 vs, 1443 m, 1402 vs, 1151 m, 1141 m, 1010 m, 936, 901, vs, ν(Mo=O), 820 s, 809 s, 758 m, 685 m, 654 s. CI-MS (98Mo), [*m*/*z*, %]: 288 ([M–2CH_3]+, 5), 160 ([M–L]+, 25), 158 ([L]+, 100), 145 ([M–CH_3–L]+, 3). ^{1}H NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 9.68 (d, 2H), 9.23 (d, 2H), 7.70 (dd, 2H), 0.56 (s, 6H).

4.7. Preparation of $MoO_2(CH_3)_2$(phen) (**6**)

To a suspension of $MoO_2(Br)_2$(phen) (0.74 g, 1.58 mmol), in THF at −20°C (isopropanol bath), 2.1 equivalents of CH_3MgBr were slowly added. The reaction was allowed to warm-up to room temperature and was stirred for 3 h. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness and the red residue was recrystallised from CH_2Cl_2/diethyl ether. Yield, 90%.

Anal. Calc. for $C_{14}H_{14}N_2O_2Mo$ (338.22): C 49.72; H 4.17; N 8.28. Found: C 49.87; H 4.15; N 8.12. IR (KBr, ν cm^{-1}): 3050 m, 2965 m, 2901 m, 1510 s, 1422 vs, 1343 m, 1140 m, 1096 m, 957, 930, 914 vs, ν(Mo=O), 891 s, 845 vs, 731 s, 625 m. ^{1}H NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 9.04 (d, 2H), 8.19 (d, 2H), 7.73 (s, 2H), 7.55 (q, 2H), 0.43 (s, 6H).

4.8. Preparation of MoO_2Br_2(phen) (**6*a***)

A solution of $MoO_2Br_2(NCCH_3)_2$ (0.38 g, 1.00 mmol) in THF (10 ml) was treated with phenanthroline (0.18 g, 1.00 mmol). The colour of the solution changed to yellow and a precipitate was formed. After 1 h, the suspension was brought to dryness to yield a powder which was washed with diethyl ether. Yield, 98%. ^{1}H NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 9.74 (d, 2H), 8.63 (d, 2H), 8.06 (s, 2H), 8.00 (q, 2H). EA and IR are in agreement with Ref. [44].

4.9. Preparation of $MoO_2(CH_3)_2$(4,7-diphenyl-1,10-phen) (**7**)

To a suspension of MoO_2Br_2(4,7-diphenyl-1,10-phen) (0.80 g, 1.29 mmol), in THF at -20°C (isopropanol bath), 2.1 equivalents of CH_3MgBr were slowly added. The reaction was allowed to warm-up to room temperature and was stirred for 4 h. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness and the red residue was recrystallised from CH_2Cl_2/diethyl ether. Yield, 92%. Anal. Calc. for $C_{26}H_{22}N_2O_2Mo$ (490.42): C 63.68; H 4.52; N 5.71. Found: C 63.62; H 4.58; N 5.76. IR (KBr, ν cm^{-1}): 3061 m, 3032 m, 2951 m, 1597 s, 1557 s, 1518 vs, 1493 s, 1421 s, 1395 m, 1233 s, 1094 m, 1018 m, 955, 932, 912 vs, ν(Mo=O), 891 s, 851 vs, 766 vs, 739 vs, 702 vs, 667 s, 633 m, 575 m, 548 m. ^{1}H NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 9.80 (d, 2H), 8.04 (s, 2H), 7.62 (d, 2H), 7.50 (m, 10H), 0.43 (s, 6H).

