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Dimeric μ-oxo bridged molybdenum(VI) dioxo complexes as catalysts in the epoxidation of internal and terminal alkenes†

Martina E. Judmaier, Chris H. Sala, Ferdinand Belaj, Manuel Volpe and Nadia C. Mösch-Zanetti*

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The preparation of the tridentate phenol based amine ligands HL**1**–HL**4** is achieved *via* a convenient one-pot synthesis by reductive amination in quantitative yield in an autoclave under 7 bar H_2 gas. Reaction of $[MoO_2(acac)_2]$ and the corresponding ligand HLX (X = **1**, **2** and **4**) in methanol–H_2O results in the formation of orange to red dimeric μ-oxo bridged $[\{MoO_2(LX)\}_2(\mu\text{-}O)]$ (X = **1**, **2** and **4**) complexes **1–3** in high yield and high purity. Complexes **1–3** are stable towards air and water. Both ligands coordinate *via* the phenolic O atom, the amine N atom and the third donor atom in the side chain (OMe for **1** and NMe_2 for **2** and **3**) in a *fac* mode to the metal center. The molybdenum atoms are linked by a bridging μ-oxo moiety to each other as confirmed by X-ray diffraction analyses of complexes **2** and **3**. All complexes have been tested in the epoxidation of several internal and terminal alkenes using TBHP as an oxidant. Depending on the nature of the substrate, the epoxides are obtained in moderate to good yields and high selectivities. In the epoxidation of cyclooctene a TOF = 467 h^{-1} with complex **1** has been observed, significantly higher compared to other dimeric complexes reported in the literature. In the more challenging epoxidation of styrene, complexes **1** and **2** have proven to be highly selective as only the formation of styrene oxide is observed. The OMe based complex **1** has also proven to be more active than the NMe_2 based counterparts **2** and **3**. The basic conditions induced by the NMe_2 groups in complexes **2** and **3** lower their catalytic activity.

Introduction

Epoxides are important organic intermediates as they allow for a wide range of further applications in synthetic organic chemistry and chemical technology.[1] The catalytic epoxidation of alkenes is an essential synthetic method and high valent oxo metal species have been demonstrated to be versatile catalysts in the presence of soft oxidants such as H_2O_2, alkyl hydro peroxides or air,[2] thus effectively overcoming the limitations connected to the use of stoichiometric amounts of peracids.

Since the late 1960's molybdenum and tungsten complexes have been playing an important role in the industrial propylene oxide production in the Arco/Halcon process using alkyl hydroperoxides as oxygen sources.[1] During the last few years, several monomeric[3–11] and dimeric μ-oxo bridged[6,7,10,12–17] molybdenum(VI) dioxo complexes coordinated by various types of ligands have been investigated as catalysts for liquid phase alkene epoxidation, usually employing *tert*-butyl hydroperoxide (TBHP) or H_2O_2 as an oxygen source. Among them, the monomeric $[CpMoO_2Cl]$ complex[3] as well as the air and water stable dimeric μ-oxo bridged $[\{MoO_2Cl(pzH)_2\}_2(\mu\text{-}O)]$ complex[15] surpass the high catalytic activity of the well-known $[CH_3ReO_3]$ (MTO) epoxidation catalyst.[18,19]

In general, molybdenum(VI) dioxo species have proven to be highly active and selective in the epoxidation of internal aliphatic alkenes (*e.g.* cyclooctene or cyclohexene). The epoxidation of terminal alkenes (*e.g.* styrene) remains challenging, as in most cases the formation of ring-opening products is preferred.[11,20] Only a limited number of highly selective molybdenum(VI) dioxo complexes in the epoxidation of styrene can be found in the literature.[3,5,8,21] Styrene oxide is often used for the manufacture of important commercial products (*e.g.* epoxy resins, cosmetics, surface coatings, sweeteners, perfumes, drugs, *etc.*).[22]

Institut für Chemie, Karl-Franzens-Universität Graz, Stremayrgasse 16, 8010 Graz, Austria. E-mail: nadia.moesch@uni-graz.at; Fax: +43 (0)316 380 9835; Tel: +43 (0)316 380 5286

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Thus, the search for highly active and selective homogenous molybdenum catalysts is still ongoing. For easy catalyst handling, the formation of air and water stable molybdenum complexes is highly preferred.

Our research group has focused in recent years on the synthesis of rhenium(V) monooxo[23] and molybdenum(VI) dioxo[11,21] complexes as catalysts in epoxidation reactions. Among them is a set of highly active and selective monomeric $[MoO_2L_2]$ complexes ligated by bidentate Schiff base ligands with pendant donor arms (D = OMe, NMe_2), influencing both the reactivity as well as the selectivity.[21] Complexes with OMe donor atoms have proven to be more reactive than complexes with an NMe_2 group despite the fact that they are not coordinated in the catalyst precursors. Furthermore, in the epoxidation of styrene, complexes with donor atoms (OMe, NMe_2) have proven to be more selective than a related complex without an additional donor. Herein, we present the synthesis and characterization of molybdenum(VI) complexes ligated by tridentate phenol based amine ligands in which the imine functionality is reduced to an amine. This led to dinuclear μ-oxo bridged complexes that were found to be air and water stable. Their interesting catalytic behaviour in the epoxidation of various internal and terminal alkenes is described.

Results and discussion

Synthesis of the ligands HL1–HL4

Ligands HL**1**–HL**4** have been prepared in a convenient one-pot synthesis by reductive amination. Inexpensive benzaldehyde derivatives are reacted with the appropriate primary amines in an autoclave under 7 bar H_2 gas (see Scheme 1). The reaction is catalyzed by Pd/C (10 wt%). After standard workup, the ligands are obtained as viscous oils in quantitative yields.

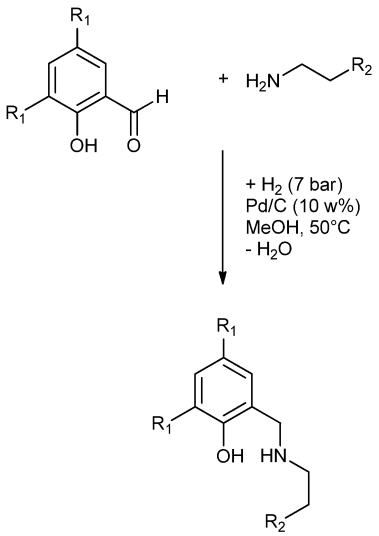
Similar ligands were previously prepared *via* the intermediate formation of the corresponding Schiff base and subsequent reduction with $M[BH_4]$ (M = Na or K) or $Na[BH_3(CN)]$.[12,13,24] However in our hands, the synthesis *via* this pathway led to a mixture of products and the desired ligands HL**1**–HL**4** could only be obtained in pure form *via* column chromatography in significant lower yields (<50%).

All ligands were characterized by common spectroscopic methods such as NMR and IR spectroscopy and mass spectrometry. The diagnostic protons of the methylene group at the aromatic ring (Ar-CH_2N) reveal a single resonance in the region between 3.93 and 4.00 ppm in ^{1}H NMR spectra, measured in chloroform-*d*, which is in good accordance with the literature.[12] The methylene C (Ar-CH_2N) atom shows a single resonance between 52.43 and 53.55 ppm in the ^{13}C NMR spectra. Due to a fast exchange, the protons of the NH group as well as of the OH moiety are not visible in ^{1}H NMR spectra. IR spectra confirm the formation of the desired ligands, as the absorption of the NH vibration is visible as a weak band between 1605 and 1612 cm^{-1}.

