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Bidentate Lewis base adducts of molybdenum(VI): Ligand impact on catalytic performance and stability

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ABSTRACT

The reaction of solvent substituted $[MoO_2Cl_2](THF)_2$ complexes with 1 equiv. of bidentate nitrogen donor ligands leads to complexes of the type $[MoO_2Cl_2L_2]$ (L_2 = 4,5-diazafluorene-9-one; 1,10-phenanthroline-5,6-dione; 2,2′-biquinoline-4,4′-dicarboxylic acid, diethyl ester; 3,6′-bis-2-pyridyl-pyridazine; 4,4′-di-ethoxycarbonyl-2,2′-bipyridine) in quantitative yields at room temperature under inert gas atmosphere within a few minutes. The catalytic activity of the $[MoO_2Cl_2L_2]$ complexes in olefin epoxidation with t-butyl hydroperoxide as oxidizing agent is strongly influenced by the nature of the ligand L and its steric demand. The complexes, with the sole exception of compound **9** [MoO_2Cl_2(1,10-phenanthroline-5,6-dione)], are very active and highly selective epoxidation catalysts. The influence of the terminal oxo ligands together with the Lewis base ligands on the Mo center obviously keeps the compounds on a quite stable level of electron density.

1. Introduction

The coordination chemistry of molybdenum continues to be the subject of considerable research efforts. This is in part due to the occurrence of Mo in the active sites of biologically important species, such as molybdoenzymes [1]. The flexibility of molybdenum to appear in a broad variety of oxidation states [2] – from Mo^{VI} to Mo^0 (and even Mo^{-II}) – makes molybdenum(VI) complexes versatile catalysts for various reactions, among them the oxidation of organic compounds [3,4]. Treatment of MoO_2Cl_2 species (X = halide, OR, $OSiR_3$) with Lewis bases, such as pyridine, 2,2′-bipyridine and 1,10-phenanthroline, and with donor solvents, such as acetonitrile and THF, gives adducts of the composition $[MoO_2X_2L_2]$ [5–8]. It has been shown that complexes of the type $[MoO_2X_2L_2]$ are excellent catalyst precursors for the epoxidation of olefins in the presence of *tert*-butyl hydroperoxide (TBHP) as a oxygen source [9–12]. TBHP has a good thermal stability and is comparatively easy to handle [13]. Furthermore, the byproduct of the reaction, *tert*-butanol, is easy to separate by distillation and can be recycled or used for other industrial processes [14]. Important properties, such as the solubility of the complex and the Lewis acidity of the metal center, can be fine-tuned by variation of either X or L. These adjustments allow highly active and selective catalysts to be prepared [15]. The first X-ray crystal structure of a $[MoO_2X_2L_2]$-type complex has been reported already in 1966 [16]. The $[MoO_2X_2L_2]$ complexes are monomeric and present a distorted octahedral geometry, with the oxo ligands *cis* to each other in order to maximize the π donation into the empty t_{2g} set orbitals [17].

Concerning the reaction mechanism, it has been generally agreed that formation of a Mo(VI) alkyl peroxide occurs, followed by transfer of the distal oxygen atom of the alkyl peroxide rather than an oxo ligand [18]. The activity of d^0 M-oxo catalysts in olefin epoxiation depends on the Lewis bases, the redox stability of the ligands, and particularly on the stability of the adduct complexes [12,19,20]. The activity was also found to be influenced by both the electronic and steric nature of the ligands [21]. In addition, substituted bipyridines can enhance the catalyst solubility in organic solvents [22–24]. Adduct stability and loss of the bipyridine ligand in solution (especially in donor solvents, such as THF or CH_3CN) is a major concern when applying these catalysts under homogeneous conditions. The release of the Lewis base ligand affects the activity of the catalyst (due to polymerization and precipitation of MoO_2X_2) and leads to the oxidation of not coordinated bipyridine [12]. Accordingly, the whole catalytic system is destroyed.

In this work, the synthesis and spectroscopic properties of $[MoO_2Cl_2L_2]$(L_2 = **5**: 4,4′-di-ethoxycarbonyl-2,2′-bipyridine; **7**: 2,2′-biquinoline-4,4′-dicarboxylic acid, diethyl ester; **8**: 4,5-diazafluorene-9-one; **9**: 1,10-phenanthroline-5,6-dione; **10**: 3,6′-bis-2-pyridyl-pyridazine) are reported. The effect of the different functional groups on the bipyridine ring to the catalytic activity is in the focus of the present study.