4.10. Preparation of MoO_2Br_2(4,7-diphenyl-1,10-phen) (**7*a***)

A solution of $MoO_2Br_2(NCCH_3)_2$ (1.50 g, 4.05 mmol) in THF (30 ml) was treated with 4,7-diphenyl-1,10-phen (1.35 g, 4.05 mmol). The colour of the solution changed immediately to orange and the reaction was stirred for further 60 min. After concentration to ca. 4 ml and addition of ether, the solid was filtered off and the powder was washed with ether and dried in an oil vacuum pump. Yield, 98%. Anal. Calcd for $C_{24}H_{16}MoBr_2O_2N_2$ (620.16): C, 46.48; H, 2.60; N, 4.52. Found: C, 46.55; H, 2.47; N, 4.39. IR (KBr, ν cm^{-1}): 3123 m, 3059 m, 1599 vs, 1555 vs, 1518 s, 1493 s, 1445 m, 1427 vs, 1396 vs, 1235 vs, 1018 m, 936, 914, vs, ν(Mo=O), 899 s, 849 s, 810 m, 764 vs, 737 vs, 700 vs, 667 s, 633 s, 573 s, 544 s. ^{1}H NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 9.81 (d, 2H), 8.13 (s, 2H), 7.94 (d, 2H), 7.53 (m, 10H).

4.11. Preparation of $MoO_2(CH_2CH_3)_2$(4,7-diphenyl-1,10-phen) (**8**)

To a suspension of MoO_2Br_2(4,7-diphenyl-1,10-phen) (1.00 g, 1.61 mmol), in THF at -20°C (isopropanol bath), 2.1 equivalents of CH_3CH_2MgBr were slowly added. The reaction was allowed to warm-up to room temperature and was stirred for 6 h. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness and the red residue was recrystallised from CH_2Cl_2/diethyl ether. Yield, 91%. Anal. Calc. for $C_{28}H_{26}N_2O_2Mo$ (518.47): C 64.87; H 5.05; N 5.40. Found: C 64.72; H 5.00; N 5.20. IR (KBr, ν cm^{-1}): 3058 m, 3030 m, 2953 m, 2916 m, 2850 m, 1599 s, 1560 s, 1520 vs, 1493 s, 1422 s, 1398 m, 1234 s, 957, 930 vs, ν(Mo=O), 885 s, 851 vs, 768 vs, 739 vs, 704 vs, 667 s, 667 m, 575 m, 548 m. ^{1}H NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 9.87 (d, 2H), 8.10 (s, 2H), 7.86 (d, 2H), 7.55 (m, 10H), 3.42 (m, 4H), 1.15 (t, 6H).

4.12. Preparation of complexes $MoO_2(Me)_2$(L), with L=CYDAB (**9**); *Me-CYDAB* (***10***); *tBu-DAB* (**11**)

To a suspension of MoO_2Cl_2(L), in diethyl ether at -20°C (isopropanol bath), 2.1 equivalents of CH_3MgCl were slowly added. The reaction was allowed to warm-up to room temperature and was stirred for 90 min. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the

organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness and the residue was recrystallised from CH_2Cl_2/diethyl ether/*n*-hexane.

$MoO_2(Me)_2$(CYDAB) (**9**): Yield, 50%. Anal. Calc. for $C_{16}H_{30}MoN_2O_2$ (378.37): C 50.79; H 7.99; N 7.40. Found: C 50.95; H 8.16; N 7.44. IR (KBr, ν cm^{-1}): 3005 s, 2936 vs, 2853 s, 1484 m, 1451 s, 1400 s, 1352 m, 1078 m, 926, 899, vs, ν(Mo=O), 822 m. CI-MS (98Mo), [*m*/*z*, %]: 365 ([M–CH_3]+, 6), 350 ([M–2CH_3]+, 38), 326 ([M–C_4H_6]+, 54), 177 ([L–C_3H_7]+, 100), 156 ([$MoC_2H_2O_2$]+, 15), 142 ([$MoCO_2$]+, 21), 126 ([L–C_6H_6O]+, 53). ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., δ ppm): 8.15 (s, 2H), 4.34–4.27 (tt, 2H), 2.10–1.30 (m, 20H), 0.50 (s, 6H).