Synthesis of the complexes 1–3

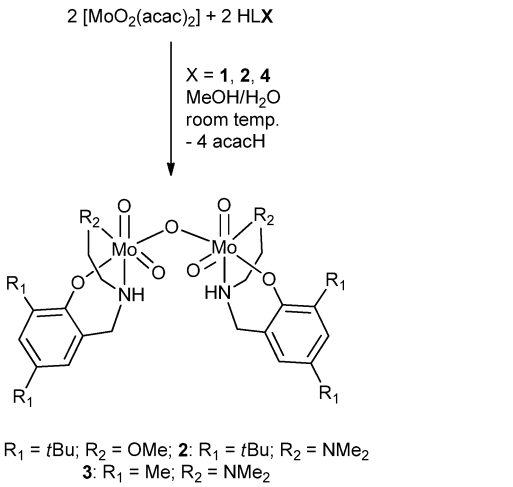
The dimeric μ-oxo bridged $[\{MoO_2(LX)\}_2(\mu\text{-}O)]$ (X = **1**, **2** and **4**) complexes (**1**–**3**) are accessible by the reaction of $[MoO_2(acac)_2]$ and the respective ligand HLX (X = **1**, **2** and **4**) in methanol in the presence of water at room temperature (see Scheme 2). The complexes precipitate as solid material after stirring overnight at room temperature. After workup, complexes **1**–**3** are isolated as yellow (**1**) to red (**2** and **3**) solids in excellent yields (79–96%).

Reaction conditions were evaluated using the example compound **3**. Equimolar reaction of $[MoO_2(acac)_2]$ and the ligand HL**4** in the presence of 2 equiv. of water in methanol at room temperature (see Table 1, entry 4) gave complex **3** in highest yields. Elevated reaction temperatures have a negligible effect on the isolated amount of complex **3** (entry 5). Lower amounts of water result in lower yields. Dry solvents (methanol or acetonitrile) often still contain residual traces of water, consequently low amounts of complex **3** are observed in these reactions, even though no water was added (entries 1 and 6).



HL**1**: R_1 = *t*Bu; R_2 = OMe; HL**2**: R_1 = *t*Bu; R_2 = NMe_2
HL**3**: R_1 = Me; R_2 = OMe; HL**4**: R_1 = Me; R_2 = NMe_2

Scheme 1 Synthetic procedure for the preparation of the ligands HL**1**–HL**4**.



1: R_1 = *t*Bu; R_2 = OMe; **2**: R_1 = *t*Bu; R_2 = NMe_2
3: R_1 = Me; R_2 = NMe_2

Scheme 2 Synthetic procedure for the preparation of dimeric μ-oxo bridged molybdenum(VI) dioxo complexes **1**–**3**.

Table 1 Optimization of reaction conditions for the synthesis of **3**

Entry[a]	Solvent	H_2O (equiv.)	T (°C)	Yield (%)
1	MeOH	0.0	25	18
2	MeOH	0.5	25	72
3	MeOH	1.5	25	80
4	MeOH	2.0	25	88
5	MeOH	2.0	50	86
6	CH_3CN	0.0	25	11
7	CH_3CN	2.0	25	74

[a] An equimolar ratio (1 : 1) of $[MoO_2(acac)_2]$ and HL**4** has been used for the synthesis of complex **3** in entries 1–7.

Also reactions performed in acetonitrile in the presence of 2 equiv. of water result in the formation of complex **3** in good yield (74%). Therefore it seems obvious that the bridging oxygen atom derives from water, as it has been previously described in the literature.[12]

Surprisingly enough, analogous reaction conditions employing ligand HL**3** and $[MoO_2(acac)_2]$ did not result in any complex formation. Monitoring the reaction *via* ^{1}H NMR spectroscopy after 24 hours of reaction time showed only the existence of the free ligand and the metal precursor. Furthermore, the formation of monomeric complexes of the type $[MoO_2L_2]$ has not proven to be successful with this type of ligand. On the other hand, we have previously published a set of such mononuclear complexes ligated by corresponding Schiff base ligands featuring an imine (Ar-CH=N) moiety.[21] With these ligands no dimeric complexes could be obtained, since in the presence of water they tend to decompose into unidentified polyoxo materials. Monomeric compounds are also formed with a ligand where the proton attached to the amine nitrogen atom is substituted by a methyl group. Reaction of this type of ligands with $[MoO_2Cl(\eta^2\text{-}t\text{Bu}_2\text{Pz})]$[25] or $[MoO_2Cl_2]$ led to complexes $[MoO_2ClL]$ in which the ligand is coordinated in a tridentate fashion.[26] Any attempt to substitute the remaining chlorine atom in the latter compounds proved to be futile. Thus, the protons at nitrogen in the here described ligands are crucial for the stability of the complexes **1–3**. This fact is supported by the molecular structure determined by X-ray diffraction analysis (*vide infra*) where strong Mo=O–H bonds are apparent.

Complexes **1–3** are well soluble in common organic solvents such as dichloromethane, chloroform, THF and methanol at room temperature, but less so in acetonitrile and water. All complexes are insoluble in aliphatic and aromatic hydrocarbons such as pentane, heptane, benzene and toluene. Complexes **1–3** are stable in air and can be stored without decomposition for several months.

All complexes have been characterized by common spectroscopic methods such as NMR and IR spectroscopy and elemental analyses. MS measurements – even with very mild ionization techniques – failed to show the molecular peak. Only free ligand could be detected. However the molecular structures of complexes **2** and **3** were determined by single crystal X-ray diffraction analyses (*vide infra*).

^{1}H and ^{13}C NMR spectroscopy confirmed the formation of the desired complexes as the resonances of the free ligand are shifted upon coordination to the metal center. The diagnostic resonance of the methylene moiety (Ar-CH_2N) at the aromatic ring splits into two multiplets (for **1** and **2**) or doublets (for **3**) with the integration of one between 3.85 and 4.77 ppm (see Table 2) upon coordination of the N atom to the metal center. The proton of the N*H* moiety is visible as a broad signal between 4.75 and 4.83 ppm. The corresponding C atom of the methylene moiety (Ar-CH_2N) occurs between 53.46 and 54.29 ppm in ^{13}C NMR spectra.

Table 2 Selected ^{1}H NMR resonances and IR vibrations of the ligands HL**1**, HL**2**, HL**4** and the dimeric molybdenum complexes **1–3**

Ligand	Ar-CH_2N[a] [ppm]	Complex	Ar-CH_2N[a] [ppm]	NH[a] [ppm]	$\nu_{Mo=O}$[b] [cm^{-1}]	$\nu_{Mo\text{-}\mu\text{-}O}$[b] [cm^{-1}]
HL**1**	4.00	**1**	3.93	4.77	897	739
			4.77		885	
HL**2**	3.97	**2**	3.95	4.75	918	711
			4.75		880	
HL**4**	3.93	**3**	3.85	4.83	912	710
			4.75		878	

[a] NMR spectra are measured in chloroform-*d*. The shifts are reported in ppm *vs.* the solvent residual peak. [b] IR spectra are measured in the solid state.

IR spectra of complexes show two strong $\nu_{Mo=O}$ absorptions at 878–885 cm^{-1} and 897–918 cm^{-1}, characteristic of the symmetric and asymmetric stretching mode of the *cis*-$[MoO_2]^{2+}$ fragment. The absorption of the $\nu_{Mo\text{-}(\mu\text{-}O)}$ vibration is visible as a broad band between 710 and 739 cm^{-1}. All absorptions are in good accordance with the literature.[12,17,27] Elemental analyses confirmed the existence of μ-oxo bridged dimeric molybdenum complexes of the type $[\{MoO_2(LX)\}_2(\mu\text{-}O)]$ (X = **1**, **2** and **4**).

Dimeric $[\{MoO_2L_n\}_2(\mu\text{-}O)]$ (n = 1 or 2) complexes are widespread in the literature.[6,7,9,10,12–15,17,27] Mitchell and Finney published in 2001 a very similar complex with a pyridine moiety in the side chain.[12] This complex has proven to be highly active in the epoxidation of aromatic alkenes in the presence of *tert*-butyl hydroperoxide (TBHP).