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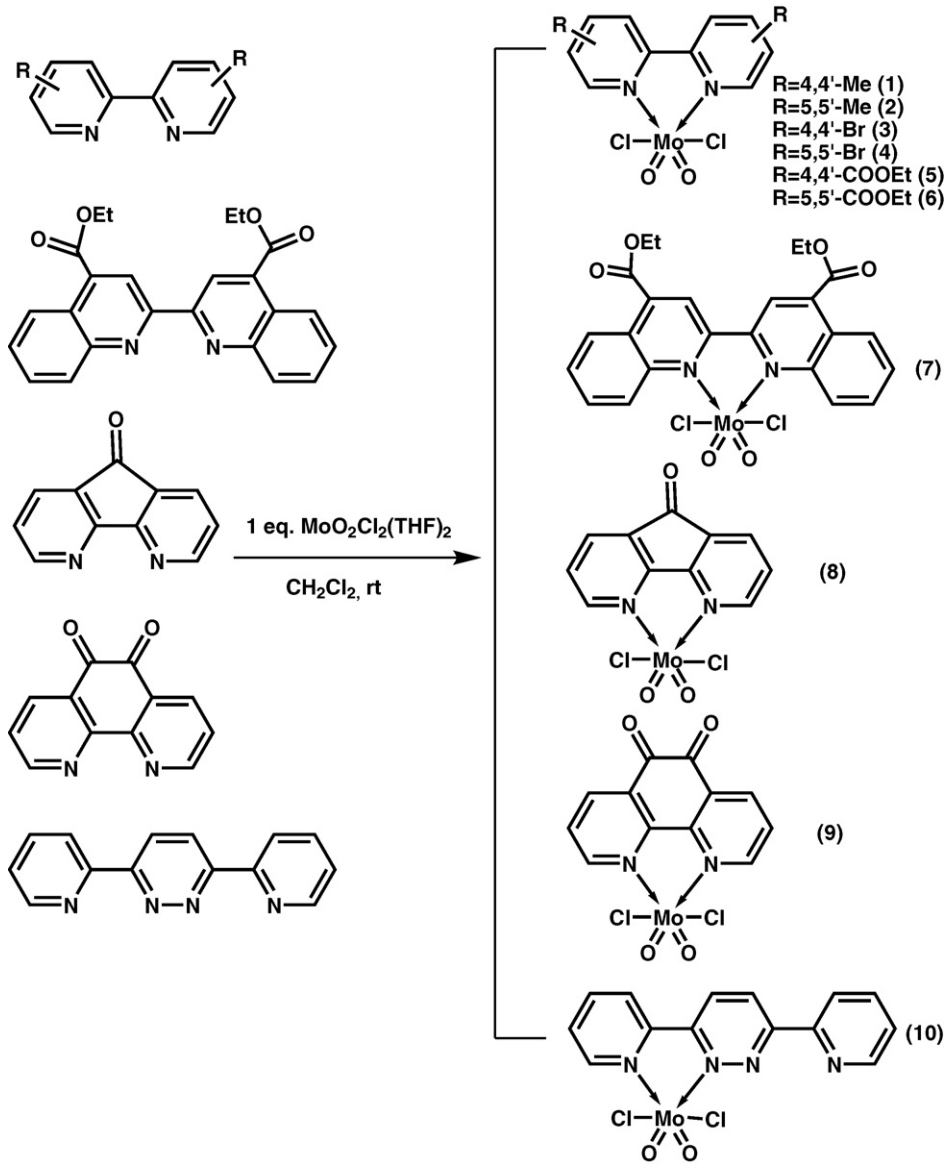


Scheme 1. Synthesis and structures of complexes **1**–**10**.

2. Results and discussion

In a previous work, the synthesis of a series of dioxomolybdenum(VI) bipyridine derived complexes, in which the ligands have different functional groups at different positions on the bipyridine rings, have been described [25]. Among the complexes described there are 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine, 4,4′-dibromo-2,2′-bipyridine, 5,5′-dibromo-2,2′-bipyridine, 5,5′-di-ethoxycarbonyl-2,2′-bipyridine, which are also included in this paper as complexes **1**–**4** and **6** for sake of a detailed comparison of their catalytic abilities in the olefin epoxidation. For the present work some other bipyridine derivatived dioxo-

Table 1
Selected FT-IR (KBr), calculated force constants f(Mo = O) for $[MoO_2Cl_2L_2]$ and ^{95}Mo NMR spectroscopic data for complexes **1**–**10**.

Complexes	υ(Mo = O) (cm^{-1})			f(Mo = O) (m dyn $Å^{-1}$)	Decomp. temp. (°C)	$\delta(^{95}Mo)$ (ppm)	Deuterated solvent
	υ_s	υ_{as}	$\upsilon_{average}$				
1	938	907	922.5	6.82	Not determined	–	–
2	904	937	920.5	6.79	375	–	–
3	912	942	927	6.89	375	–	–
4	908	941	924.5	6.85	300	–	–
5	950	914	932	6.97	250	202	$CDCl_3$
6	945	911	928	6.91	275	194	CD_3NO_2
7	951	918	934.5	7.00	300	198	$CDCl_3$
8	949	916	932.5	6.97	250	–	–
9	943	916	929.5	6.93	325	207	CD_3NO_2
10	943	916	929.5	6.93	400	–	–

molybdenum(VI) complexes have been prepared. Scheme 1 shows the reactions of $[MoO_2Cl_2(THF)_2]$ with various bidentate Lewis bases.