$MoO_2(Me)_2$(Me-CYDAB) (**10**): Yield, 40%. Anal. Calc. for $C_{18}H_{34}MoN_2O_2$ (406.42): C 53.20; H 8.43; N 6.89. Found: C 53.20; H 8.31; N 6.73. IR (KBr, νcm−1): 2928 vs, 2855 s, 1454 m, 1397 m, 1368 m, 1171 m, 934, 907, vs, ν(Mo=O). CI-MS (98Mo), [*m*/*z*, %]: 314 ([M–C_6H_8N]+, 4) 300 ([M–$C_7H_{10}N$]+, 100), 218 ([M–$C_{14}H_{22}$]+, 29), 160 ([$Mo(CH_3)_2O_2$]+, 4), 145 ([$Mo(CH_3)O_2$]+, 4), 140 ([MoN_2CH_2]+, 11), 130 ([MoO_2]+, 2). ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., δ ppm): 4.11–4.03 (tt, 2H), 2.36 (s, 6H), 2.10–1.10 (m, 20H), 0.50 (s, 6H).

$MoO_2(Me)_2$(*t*Bu-DAB) (**11**): Yield, 35%. Anal. Calc. for $C_{12}H_{26}MoN_2O_2$ (326.29): C 44.17; H 8.03; N 8.59. Found: C 44.07; H 7.99; N 8.63. IR (KBr, ν cm^{-1}): 2976 s, 2922 m, 1398 s, 1238 m, 1201 m, 936, 908, vs, ν(Mo=O), 824 m, 698 m, 530 m. CI-MS (98Mo), [*m*/*z*, %]: 313 ([M–CH_3]+, 6), 241 ([M–$C(CH_3)_3$–2CH_3]+, 16), 227([M–$C(CH_3)_3$–3CH_3]+, 10), 209 ([M–2$C(CH_3)_3$] +, 25), 167([M–CO_2–2$C(CH_3)_3$–H_2]+, 29), 138 ([M–CO_2–2CH_3–2$C(CH_3)_3$–H_2]+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz, r.t., δ ppm): 8.57 (s, 2H), 1.69 (s, 18H), 0.85 (s, 6H).

5. X-ray crystallography

Suitable single crystals of **5** for the X-ray diffraction studies were grown by standard techniques from CH_2Cl_2/diethyl ether. Preliminary examination and data collection were carried out on a NONIUS CAD4 four circle diffractometer equipped with a sealed tube (50 kV; 40 mA) and graphite monochromated MoK_α radiation. Data collection were performed at 193 K within the Θ-range of $2.49^\circ < \Theta < 26.29^\circ$. The unit cell parameters were obtained by full-matrix least-squares refinements of 25 accurate centered high angle reflections. A total number of 2612 reflections were collected. A total of 327 systematic absent reflections were rejected from the original data set. After merging, a sum of 2285 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Within the measuring time three check reflections (45 h, monitored every 3600 s) indicated no loss of the initial intensity. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All "heavy atoms" of the asymmetric unit were refined anisotropically. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_0^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at $R1 = 0.0357$, $wR2 = 0.0859$, and shift/err < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for X-Ray Crystallography [45]. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V [46] system, including the programs PLATON [47], SIR92 [48], and SHELXL-97 [49]. A summary of the crystal and experimental data is reported in Table 1. 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-14133. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

5.1. Catalytic reactions with compounds (1–11 and 3a, 5a–7a) and their bromo precursors as catalysts

800 mg (7.3 mmol) *cis*-cyclooctene, 800 mg *n*-dibutylether (internal standard), 1 mol% (73 μmol) **1**–**11** (as catalyst), and 2 ml 5.5 M *t*-butylhydroperoxide in decane were added to a thermostated reaction vessel and stirred for 4 h at 55°C.

The course of the reaction was monitored by quantitative GC-analysis. Samples were taken every 30 min, diluted with dichloromethane, and chilled in an

icebath. For the destruction of hydroperoxide and removal of water, a catalytic amount of manganese dioxide and magnesium sulfate was added. After the gas evolution ceased, the resulting slurry was filtered over a filter equipped Pasteur pipette and the filtrate injected in the GC column.

The conversion of cyclooctene and formation of cyclooctene oxide was calculated from a calibration curve (r^2=0.999) recorded prior to the reaction course. In the case of cyclohexene and styrene, the procedure was similar to the one described for cyclooctene (see above).

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