Molecular structure in the solid state

Single crystals suitable for X-ray diffraction analyses of complex **2** were obtained from dilute acetonitrile solutions at room temperature and those for complex **3** were obtained from concentrated dichloromethane solutions at −30 °C, in both cases in the form of orange blocks. Complex **1** also crystallized from an acetonitrile solution, however the crystals were found to be unsuitable for X-ray diffraction analysis. A molecular view of each of the two complexes is shown in Fig. 1. Selected bond lengths and angles are given in Table 3 and crystallographic data in Table 7.

The molecular structures of complexes **2** and **3** are quite similar and both complexes reveal a μ-oxo bridging moiety. The two molybdenum atoms are six coordinated in a distorted octahedral environment. Each molybdenum atom is ligated by a tridentate ligand, two terminal oxygen atoms and a bridging μ-oxo atom.

The tridentate ligand coordinates *via* its phenolic O atom and both N atoms (NH and NMe_2) to the metal center.

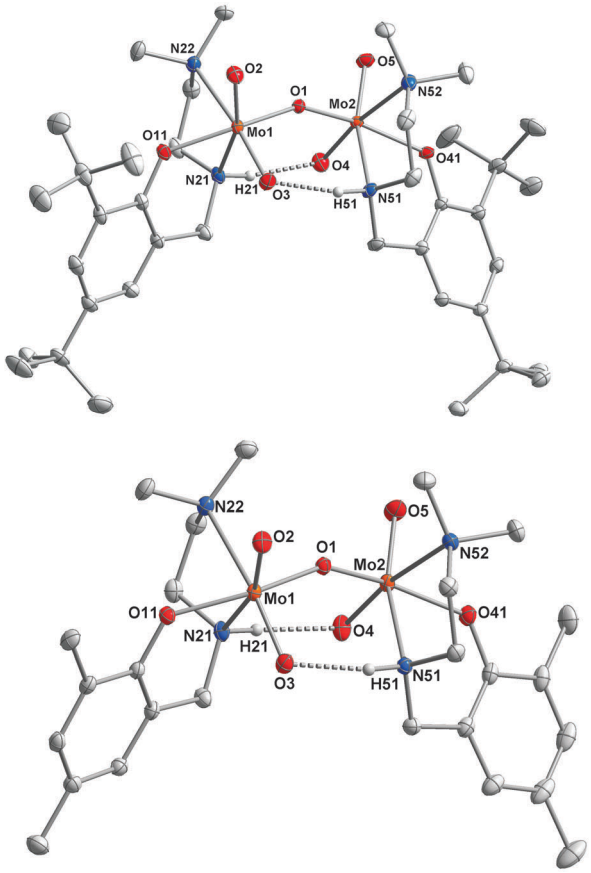


Fig. 1 Molecular structure and atom labeling scheme for complexes **2** (top) and **3** (bottom). Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms (except those involved in hydrogen bonding) are omitted for clarity.

Table 3 Selected bond lengths [Å] and angles [°] of complexes **2** and **3**

	2	**3**
Mo1–O1	1.9148(10)	1.9104(12)
Mo1–O2	1.7113(11)	1.7178(13)
Mo1–O3	1.7258(11)	1.7206(13)
Mo1–O11	1.9515(11)	1.9548(12)
Mo1–N21	2.3276(13)	2.3298(15)
Mo1–N22	2.4168(13)	2.4138(15)
Mo2–O1	1.9104(10)	1.9055(12)
Mo2–O4	1.7203(12)	1.7256(14)
Mo2–O5	1.7122(11)	1.7091(14)
Mo2–O41	1.9537(11)	1.9577(13)
Mo2–N51	2.3350(13)	2.3233(14)
Mo2–N52	2.4429(14)	2.4221(16)
Mo1···Mo2	3.7110	3.6954
O1–Mo1–O11	155.96(5)	154.87(5)
O2–Mo1–N21	158.13(5)	160.08(6)
O3–Mo1–N22	166.71(5)	165.45(6)
O1–Mo2–O41	155.21(5)	155.63(6)
O4–Mo2–N52	167.50(5)	166.28(6)
O5–Mo2–N51	157.81(6)	158.91(6)
Mo1–O1–Mo2	151.93(6)	151.12(8)
O3–Mo1–O1	96.39(5)	96.64(6)
O3–Mo1–O2	108.36(6)	108.13(7)
O3–Mo1–O11	94.64(5)	95.08(6)
O3–Mo1–N21	92.93(5)	91.42(6)
O4–Mo2–O1	96.86(5)	96.32(6)
O4–Mo2–O5	107.63(6)	108.20(7)
O4–Mo1–O41	94.25(5)	95.82(6)
O4–Mo2–N51	94.15(5)	92.54(6)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
Hydrogen bonds for complex **2**				
N21–H21···O4	0.93	1.99	2.9093(17)	167.7
N51–H51···O3	0.93	1.99	2.9126(17)	168.8
Hydrogen bonds for complex **3**				
N21–H21···O4	0.93	1.99	2.899	166.09
N51–H51···O3	0.93	1.98	2.900	167.92

The molybdenum oxo groups show the expected mutual *cis* configuration and are located *trans* to the NH and NMe_2 moieties. The phenolic O atom and the μ-oxo bridged O atom are found to be *trans* to each other. The conformation of complexes **2** and **3** is locked in position by two intra-molecular hydrogen bonds, as protons of the NH group weakly coordinate to a terminal oxygen atom close by.

All Mo–O bond lengths (ranging from 1.9515(11) to 1.9577(13) Å) as well as all Mo=O bond lengths (ranging from 1.7091(14) to 1.7258(11) Å) are in the expected range of *cis*-$[MoO_2]^{2+}$ complexes. The Mo–(μ-O) bond lengths (ranging from 1.9104(10) to 1.9148(10) Å) are slightly longer than those reported in the literature.[9,12,27] The Mo–NH bond lengths (ranging from 2.3233(14) to 2.3350(13) Å) as well as the Mo–NMe_2 bond lengths (ranging from 2.4138(15) to 2.4429(14) Å) are somewhat longer due to the influence of the *trans* coordinated Mo=O ligands.[9,12,27]

Bond angles around the metal centers deviate in both complexes considerably from those of an ideal octahedron (see Table 3). The distorted octahedral geometry is also evident by the obtuse angles of the apical ligands (*e.g.* O3–Mo1–O2 108.36(6)° for **2** and O1–Mo1–O2 108.13(7)° for **3**). The angle around the μ-O bridge (*e.g.* Mo1–O1–Mo2 151.93(6)° for **2** and Mo1–O7–Mo2 151.12(8)° for **3**) promotes a short intermetallic distance (*e.g.* Mo1···Mo2 3.7110 Å for **2** and 3.6954 Å for **3**). Both, the angle around the μ-oxo bridge as well as the intermetallic distances are in good accordance with the literature.[9,12,15]

Epoxidation of alkenes

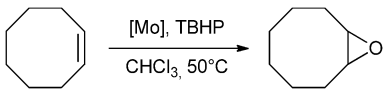
All dimeric molybdenum(VI) dioxo complexes **1–3** have been tested as catalysts in the epoxidation of several internal and terminal alkenes using *tert*-butyl hydroperoxide (TBHP, 5.5 M in decane) as an oxidant. Optimal reaction conditions regarding temperature, oxidant loading and catalyst loading were evaluated using the substrate cyclooctene and complex **1** as a catalyst.

Table 4 summarizes the results of temperature and solvent screening. In accordance with the literature, chlorinated solvents proved to be the best cosolvent. Full conversion to the corresponding epoxide was obtained in chloroform at 50 °C within one hour of reaction time. With heptane and toluene as co-solvents, acceptable conversions at higher temperature (75 °C) were obtained. Lower conversions are observed in methanol and *tert*-butyl alcohol, whereas no conversion of epoxide is reached in THF and diethyl ether. Again, these results are in good accordance with the literature, where higher temperatures and chlorinated solvents are preferred. All further experiments were performed in chloroform at 50 °C (Scheme 3).