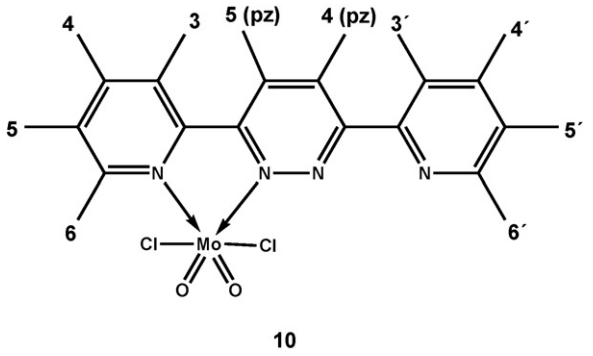
2.1. Synthesis and spectroscopic characterization of complexes **1–10**

Scheme 1 exhibits the complexes **1**–**10**, which were obtained as microcrystalline powders in good yields by addition of 1 equiv. of the bidentate Lewis bases to a solution of adduct $[MoO_2Cl_2(THF)_2]$ in dichloromethane solution at room temperature. Due to the poor solubility of newly synthesized complexes, no crystal structure was obtained. In contrast to some of the monodentate Lewis base adducts of dichlorodioxomolybdenum(VI), and solvent stabilized starting materials, all synthesized bidentate $[MoO_2Cl_2L_2]$-type complexes are stable under laboratory atmosphere and can be handled in air. This represents a remarkable difference to monodentate Lewis base adducts of dichlorodioxomolybdenum(VI) and the THF substituted starting materials, which are in most cases both air- and moisture-sensitive and can only be handled and stored under moisture-free inert gas atmosphere. The better donor capabilities and presumably also the greater steric demand of the chelating product complexes **5**, **7**–**10** stabilize these molecules significantly.

The characterization of the compounds presented here is straightforward and exhibits no unusual features in comparison with other Lewis base adducts of bis(halogeno)dioxomolybdenum(VI) prepared using the same method [18b]. The FT-IR spectra of the complexes display a very strong symmetric Mo=O stretching vibration in the region of 943–950 cm^{-1} while the asymmetric Mo=O stretching vibration lies between 914 and 918 cm^{-1} (see Table 1). The corresponding force constants of the Mo=O bonds can be derived from the υ (Mo=O) values. The force constants of the complexes **5** and **7**–**10** range from 6.93 to 7.00 m dyn $Å^{-1}$. However, when compared to the force constant of $[MoO_2Cl_2(bipy)]$ (6.73 m dyn $Å^{-1}$) [18b] the values obtained for the complexes described in this work are higher, indicating stronger Mo=O bonds in the case of the MoO_2Cl_2–Lewis base adducts presented here. Lewis base ligands (except L**5**) used in this work were also studied ligating methyltrioxorhenium(VII) (MTO) [26]. In the Mo case, the nitrogen atoms of the organic ligands are bound more strongly. In the MTO case reactions with the ligands used to obtain compounds **9** and **10** gave isolable adducts. The *f*(Re=O) force constant of the MTO adducts with L**9** (7.46 m dyn $Å^{-1}$) and with L**10** (7.49 m dyn $Å^{-1}$) are considerably stronger than their molybdenum adducts. This is most likely due to the weaker Re–L interactions and its stronger Lewis acidity, leading to stronger Re=O bonds.

The ^{1}H NMR spectra of complexes **5**, **7**–**10** were measured at room temperature using either CD_3NO_2 or $CDCl_3$ as solvent. Complexes **8** and **10** however, are only fairly soluble in CD_3NO_2. Nevertheless, the majority of the prepared complexes are soluble enough in polar, non-coordinating organic solvents to give ^{1}H NMR spectra of sufficient resolution. In general, the spectroscopic data for these complexes are in good agreement with those obtained for previously described Lewis base adducts [18b]. The proton signals of all examined compounds are shifted to lower field after complexation.

Upon coordination, the ligand affects both the electronic and the steric environment of the molybdenum(VI) complex. The chemical shift differences between the free ligands and the corresponding ligated complexes largely depend on the electron-donating ability of each ligand to the metal center. The presence of electron-donating or withdrawing group(s) on the bidentate ligands of course influences the stability of the adduct [20]. Complex **9** is considerably more stable than complex **8**. Consequently, the ^{1}H NMR signals of complex **9** display higher shielding compared to complex **8**.



10

Scheme 2. Numbering scheme for the assignment of the ^{1}H NMR spectra of complex **10**.

The ^{95}Mo NMR shift differences between the synthesized complexes under investigation are comparatively small. Complexes of the composition $[MoO_2Cl_2L_2]$ generally display their ^{95}Mo NMR signals in the range of 160–220 [27]. For example, the difference of the chemical shift of complex **6** and complex **7** (determined, however, in different solvents (CD_3NO_2 and $CDCl_3$)) is less than 5 ppm (see Table 1).