Table 4 Epoxidation of cyclooctene catalyzed by **1**; the effect of cosolvent and temperature

Cosolvent[a]		35 °C		50 °C		75 °C
Chlorinated	CH_2Cl_2	82	$CHCl_3$	98	$C_2H_4Cl_2$	87
Heptane				63		69
Toluene				72		81
Diethyl ether		<10				
THF				<10		
MeOH				27		
*t*BuOH				12		

[a] Reaction conditions: 0.5 mol% complex **1**, 1.41 mmol cyclooctene, 2.82 mmol TBHP (2 equiv.). Conversions were determined by GC-MS measurements after 60 minutes. Mesitylene was used as internal standard. Complete selectivity towards the epoxide was observed.



Scheme 3 Epoxidation of cyclooctene.

Complex **1** allows for a catalyst loading down to 0.25 mol% in the presence of two equivalents of TBHP without loss of activity (TOF = 467 h^{-1}). After one hour of reaction time, full conversion to the corresponding epoxide is observed. A further catalyst lowering to 0.1 mol% with a similar TBHP amount results in lower epoxide yield (87%). Reactions performed with 1 equiv. of TBHP are slower. Only 50% conversion is obtained with a catalyst : substrate ratio of 1 : 200. After 3 hours of reaction time, 65% of epoxide yield is observed. For subsequent epoxidation reactions we chose 0.5 mol% of catalyst loading and 2 equiv. of TBHP at 50 °C in chloroform as the standard conditions (Table 5).

The stability of complex **1** under catalysis conditions was tested in four consecutive runs in the epoxidation of cyclooctene using TBHP (5.5 M in decane) as an oxidant (see Fig. 2). After 90 minutes, 24 hours and 48 hours, catalysis was restarted by the addition of cyclooctene and TBHP (ratio 1 : 2). Full conversion to the corresponding epoxide was obtained in the first two runs after 60 minutes of reaction time. After 24 hours, complex **1** is still active, but the conversion rate is lower than in the former two runs (*e.g.* after 60 minutes 58% of epoxide are obtained),

Table 5 Epoxidation of cyclooctene catalyzed by **1**; the effect of catalyst and oxidant (TBHP) loading

		Conversion[a] (%)	
mol% **1**	[Mo] : alkene ratio	TBHP[b] (1 equiv.)	TBHP[b] (2 equiv.)
0.5	1 : 200	50	98
0.25	1 : 400	48	96
0.1	1 : 1000	33	87
0.05	1 : 2000	22	80
0.01	1 : 10 000	18	21

[a] Reactions were carried out at 50 °C in chloroform (5 ml) using 1.41 mmol cyclooctene, 1.41 mmol mesitylene (internal standard) and 1.41 (1 equiv.) or 2.82 (2 equiv.) TBHP. Conversions were determined by GC-MS measurements after 60 minutes. Mesitylene was used as internal standard. [b] Complete selectivity towards the epoxide was observed.

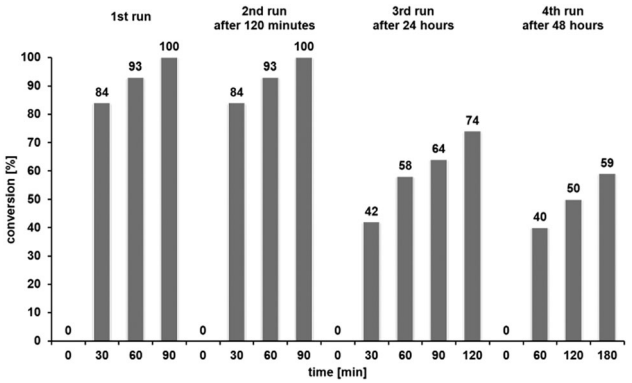


Fig. 2 Activity test of complex **1** *via* the epoxidation of cyclooctene in four consecutive runs. After 120 minutes, 24 and 48 hours 1.41 mmol cyclooctene and 2.82 mmol TBHP are added to the initial reaction mixture. Reactions are performed in chloroform (5 ml) at 50 °C and 0.5 mol% catalyst loading.

most probably due to the increasing concentration of *tert*-butyl alcohol in solution, which may act as a competitive inhibitor for the attack of TBHP at the molybdenum(VI) center.[28] After 48 hours, the catalytic activity of complex **1** is significantly lower and only 40% of epoxide is obtained after 60 minutes of reaction time.

Complexes **1–3** have been used as precatalysts in the epoxidation of different aliphatic and aromatic alkenes. All reactions were performed in chloroform at 50 °C using 0.5 mol% catalyst, 1.41 mmol substrate and 2.82 mmol TBHP. In all cases control experiments confirmed a low conversion of the substrate (<10%) in the absence of a catalyst.

The different alkenes are generally oxidized in moderate to good yields with high selectivities (see Table 6). Complete conversion to the corresponding epoxide is observed for both cyclic alkenes (cyclohexene and cyclooctene) after one hour of reaction time for the OMe based complex **1**. Lower conversions are observed after 24 hours for both NMe_2 based complexes **2** and **3**. These complexes possess similar catalytic activities. Sterically more demanding substituents (*t*Bu in **2** *vs.* Me in **3**) in the ligand backbone have a negligible effect.

Further epoxidation reactions were performed with complexes **1** and **2**. Both complexes have sterically demanding *t*Bu substituents at *ortho* and *para* positions on the phenyl ring, but differ in the donor atoms in the side chain (OMe for **1** and NMe_2 for **2**).

Conversions for linear alkenes are in general somewhat lower, but the best catalyst **1** reaches 70% of 1,2-epoxyoctane and 83% of 2,3-epoxy-1-propanol after 24 hours. More challenging are aromatic alkenes, such as styrene, *cis*-stilbene and *trans*-stilbene, as these substrates are less electron rich. Moderate conversions, but always with excellent selectivities, are obtained in the epoxidation of styrene. The formation of ring opening products is negligible. Again, complex **1** is somewhat more active (*e.g.* after 24 hours 44% for **1** *vs.* 36% for **2**). In the epoxidation of *cis*-stilbene and *trans*-stilbene significantly higher conversions are obtained with complex **1**. Complex **2** is less active and only in the case of *cis*-stilbene, epoxide formation

Table 6 Epoxidation of aliphatic and aromatic alkenes using complexes **1–3** as precatalysts

Substrate	Catalyst[a]	Epoxide yield (%)	Time (h)	Selectivity[b] (%)
Cyclohexene[c]	**1**	98	1	99
	2	90	24	99
	3	95	24	99
Cyclooctene[c]	**1**	98	1	99
	2	9/88	1/24	99
	3	7/90	1/24	99
1-Octene[d]	**1**	34/70	4/24	99
	2	26	24	99
2-Propenol[d]	**1**	66/83	8/24	99
	2	21	24	99
Styrene[c]	**1**	35/44	5/24	99
	2	36	24	99
cis-Stilbene[e]	**1**	36/62	4/24	99
	2	17	24	99
trans-Stilbene[e]	**1**	32/55	4/24	99
	2	—	24	—
α-Terpineol[c]	**1**	55/100	0.25/1	99
	2	36/86	4/24	99
R-(+)-Limonene[e]	**1**[f]	53/98/53	0.25/2/4	53
	2	37/77	4/24	99

[a] Reactions were carried out at 50 °C in chloroform using 1.41 mmol (1 equiv.) alkene, 1.41 mmol internal standard, 2.82 mmol (2 equiv.) TBHP. [b] Selectivity after 24 hours. [c] Reaction yields were determined by integration of GC-MS chromatograms; mesitylene was used as internal standard. [d] Isolated yields: determined by integration of ^{1}H NMR spectra in $CDCl_3$ *vs.* dichloroethane as internal standard. [e] Reaction yields were determined by integration of HPLC chromatograms; mesitylene was used as internal standard. [f] Dipentene dioxide (limonene dioxide) as a side product.

is observed (*e.g.* after 24 hours 17%). In the epoxidation of α-terpineol the oxidizable OH group is not affected and after one hour of reaction time full conversion is obtained with complex **1**, whereas 86% of epoxide is obtained after 24 hours with **2**. The epoxidation of limonene is more challenging as the substrate includes two different alkene moieties – one internal and one terminal double bond. Full conversion within two hours of reaction is observed for the OMe based complex **1**. Nevertheless, the selectivity after 24 hours is low as the formation of the double epoxide (dipentene dioxide) is preferred. Reactions catalyzed by **2** are slower, but more selective. After 24 hours, only 1,2-epoxy-limonene (77%) as a single product is obtained.

Complex **1** could definitely not surpass the high catalytic activity of the dimeric $[\{MoO_2Cl(pzH)_2\}_2(\mu\text{-}O)]$ complex published by Gonçalves and coworkers in 2007.[15] This complex reaches under the best reaction conditions a TOF = 32 000 h^{-1} in the epoxidation of cyclooctene, which is even higher than the TOFs recorded for the $[ReO_3CH_3]$–H_2O_2 catalytic epoxidation system.[18,29] Compared to other dimeric $[\{MoO_2L_n\}_2(\mu\text{-}O)]$ complexes (n = 1, 2) in the literature,[6,7,12,14,17] the catalytic activity of complex **1** is higher. Under the best reaction conditions a TOF = 467 h^{-1} in the epoxidation of cyclooctene is observed. For example, the $[\{MoO_2Cl(dmf)_2\}_2(\mu\text{-}O)]$ complex[7] representing one of the more active dimeric catalysts reaches a TOF = 102 h^{-1} in the epoxidation of cyclooctene. In the epoxidation of *R*-(+)-limonene similar conversions to the literature are obtained,[6,14] but complex **2** has proven to be more selective as the formation of 1,2-epoxy-limonene as a single product is preferred.

Recently we published a set of monomeric $[MoO_2L_2]$ complexes ligated by bidentate Schiff base ligands (Ar-CH=N moiety) including the same donor atoms in the side chain (OMe and NMe_2).[21] For both complex types (monomeric *vs.* dimeric), the OMe based compounds have proven to be more active than their NMe_2 based counterparts. The more basic NMe_2 donor group is obviously more prone towards protonation leading to the formation of a less active species and hence slowing down the catalytic activity.[21] The higher catalytic activity of OMe based complexes may be explained by the influence of the OMe group in the formation of hydrogen bonds. Such bonds may be stable enough to lower the activation barriers during the catalytic cycle.[30,31] Moreover, the catalytic activity of both, the monomeric and dimeric complexes, is influenced by the nature of the substrate. In the epoxidation of internal aliphatic alkenes the dimeric complex **1** has proven to be more active than the monomeric $[MoO_2L_2]$ complexes (*e.g.* in the epoxidation of cyclooctene TOF = 467 h^{-1} for **1** *vs.* TOF = 359 h^{-1} for the best $[MoO_2L_2]$ complex[21]). In the epoxidation of terminal alkenes (*e.g.* styrene) higher conversions are observed in reactions catalyzed by the monomeric complexes.

The reaction mechanism in the epoxidation of alkenes is still under debate.[17,30–32] However, the more likely mechanism includes the addition of TBHP across a terminal Mo=O group, resulting in the formation of Mo–OH and Mo–O–O–*t*Bu moieties. The α-O atom of the latter moiety is then transferred to the alkene, producing the epoxide under concomitant elimination of *tert*-butyl alcohol, yielding the initial complex. Theoretical studies evidence the importance of H bond formations at various steps during the catalytic cycle.[30,31] Both the oxygen atom transfer as well as the H atom transfer represent a barrier. Single crystal X-ray diffraction analyses of complexes **2** and **3** indicate the existence of Mo=O···H bonds.

In the case of dimeric complexes, a splitting across the μ-oxo bridge prior to the coordination of TBHP seems to be necessary. It has previously been described in the literature that in comparative studies related monomeric and dimeric complexes exhibit similar epoxidation activities after 24 hours of reaction time pointing to a common monomeric catalytically active species.[7,12,16,17] ATR-IR spectroscopic investigations of the epoxidation of cyclooctene employing complex **1** were performed by taking aliquots of the reaction solution. The absorption of the Mo–(μ-O) vibration in the IR spectrum at 739 cm^{-1} disappears during the catalytic cycle indicating the transformation of the catalyst precursor. Both, the symmetric and the asymmetric absorption of the Mo=O vibration are shifted and appear now as broad overlapping bands at 907 cm^{-1}. The formation of a monomeric active species is likely, but the real nature of the compound is as yet unclear. Furthermore, it is unknown whether both metal atoms of the dinuclear compounds represent active centers. Comparison of the activity of compounds **1–3** to related mononuclear compounds would be helpful. However, such compounds are as yet elusive

Table 7 Crystal data and structure refinement of complexes **2** and **3**

	2	**3**
Empirical formula	$Mo_2O_7N_4C_{38}H_{66}\cdot 2\ C_2H_3N$	$Mo_2O_7N_4C_{26}H_{42}\cdot 2\ CH_2Cl_2$
Formula weight	964.94	884.37
Crystal description	Block, orange	Block, orange
Crystal size (mm)	0.29 × 0.22 × 0.20	0.46 × 0.34 × 0.29
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Unit cell dimensions, a (Å)	13.8832(5)	7.4666(6)
b (Å)	11.6611(4)	14.8332(11)
c (Å)	30.2445(9)	16.7476(12)
α (°)	90	98.171(2)
β (°)	94.1130(10)	90.647(2)
γ (°)	90	92.937(2)
Volume (Å^3)	4883.8(3)	1833.3(2)
Z, calculated density (g cm^{-3})	4, 1.312	2, 1.602
F(000)	2024	900
Linear absorption coefficient μ (mm^{-1})	0.563	1.022
Absorption correction	Semi-empirical from equivalents	Multi-scan
Temperature (K)	100	100
Wavelength (MoKα) (Å)	0.71073	0.71073
Theta range for data collection (°)	1.87 to 30.00	2.46 to 34.35
Limiting indices	$-19 \le h \le 11$ $-16 \le k \le 14$ $-42 \le l \le 42$	$-11 \le h \le 11$ $-21 \le k \le 23$ $-24 \le l \le 25$
Reflections collected/unique	44 653/14 241	360 456/12 236
Reflections with $I > 2\sigma(I)$	12 714	11 100
R(int), R(sigma)	0.0216, 0.0229	0.0425, 0.0270
Completeness to theta max.	0.999	0.983
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2
Data/restraints/parameters	14 241/585/1	12 236/5/441
Goodness-of-fit on F^2	1.060	1.071
Final R_1 [a] wR_2 [b] [$I > 2\sigma(I)$]	R_1 = 0.0268 wR_2 = 0.0657	R_1 = 0.0297 wR_2 = 0.0754
R indices (all data)	R_1 = 0.0322 wR_2 = 0.0686	R_2 = 0.0340 wR_2 = 0.0790
Largest diff. peak and hole (e Å^{-3})	1.200 and −0.691	1.364 and −1.380
CCDC deposition no.	909614	909615

[a] $R_1 = \sum \|F_o\|-|F_c\| / \sum |F_o|$. [b] $wR_2 = \left\{ \sum \left[w\left(wF_o^2 - F_c^2\right)^2 \right] / \sum \left[w\left(F_o^2\right)^2 \right] \right\}^{1/2}$.

preventing the elucidation of this question. Attempts to isolate any intermediate molybdenum(VI) *tert*-butyl hydroperoxide complex have not been successful as yet. Unfortunately, the use of H_2O_2 as a terminal oxidant in the epoxidation of cyclooctene did not yield significant amounts of the corresponding epoxide (17% of cyclooctene oxide for **1**).