In the case of complex **10** with four nitrogen atoms, elemental analysis indicates a 1:1 coordination. It is assumed that the Mo atom of MoO_2Cl_2 coordinates as shown in Scheme 2. Nevertheless, in the NMR spectrum in DMSO recorded at room temperature, comparatively broad proton peaks can be observed, representing the pyridazine protons and the $H^{3,3'}$, $H^{4,4'}$, $H^{5,5'}$, $H^{6,6'}$ protons of the pyridines. This can be interpreted as a (slow) exchange of the MoO_2Cl_2 moiety between the two bidentate ligand sites at room temperature. In order to clarify this, a temperature-dependent ^{1}H NMR experiment was also performed in CD_2Cl_2. The spectrum shows that the original peak groups get much more defined into well resolved 10 distinctive groups when the temperature is lowered to −90 °C (see Fig. 1). Accordingly it can be concluded that below room temperature the MoO_2Cl_2 moiety is bonded to one distinctive coordination site at the ligand. This contrasts somewhat with the situation of a coordinating MTO unit, where the molecule does not undergo exchange phenomena only at lower temperature. This is in good agreement with the notion that bidentate ligands coordinate much stronger to MoO_2Cl_2 than to MTO [25,27,28].

Thermogravimetric analysis (TGA) was performed for all compounds (see Table 1). The onset of the first decomposition temperature for the compound **9** (325 °C) is higher than compound **8** (250 °C), which also proves the high stability of the former complex. In the case of ethoxycarbonyl substituted complexes, complex **6** is more stable than **5**. The electron withdrawing effect of ethoxycarbonyl ligands is more effective in the 4,4′ than the 5,5′-positions, therefore, the donor ability of ligand **5** is weaker than that of ligand **6**. Concerning the different functional groups in 4,4′-positions, the onset of the first decomposition temperature for complex **5** (250 °C), is lower than for compound **3** (375 °C). Accordingly, **3** is more temperature stable than **5** and **3** has a weaker Mo=O bond (smaller force constant) than **5**. Accordingly, the Mo–N bonds should be stronger in **3**, consistent with the observed decomposition onset.

2.2. Application in epoxidation catalysis

The synthesized molybdenum(VI) compounds were tested as catalysts for the epoxidation of cyclooctene with TBHP (Figs. 2 and 3). A detailed description of the catalytic reactions is given in Section 4. In the absence of a catalyst, no significant amount of epoxide is formed. Two series of experiments with different cat-

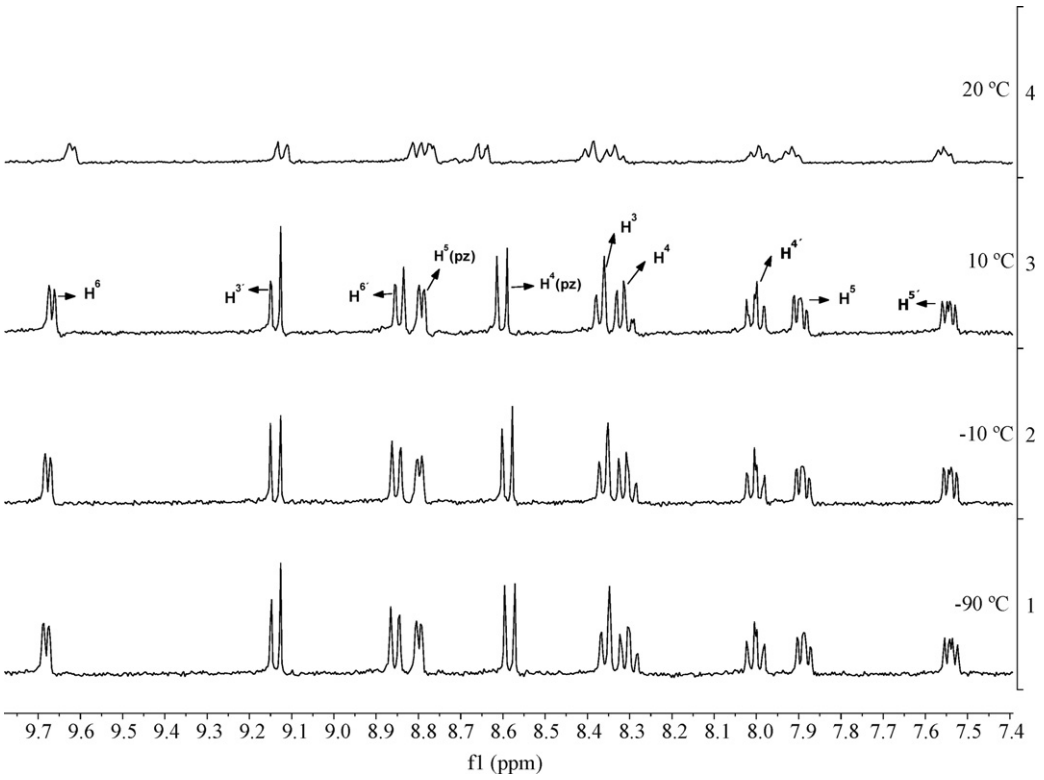


Fig. 1. Temperature-dependent ^{1}H NMR spectra of complex **10**.