Conclusions

Here we presented a set of new dimeric μ-oxo bridged molybdenum(VI) dioxo complexes ligated by tridentate phenol based ligands including an NH moiety. Complexes **1–3** are obtained by a simple procedure in high yield and high purity. The stability of complexes **1–3** towards moisture and air simplifies the handling. X-ray diffraction analyses of complexes **2** and **3** prove the existence of a bridging O atom, which most probably occurs from water. Complexes **1–3** act as precatalysts in the epoxidation of aliphatic and aromatic alkenes. The OMe based complex **1** has proven to be more active than the NMe_2 based counterparts **2** and **3**. However, consecutive catalytic runs with **1** showed after two cycles reduced activity. Terminal as well as internal alkenes including challenging substrates such as 1-octene and styrene are cleanly converted to the corresponding epoxides in moderate to good yields with high selectivities. Complex **1** has proven to be less selective in the epoxidation of *R*-(+)-limonene as the formation of the double epoxide (dipentene dioxide) is observed after 24 hours of reaction time. These results revealed complex **1** to be a highly active catalyst in comparison to other published molybdenum complexes but could not surpass the high catalytic activity of the dimeric $[\{MoO_2Cl(pzH)_2\}_2(\mu\text{-}O)]$ complex published by Gonçalves and coworkers in 2007.[15] Furthermore, compounds **1** and **2** proved to be highly selective in the epoxidation of more challenging substrates such as 1-octene and styrene as no further oxidation products were observed. The nature of the real catalyst is as yet unclear, but IR measurements of complex **1** indicate a splitting of the dimeric μ-oxo bridged compound during the catalytic cycle.

Experimental

General remarks

3,5-Di-methyl-2-hydroxybenzaldehyde was prepared according to the literature.[33] $[MoO_2(acac)_2]$ was purchased from Aldrich and used as received. All other chemicals were obtained from different suppliers and used without further purification. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III Spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C NMR).

The ^{1}H NMR spectroscopic data are reported as s = singlet, d = doublet, t = triplet, m = multiplet, coupling constants are reported in Hz and chemical shifts are given in ppm relative to the solvent residual peak. All deuterated solvents were purchased from Deutero GmbH and dried over molecular sieves. IR spectra were measured as solid samples on a Bruker Alpha P Diamond FTIR-ATR spectrometer. Mass spectra have been measured on an Agilent 5973 MSD-Direct Probe using the EI ionisation technique. GC-MS measurements were performed on an Agilent 7890A with an Agilent 19091J-433 column coupled to a mass spectrometer type Agilent 5975C. HPLC measurements were performed on an Agilent 1200 Series with a Zorbax eclipse XDB-C18 column and a UV/Vis detector. Elemental analyses were carried out using a Heraeus Vario Elementar automatic analyzer at the Institute of Inorganic Chemistry at the University of Technology in Graz.

General procedure for the synthesis of the ligands

The aromatic benzaldehyde (12.8 mmol, 1 equiv.) and the appropriate primary amine (16.6 mmol, 1.3 equiv.) were dissolved in methanol (80 ml) and placed in a stainless steel 250 ml autoclave. Pd/C (10 %wt) as a catalyst was added. The mixture was degassed several times and saturated with H_2. The hydrogenation was carried out at 7 bar H_2 with stirring at 50 °C for 24 hours. The hydrogen gas was then carefully released and the Pd/C catalyst was filtered off. The solution of the product was dried over Na_2SO_4 and again filtered. The solvent was removed under vacuum affording the corresponding ligand as colorless oils in quantitative yield. The ligands were used without further purification.

Reduction of the respective Schiff base ligands with $M[BH_4]$ (M = Na or K) or $Na[BH_3(CN)]$ according to the literature results as well in the formation of the desired amine based ligands.[12] Nevertheless, as purification *via* column chromatography on aluminium oxide was needed, yields were significantly lower (<50%).

Ligand HL1. In a 250 ml stainless steel autoclave 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (4.69 g, 20 mmol) and 2-methoxyethylamine (1.96 g, 26 mmol) were dissolved in methanol (80 ml). Pd/C (0.47 g) was added and the mixture was exposed to H_2 gas (7 bar). After purification, the ligand was obtained as a colorless viscous oil. Yield: 5.63 g (96%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, ppm) δ 1.32 (s, 9H, C(CH_3)$_3$), 1.46 (s, 9H, C(CH_3)$_3$), 2.88 (t, $^3J_{H\text{-}H}$ = 5.1 Hz, 2H, N(CH_2)$_2$O), 3.40 (s, 3H, OCH_3), 3.56 (t, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, N(CH_2)$_2$O), 4.00 (s, 2H, Ar-CH_2N), 6.90 (d, $^4J_{H\text{-}H}$ = 2.4 Hz, 1H, Ar-H), 7.24 (d, $^4J_{H\text{-}H}$ = 2.4 Hz, 1H, Ar-H). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, ppm) δ 29.77 (C(CH_3)$_3$), 31.83 (C(*C*H_3)$_3$), 34.26 (*C*(CH$_3$)$_3$), 35.02 (C(*C*H$_3$)$_3$), 48.07 (N(*C*H$_2$)$_2$O), 53.33 (Ar-*C*H$_2$N), 58.96 (O*C*H$_3$), 71.22 09 (N(*C*H$_2$)$_2$O), 122.04 (*Ar*), 123.02 (*Ar*-H), 123.31 (*Ar*-H), 135.93 (*Ar*), 140.49 (*Ar*), 154.83 (*Ar*-OH). The protons of the N*H* and O*H* group were not detected in benzene-d_6 or in chloroform-*d*. IR (ATR, cm^{-1}): ν 2952 (s), 1605 (w, NH), 1441 (s), 1360 (m), 1237 (s), 1128 (m), 1098 (m), 877 (m), 724 (m). MS (EI) (70 eV) *m*/*z* (%): 293.3 (50) [M]$^+$, 248.2 (30) [M-CH$_2$OCH$_3$]$^+$, 219.3 (100) [M-NH(CH$_2$)$_2$OCH$_3$]$^+$. Anal. calcd for $C_{18}H_{31}NO_2$ (293.4): C 73.17, H 10.65, N 4.77%; found: C 72.80, H 9.77, N 4.90%.

Ligand HL2. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (4.69 g, 20 mmol) and *N*,*N*-dimethylethylene-diamine (2.29 g, 26 mmol) were dissolved in methanol (80 ml). Pd/C (0.47 g) was added and the mixture was exposed to H_2 gas (7 bar). After purification, the ligand was obtained as a colorless viscous oil. Yield: 6.00 g (98%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, ppm): δ 1.30 (s, 9H, C(CH_3)$_3$), 1.44 (s, 9H, C(CH_3)$_3$), 2.24 (s, 6H, N(CH_3)$_2$), 2.46 (t, $^3J_{H\text{-}H}$ = 5.9 Hz, 2H, N(CH_2)$_2$N), 2.75 (t, $^3J_{H\text{-}H}$ = 5.9 Hz, 2H, N(CH_2)$_2$N), 3.97 (s, 2H, Ar-CH_2N), 6.88 (d, $^4J_{H\text{-}H}$ = 2.4 Hz, 1H, Ar-H), 7.23 (d, $^4J_{H\text{-}H}$ = 2.5 Hz, 1H, Ar-H). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, ppm): δ 29.77 (C(*C*H$_3$)$_3$), 31.83 (C(*C*H$_3$)$_3$), 34.25 (*C*(CH$_3$)$_3$), 35.01 (*C*(CH$_3$)$_3$), 45.59 (2× N(*C*H$_3$)$_2$), 46.09 (N(*C*H$_2$)$_2$N), 53.55 (Ar-*C*H$_2$N), 58.41 (N(*C*H$_2$)$_2$N), 122.22 (*Ar*), 122.90 (*Ar*-H), 123.21 (*Ar*-H), 135.86 (*Ar*), 140.35 (*Ar*), 154.90 (*Ar*-OH). The protons of the N*H* and O*H* group were not detected in benzene-d_6 or in chloroform-*d*. IR (ATR, cm^{-1}): ν 2950 (s), 1606 (w, NH), 1458 (s), 1438 (s), 1360 (m), 1236 (s), 1202 (m), 1040 (m), 876 (m), 821 (m), 761 (m). MS (EI) (70 eV) *m*/*z* (%): 306.3 (23) [M]$^+$, 247.3 (17) [M-(CH$_2$N(CH$_3$)$_2$)-H]$^+$, 219.3 (100) [M-NH(CH$_2$)$_2$N(CH$_3$)$_2$]$^+$. Anal. calcd for $C_{19}H_{34}N_2O$ (306.5): C 74.46, H 11.18, N 9.14%; found: C 74.09, H 11.02, N 9.08%.

Ligand HL3. 3,5-Di-methyl-2-hydroxybenz-aldehyde[33] (3.00 g, 20 mmol) and 2-methoxyethylamine (1.96 g, 26 mmol) were dissolved in methanol (80 ml). Pd/C (0.30 g) was added and the mixture was exposed to H_2 gas (7 bar). After purification, the ligand was obtained as a colorless viscous oil. Yield: 4.06 g (97%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, ppm) δ 2.21 (s, 3H, Ar-CH_3), 2.22 (s, 3H, Ar-CH_3), 2.82 (t, $^3J_{H\text{-}H}$ = 5.1 Hz, 2H, N(CH_2)$_2$O), 3.37 (s, 3H, OCH_3), 3.52 (t, $^3J_{H\text{-}H}$ = 5.1 Hz, 2H, N(CH_2)$_2$O), 3.95 (s, 2H, Ar-CH_2N), 6.66 (s, 1H, Ar-*H*), 6.87 (s, 1H, Ar-*H*). ^{1}^{3}C NMR (75 MHz, chloroform-*d*, 298 K, ppm) δ 15.73 (Ar-*C*H$_3$), 20.50 (Ar-*C*H$_3$), 47.96 (N(*C*H$_2$)$_2$N), 52.43 (Ar-*C*H$_2$N), 58.95 (O*C*H$_3$), 71.13 (N(*C*H$_2$)$_2$N), 121.46 (*Ar*), 124.93 (*Ar*), 126.57 (*Ar*-H), 127.57 (*Ar*), 130.55 (*Ar*-H), 153.97 (*Ar*-OH). The protons of the N*H* and O*H* group were not detected in benzene-d_6 or in chloroform-*d*. IR (ATR, cm^{-1}): ν 2917 (m), 1612 (w, NH), 1481 (s), 1244 (s), 1192 (m), 1157 (m), 1124 (s), 1097 (s), 857 (s), 770 (s). MS (EI) (70 eV) *m*/*z* (%): 209.2 (43) [M]$^+$, 164.2 (46) [M-CH$_2$OCH$_3$]$^+$, 135.2 (100) [M-NH(CH$_2$)$_2$OCH$_3$]$^+$. Anal. calcd for $C_{12}H_{19}NO_2$ (209.3): C 68.87, H 9.15, N 6.69%; found: C 68.68, H 8.78, N 6.32%.

Ligand HL4. 3,5-Di-methyl-2-hydroxybenz-aldehyde[33] (3.00 g, 20 mmol) and *N*,*N*-dimethylethylenediamine (2.29 g, 26 mmol) were dissolved in methanol (80 ml). Pd/C (0.30 g) was added and the mixture was exposed to H_2 gas (7 bar). After purification, the ligand was obtained as a colorless viscous oil. Yield: 4.06 g (97%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, ppm) δ 2.21 (s, 3H, Ar-CH_3), 2.22 (s, 3H, Ar-CH_3), 2.23 (s, 6H, N(CH_3)$_2$), 2.44 (t, $^3J_{H\text{-}H}$ = 5.7 Hz, 2H, N(CH_2)$_2$N), 2.70 (t, $^3J_{H\text{-}H}$ = 5.7 Hz, 2H, N(CH_2)$_2$N), 3.93 (s, 2H, Ar-CH_2N), 6.65 (s, 1H, Ar-*H*), 6.86 (s, 1H, Ar-*H*). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, ppm) δ 15.71 (Ar-*C*H$_3$),

20.48 (Ar-CH_3), 45.49 (2× N(CH_3)$_2$), 45.87 (N(CH_2)$_2$N), 52.64 (Ar-CH_2N), 58.31 (N(CH_2)$_2$N), 121.70 (*Ar*), 124.82 (*Ar*), 126.42 (*Ar*-H), 127.37 (*Ar*), 130.39 (*Ar*-H), 154.07 (*Ar*-OH). The protons of the N*H* and O*H* group were not detected in benzene-d_6 or in chloroform-*d*. IR (ATR, cm^{-1}): ν 2856 (m), 1612 (w, NH), 1482 (s), 1245 (s), 1156 (m), 1039 (m), 856 (s), 774 (s), 735 (m). MS (EI) (70 eV) *m*/*z* (%): 222.2 (27) [M]$^+$, 163.1 (100) [M-(CH$_2$N(CH$_3$)$_2$)-H]$^+$, 135.2 (38) [M-NH(CH$_2$)$_2$N(CH$_3$)$_2$]$^+$. Anal. calcd for $C_{13}H_{22}N_2O$ (222.3): C 70.23, H 9.97, N 12.60%; found: C 70.50, H 10.52, N 12.36%.

General procedure for the synthesis of the complexes

The appropriate ligand (1 mmol, 1 equiv.) was dissolved in methanol (3 ml) and slowly added to a solution of 326 mg [MoO_2(acac)$_2$] (1 mmol, 1 equiv.) in methanol (3 ml). Distilled water (0.36 ml, 2 mmol, 2 equiv.) was added *via* syringe. The solution was stirred over-night at 25 °C. The resulting precipitate was filtered and washed twice with cold methanol (2 × 3 ml). The complex was dissolved in CH_2Cl_2 (5 ml) and filtered over a pad of Celite. The pure complex was dried under vacuum.

[{MoO$_2$(L1)}$_2$(μ-O)] (1). Synthesis of complex **1** followed the general procedure described above. A solution of the ligand HL**1** (0.29 g, 1 mmol) in methanol (1 ml) was added to a solution of [MoO_2(acac)$_2$] (0.33 g, 1 mmol) in methanol (3 ml). After purification, complex **1** was obtained as yellow solid. Yield: 0.68 g (79%).