alyst:substrate:oxidant ratios (1:100:150 and 1:1000:1500) were undertaken at 55 °C in order to compare the catalytic potential of the systems. The catalytic reactions show time dependent curves in which the yield increases quickly in the initial part of the reaction and thereafter slows down when the reaction approaches completeness, due to an increasing lack of substrate (Figs. 2 and 3). All examined compounds except complex **9** show quite high catalytic activity. Particularly complexes **5**, **7**, **8** and **10** display TOFs higher than 900 h^{-1} and reach yields well exceeding 80% within the first hour of reaction time (see Table 2). Yet, complex **9** shows a very low activity during an initial phase at the reaction, lasting for more than 1 h.

When comparing a series of complexes with the functional groups in the same positions of the bipy-rings, the -Br ligated compounds are more active than the COOEt ligated complexes and all of them are more active than the $-CH_3$ ligated complexes. This is in accord with the donor/acceptor capabilities of these complexes. The effect of the ring substituents is most pronounced when they are *trans*-positioned to the oxo ligands. Only compound **3** is more catalytically active than the not ligated compound MoO_2Cl_2, which is however by far the most sensitive compound and cannot be handled in air or in the presence of moisture without (at least partial) decomposition, associated with a drastic reduction of its activity. The somewhat lower catalytic activity of compound **7** in comparison to compound **5** can be ascribed both the sterical reasons (larger ligands, blocking the equatorial plane) and to electronic reasons. The particularly low activity of compound **9**, however, seems to be due to electronical reasons. In case of compound **10**, a certain sterical hindrance may also play a role.

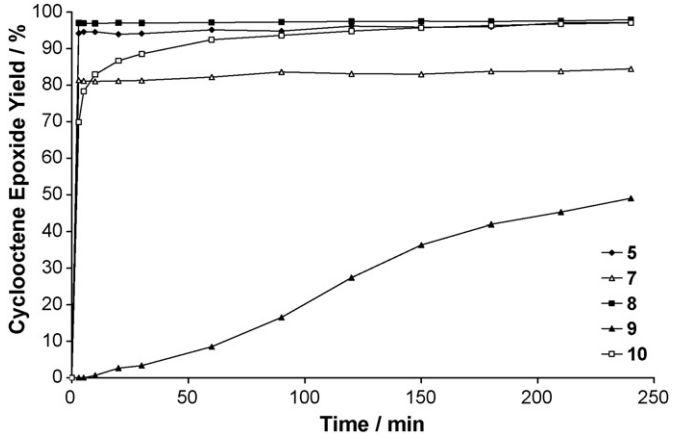


Fig. 2. Time dependent yield of cyclooctene epoxide in the presence of MoO_2Cl_2 and compounds **5**, **7**–**10** as catalysts at 55 °C with 1 mol% catalyst concentration between 0 and 4 h.

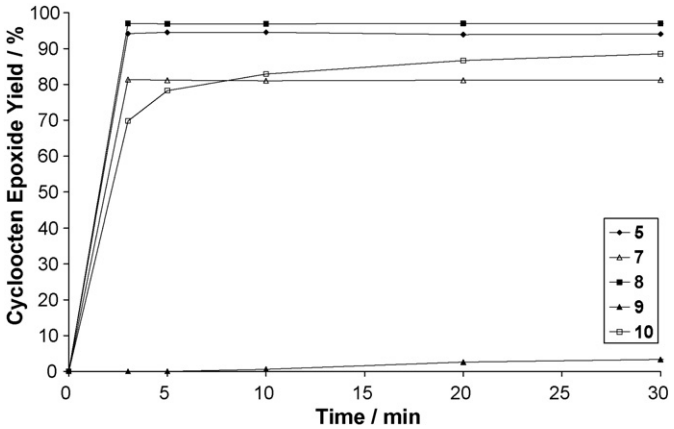


Fig. 3. Time dependent yield of cyclooctene epoxide in the presence of MoO_2Cl_2 and compounds **5**, **7**–**10** as catalysts at 55 °C with 1 mol% catalyst concentration between 0 and 30 min.

Table 2
Approximate TOF values after 5 min for MoO_2Cl_2 and complexes **1**–**8** and **10** using cyclooctene as substrate (catalyst concentration 1 mol%).

Compound	TOF [h^{-1}]
MoO_2Cl_2	1181
1	923
2	862
3	1583
4	1124
5	1135
6	1069
7	974
8	1163
9	10
10	939

The TOF of complex **9** was calculated at the time interval of highest conversion. The TOF value for MoO_2Cl_2 has been determined under argon atmosphere and strict exclusion of water. The TOF value for complex **1** has been re-measured and turns out to be higher than reported before [21].

When changing the catalyst:substrate:oxidant ratio from 1:100:150 to 1:1000:1500 for most active complexes **5** and **8** do not change the activity significantly. The TOF changes from ca. 1135 h^{-1} (catalyst:substrate:oxidant ratio 1:100:150) to ca. 1102 h^{-1} (catalyst:substrate:oxidant ratio 1:1000:1500) for complex **5** and ca. 1163 h^{-1} (catalyst:substrate:oxidant ratio 1:100:150) to ca. 1156 h^{-1} (catalyst:substrate:oxidant ratio 1:1000:1500) for complex **8**. It appears that optimal activities for the system have been reached with a 1:1000:1500 ratio. Lowering the reaction temperature to 25 °C however lowers the activity. In the case of compound **5**, using a catalyst:substrate:oxidant ratio 1:100:150, the TOF decreases from ca. 1135 h^{-1} (at 55 °C) to ca. 78 h^{-1} (at 25 °C).

Adding a second batch of substrate after the first run in the catalyst:substrate:oxidant ratio 1:100:150 system, the reaction reaches still more than 90% product yield within 4 h. However, the reaction is not as fast as observed for the first run. This phenomenon is already known from related complexes and has been ascribed to a reaction of the catalyst with the byproduct *t*-BuOH, rather than a catalyst decomposition [10]. It is important to note that the reaction is selective to the desired epoxide and that no diol formation is observed.

3. Conclusions

Molybdenum(VI) complexes of general formula $[MoO_2Cl_2L_2]$ are synthesized from $[MoO_2Cl_2(THF)_2]$ and substituted 2,2′-bipyridine ligands. The coordination of bidentate Lewis base ligands to Mo(VI) is governed by both electronic and steric effects due to the contributions of different functional groups on the bipyridine ligands. The ^{1}H NMR spectra clearly reflect the electron-donating capabilities of the ligands. The stronger the donor ability of the Lewis base, the larger is the observed shift. The bipyridine derived complexes show high selectivities and/in most cases/good catalytic activities for olefin epoxidation. The best catalysts among the examined ones are those with only moderate donating capabilities and without steric hindrance of the ring sustituents with respect to the MoO_2Cl_2 moiety.

4. Experimental

General: All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere with standard Schlenk techniques. MoO_2Cl_2 and 3,6′-bis-2-pyridyl-pyridazine were purchased from Aldrich and used as received. Solvents were dried by standard procedures, distilled, and kept under argon over molecular sieves (THF, and diethyl ether over Na/benzophenone ketyl; CH_2Cl_2 over CaH_2). The ligands 4,5-diazafluoren-9-one; 1,10-phenanthroline-5,6-dione; 2,2′-biquinoline-4,4′-dicarboxylic acid, diethyl ester; 4,4′-di-ethoxycarbonyl-2,2′-bipyridine, were prepared according to published procedures [29]. Elemental analyses were performed with a Flash EA 1112 series elemental analyzer. ^{1}H, ^{13}C NMR and ^{95}Mo NMR spectra were measured in either $CDCl_3$ or CD_3NO_2 with a 400 MHz Bruker Avance DPX-400 and Varian 400 spectrometer. IR spectra were recorded with a Perkin Elmer FT-IR spectrometer using KBr pellets as the IR matrix. Catalytic runs were monitored by GC methods on a Varian CP-3800 instrument equipped with a FID and a VF-5ms column. Thermogravimetric analyses were performed using a Netzsch TG209 system at a heating rate of 10 K min^{-1} under argon.

Warning: TBHP (in decane) is toxic, possibly mutagen, corrosive and a strong oxidizer. It is a combustible liquid and is readily absorbed through the skin and must be stored below 38 °C.

Synthesis of the complexes: The complex $[MoO_2Cl_2(THF)_2]$ was dissolved in CH_2Cl_2 (5 mL) and treated with 1 equiv. of ligands that were also dissolved in CH_2Cl_2 (10 mL). The resulting turbid solutions were each stirred for 1 h. The solvent was removed in vacuo, and the product washed with diethyl ether (2× 5 mL) and dried under vacuum.