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, ppm) δ 1.29 (s, 3H, C(CH_3)$_3$), 1.44 (s, 3H, C(CH_3)$_3$), 2.77–2.98 (m, 2H, N(CH_2)$_2$O), 3.58 (dd, *J* = 9.5, 2.9 Hz, 1H, N(CH_2)$_2$O), 3.88 (s, 1H, OCH_3), 3.93 (m, 1H, Ar-CH_2N), 4.06 (dt, *J* = 12.4, 9.5, 3.0 Hz, 1H, N(CH_2)$_2$O), 4.77 (m, 2H, Ar-CH_2N*H*), 6.87 (d, *J* = 2.5 Hz, 1H, Ar-*H*), 7.28 (d, *J* = 2.4 Hz, 1H, Ar-*H*). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, ppm) δ 29.79 (Ar-C(*C*H$_3$)$_3$), 31.75 (Ar-C(*C*H$_3$)$_3$), 34.47 (Ar-*C*(CH$_3$)$_3$), 35.28 (Ar-*C*(CH$_3$)$_3$), 45.98 (N(*C*H$_2$)$_2$O), 54.09 (Ar-*C*H$_2$N), 62.42 (O*C*H$_3$), 70.74 (N(*C*H$_2$)$_2$O), 120.31 (*Ar*), 123.47 (*Ar*-H), 124.19 (*Ar*-H), 138.21 (*Ar*), 142.98 (*Ar*), 155.65 (*Ar*-O). IR (ATR, cm^{-1}): ν 1468 (w), 1442 (w), 1244 (m), 1055 (m), 933 (m), 919 (m), 897 (Mo═O, s), 885 (Mo═O, s), 854 (s), 739 (Mo-(μ-O), s, br), 554 (m). Found: C, 48.23; H, 6.78; N, 3.39%; calcd for $Mo_2O_9N_2C_{36}H_{60}$·0.74 CH_2Cl_2: C, 48.00; H, 6.74; N, 3.05%.

[{MoO$_2$(L2)}$_2$(μ-O)] (2). Synthesis of complex **2** followed the general procedure described above. A solution of the ligand HL**2** (0.31 g, 1 mmol) in methanol (1 ml) was added to a solution of [MoO_2(acac)$_2$] (0.33 g, 1 mmol) in methanol (3 ml). After purification, complex **2** was obtained as light red solid. Yield: 0.85 g (96%). Crystals suitable for X-ray diffraction analyses were obtained from diluted acetonitrile solutions at room temperature.

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, ppm) δ 1.27 (s, 3H, C(CH_3)$_3$), 1.47 (s, 3H, C(CH_3)$_3$), 2.39 (d, *J* = 13.0 Hz, 1H, N(CH_2)$_2$N), 2.59 (s, 3H, N(CH_3)$_2$), 2.80 (m, 2H, N(CH_2)$_2$N), 2.86 (s, 3H, N(CH_3)$_2$), 3.12 (m, 1H, N(CH_2)$_2$N), 3.95 (d, *J* = 14.8 Hz,1H, Ar-CH_2N), 4.75 (d, *J* = 14.5 Hz, overlapping signals, 2H, Ar-CH_2N*H*), 6.82 (s, 1H, Ar-*H*), 7.25 (s, 1H, Ar-*H*). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, ppm) δ 30.44 (Ar-C(*C*H$_3$)$_3$), 31.73 (Ar-C(*C*H$_3$)$_3$), 34.40 (Ar-*C*(CH$_3$)$_3$), 35.38 (Ar-*C*(CH$_3$)$_3$), 45.96 (N(*C*H$_2$)$_2$N), 47.93 (N(CH$_3$)$_3$), 50.76 (N(CH$_3$)$_3$), 54.29 (Ar-*C*H$_2$N), 58.77 (N(*C*H$_2$)$_2$N), 120.43 (*Ar*), 122.97 (*Ar*-H), 123.92 (*Ar*-H), 137.80 (*Ar*), 142.70 (*Ar*), 157.73 (*Ar*-O). IR (ATR, cm^{-1}): ν 1439 (w), 1241 (m), 918 (Mo═O, m), 880 (Mo═O, s), 842 (s), 711 (Mo-(μ-O), s, br), 547 (s). Found: C, 50.02; H, 6.34; N, 7.32%; calcd for $Mo_2O_7N_4C_{38}H_{66}$·0.49 CH_2Cl_2: C, 50.00; H, 6.06; N, 7.30%.

[{MoO$_2$(L4)}$_2$(μ-O)] (3). Synthesis of complex **3** followed the general procedure described above. A solution of the ligand HL**3** (0.22 g, 1 mmol) in methanol (1 ml) was added to a solution of [MoO_2(acac)$_2$] (0.33 g, 1 mmol) in methanol (3 ml). After purification, complex **3** was obtained as orange solid. Yield: 0.39 mg (88%). Crystals suitable for X-ray diffraction analyses were obtained from concentrated dichloromethane solutions at −30 °C.

^{1}H NMR (300 MHz, chloroform-*d*, 298 K, ppm) δ 2.22 (s, 3H, Ar-CH_3), 2.23 (s, 3H, Ar-CH_3), 2.32 (dd, *J* = 13.0, 2.6 Hz, 1H, N(CH_2)$_2$N), 2.47 (s, 3H, N(CH_3)$_2$), 2.63 (dt, *J* = 13.6, 10.9, 3.0 Hz, 1H, N(CH_2)N), 2.76 (m, 1H, N(CH_2)$_2$N), 2.84 (s, 3H, N(CH_3)$_2$), 3.11 (dt, *J* = 13.0, 3.5 Hz, 1H, N(CH_2)N), 3.85 (dd, *J* = 14.7, 1.9 Hz, 1H, Ar-CH_2N), 4.75 (dd, *J* = 14.6, 3.0 Hz, 1H, Ar-CH_2N), 4.83 (m, 1H, Ar-CH$_2$N*H*), 6.67 (s, 1H, Ar-H), 6.91 (s, 1H, Ar-H). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K, ppm) δ 16.78 (Ar-*C*H$_3$), 20.62 (Ar-*C*H$_3$), 44.58 (N(*C*H$_2$)$_2$N), 46.66 (N(*C*H$_3$)$_2$), 50.85 (N(*C*H$_3$)$_2$), 53.46 (Ar-*C*H$_2$N), 58.54 (N(*C*H$_2$)$_2$N), 120.63 (*Ar*), 127.26 (*Ar*), 127.63 (*Ar*-H), 129.62 (*Ar*), 130.63 (*Ar*-H), 155.69 (*Ar*-O). IR (ATR, cm^{-1}): ν 1475 (m), 1231 (m), 1161 (m), 912 (Mo═O, s), 878 (Mo═O, s), 828 (s), 710 (Mo-(μ-O), s, br), 589 (m), 536 (s). Found: C, 43.26; H, 5.78; N, 7.68%; calcd for $Mo_2O_7N_4C_{26}H_{42}$·0.21 CH_2Cl_2: C, 43.00; H, 5.84; N, 7.65%.

Epoxidation of alkenes

In a typical epoxidation reaction, the catalyst (7.05×10^{-3} mmol, 0.5 mol%), the corresponding alkene (1.41 mmol, 1 equiv.) and internal standard (1.41 mmol, 1 equiv.) were combined in chloroform (5 ml). After stirring the mixture for 5 minutes, the epoxide reaction was started with the addition of TBHP (0.5 ml of a 5.5 M solution in decane, 2.82 mmol, 2 equiv.). The reactions were monitored quantitatively by GC-MS (cyclooctene, cyclohexene, styrene, α-terpineol, *R*-(+)-limonene), HPLC (*cis*-stilbene, *trans*-stilbene) or ^{1}H NMR (1-octene and 2-propenol) analyses. At fixed intervals samples were taken and residual TBHP traces were quenched with MnO_2. After centrifugation, sample aliquots were diluted with ethyl acetate (for GC-MS) or acetonitrile (for HPLC). Mesitylene was used as internal standard for GC-MS and HPLC measurements. ^{1}H NMR spectra were measured in chloroform-*d* using dichloroethane as internal standard.

X-ray structure determination

For X-ray structure analyses the crystals were mounted on the tip of glass fibres and data collection was performed at 100 K using graphite monochromated MoKα radiation (λ = 0.71073 Å) with a BRUKER-AXS SMART APEX II diffractometer equipped with a CCD detector. The structures were solved by direct methods (SHELXS-97 (ref. 34) or SIR92 (ref. 35)) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[36]

If not otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. All hydrogen atoms were fixed in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 50% probability thermal ellipsoids, and all H atoms, except for the H atom of the NH moiety, were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **2** and **3** are reported.†

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