[*MoO_2Cl_2(4,4′-di-ethoxycarbonyl-2,2′-bipyridine)*](**5**): $[MoO_2Cl_2(THF)_2]$ (1.08 mmol) Yield: 0.53 g (98%) color: white. Selected IR (KBr): ν(cm^{-1}) = 1730(vs), 1616(w), 1487(w), 1093(w), 950(vs) (Mo=O_{sym}), 914(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ (ppm) = 9.68 (d, $J_{H,H}$ = 4.98 Hz 2H, py-$H^{3,3'}$), 8.88 (s, 2H, py-$H^{6,6'}$), 8.27 (d, $J_{H,H}$ = 5.23 Hz 2H, py-$H^{5,5'}$), 4.55(q, 4H, CH_2), 1.48(t, $J_{H,H}$ = 7.61 6H, CH_3). ^{13}C NMR (100.28 MHz, $CDCl_3$, 20 °C): δ (ppm) = 163.18 (C=O), 153.06 (py-$C^{2,2'}$), 150.29 (py-$C^{6,6'}$), 142.53 (py-$C^{4,4'}$), 126.77 (py-$C^{5,5'}$), 122.70 (py-$C^{3,3'}$), 63.42 (CH_2), 14.41(CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 201.72 ppm. Anal. Calc. For $C_{16}H_{16}Cl_2MoN_2O_6$ (499.94): C 38.5, H 3.23, N 5.61. Found C 37.6, H 3.17, N 5.41.

[*MoO_2Cl_2(2,2′-biquinoline-4,4′-dicarboxylic acid, diethyl ester)*](**7**): $[MoO_2Cl_2(THF)_2]$ (0.2 mmol) Yield: 0.11 g (93%) color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1733(vs), 1591(s), 1458(w), 1385(vs), 1027(s), 951(vs) (Mo=O_{sym}), 918(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ (ppm) = 9.77 (d, $J_{H,H}$ = 9.68 Hz 2H, py-$H^{3,3'}$), 8.89 (d, $J_{H,H}$ = 10.67 Hz, 4H, benzyl-H), 8.09 (t, $J_{H,H}$ = 9.72 Hz, 2H, benzyl-H), 7.91 (t, $J_{H,H}$ = 8.84 Hz, 2H benzyl-H′), 4.66 (q, 4H CH_2), 1.60 (t, 3H CH_3). ^{13}C NMR (100.28 MHz, $CDCl_3$, 20 °C): δ (ppm) = 165.12 (C=O), 152.65 (py-$C^{2,2'}$), 147.51 (py-$C^{6,6'}$), 141.16 (py-$C^{4,4'}$), 133.20 (C-benzyl), 130.88 (C-benzyl) 129.92 (C-benzyl), 126.84 (C-benzyl), 126.10 (py-$C^{3,3'}$), 120.97 (py-$C^{5,5'}$) 63.35 (CH_2), 14.54 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 198.20 ppm. $C_{12}H_{12}Cl_2MoN_2O_2$ (615.00): calc. C 48.05, H 3.34, N 4.67; found C 46.28, H 3.60, N 4.22.

[*MoO_2Cl_2(4,5-diazafluoren-9-one)*](**8**): $[MoO_2Cl_2(THF)_2]$ (1.3 mmol) Yield: 0.47 g (95%) color: white. Selected IR (KBr): ν(cm^{-1}) = 1739(vs), 1584(vs), 1418(vs), 1106(s), 949(vs) (Mo=O_{sym}), 916(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, CD_3NO_2, 20 °C): δ (ppm) = 9.06 (d, $J_{H,H}$ = 5.40 Hz, 2H, py-$H^{6,6'}$), 8.38 (d $J_{H,H}$ = 7.36 Hz 2 H, py-$H^{4,4'}$), 7.90 (t, $J_{H,H}$ = 7.67 Hz 2 H, py-$H^{5,5'}$). $C_{11}H_6Cl_2MoN_2O_3$ (381.13): calc. C 34.66, H 1.57, N 7.35; found C 34.64, H 1.89, N 7.05.

[*MoO_2Cl_2(1,10-phenanthroline-5,6-dione)*](**9**): $[MoO_2Cl_2(THF)_2]$ (0.8 mmol) Yield: 0.27 g (87%) color: orange. Selected IR (KBr): ν(cm^{-1}) = 1700(vs), 1577(vs), 1482(s), 1022(s), 943(vs) (Mo=O_{sym}), 916(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, CD_3NO_2 20 °C): δ (ppm) = 9.65 (d, $J_{H,H}$ = 4.50 Hz 2H, py-$H^{6,6'}$), 8.87 (dd, $J_{H,H}$ = 8.06 Hz 2 H, py-$H^{4,4'}$) 8.15 (q, 2 H, py-$H^{5,5'}$). ^{13}C NMR (100.28 MHz, CD_3NO_2,

20 °C): δ (ppm) = 177.28 (C=O), 157.60 (py-$C^{6,6'}$), 150.17 (py-$C^{2,2'}$), 142.03 (py-$C^{4,4'}$), 131.67 (py-$C^{3,3'}$), 130.65 (py-$C^{5,5'}$). ^{95}Mo NMR (26 MHz, CD_3NO_2, 20 °C): δ = 206.61 ppm. $C_{12}H_6C_{l2}MoN_2O_4$ (409.88) calc C 35.24, H 1.48, N 6.85; found C 36.34, H 2.05, N 6.83.

[*MoO_2Cl_2*(3,6′-*bis*-2-*pyridyl-pyridazine*)](**10**): [$MoO_2Cl_2(THF)_2$] (0.8 mmol) Yield: 0.21 g (63%) color: white. Selected IR (KBr): ν(cm^{-1}) = 1700(vs), 1577(vs), 1482(s), 1022(s), 943(vs) (Mo=O_{sym}), 916 (vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, CD_3NO_2 20 °C): δ (ppm) = 9.61 (d, $J_{H,H}$ = 4.88 Hz 1H, py-H^6), 9.15 (d, $J_{H,H}$ = 9.17 Hz 1 H, py-H^3), 8.90 (d, $J_{H,H}$ = 8.89 Hz 1 H, py-$H^{6'}$), 8.81 (d, $J_{H,H}$ = 3.96 Hz 1H, pz-H^5), 8.76 (d, $J_{H,H}$ = 8.11 Hz 1H, pz-H^4), 8.63 (d, $J_{H,H}$ = 8.17 Hz 1H, py-H^3), 8.44 (t, $J_{H,H}$ = 9.35 Hz 1H, py-H^4), 8.08 (t, $J_{H,H}$ = 8.84 Hz 1H, py-$H^{4'}$), 7.99 (t, $J_{H,H}$ = 7.83 Hz 1H, py-H^5), 7.61 (t, $J_{H,H}$ = 7.83 Hz 1H, py-$H^{5'}$). $C_{14}H_{10}Cl_2MoN_4O_2$ (433.21): calc. C 38.81, H 2.31, N 12.93; found C 38.47, H 2.79, N 12.31.

4.1. Catalytic reactions

Cis cyclooctene (7.3 mmol), mesitylene (2.00 g, internal standard), and 1 mol% of compounds **5**, **7**–**10** (73 μmol, catalyst) were mixed in the reaction vessel under air at 55 °C. With the addition of TBHP (11 mmol, 5.5 M in decane) the reaction was started.

The course of the reaction was monitored by quantitative GC analysis. Samples were taken in regular time intervals, diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of cyclooctene and the formation of the according oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

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References

[1] J.M. Tunney, J. McMaster, C.D. Garner, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 8, Elsevier, Amsterdam, 2003, p. 459.
[2] M.B. Hursthouse, W. Levason, R. Ratnani, G. Reid, Polyhedron 23 (2004) 1915.
[3] K.A. Jørgensen, Chem. Rev. 89 (1989) 431.
[4] M.H. Dickman, M.T. Pope, Chem. Rev. 94 (1994) 569.
[5] G.-S. Kim, D. Huffman, C.W.D. Kock, Inorg. Chem. 28 (1989) 1279.
[6] M.H. Chisholm, K. Folting, J.C. Huffman, C.C. Kirkpatrick, Inorg. Chem. 23 (1984) 1021.
[7] F.E. Kühn, A.M. Santos, M. Abrantes, Chem. Rev. 106 (2006) 2455.
[8] Z. Petrovski, M. Pillinger, A.A. Valente, I.S. Gonçalves, A. Hazell, C.C. Romão, J. Mol. Catal. A: Chem. 227 (2005) 67.
[9] F.E. Kühn, E. Herdtweck, J.J. Haider, W.A. Herrmann, I.S. Gonçalves, A.D. Lopes, C.C. Romão, J. Organomet. Chem. 583 (1999) 3.
[10] F.E. Kühn, A.D. Lopes, A.M. Santos, E. Herdtweck, J.J. Haider, C.C. Romão, A.G. Santos, J. Mol. Catal. A: Chem. 151 (2000) 147.
[11] F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Gonçalves, E. Herdtweck, C.C. Romão, J. Mol. Catal. A: Chem. 164 (2000) 25.
[12] F.E. Kühn, A.M. Santos, I.S. Gonçalves, C.C. Romão, A.D. Lopes, Appl. Organomet. Chem. 15 (2001) 43.
[13] J.-M. Brègeault, J. Chem. Soc., Dalton Trans. (2003) 3289.
[14] S. Gago, J.E. Rodriguez-Borges, C. Teixeira, A.M. Santos, J. Zhao, M. Pillinger, C.D. Nunes, Z. Petrovski, T.M. Santos, F.E. Kühn, C.C. Romão, I.S. Gonçalves, J. Mol. Catal. A: Chem. 236 (2005) 1.
[15] S. Gago, M. Pillinger, A.A. Valente, T.M. Santos, J. Rocha, I.S. Gonçalves, Inorg. Chem. 43 (2004) 5422.
[16] C.G. Hull, M.B.H. Stiddard, J. Chem. Soc. A (1966) 1633.
[17] G. Barea, A. Lledos, F. Maseras, Y. Jean, Inorg. Chem. 37 (1998) 3321.
[18] (a) J.M. Mitchell, N.S. Finney, J. Am. Chem. Soc. 123 (2001) 862;
(b) F.E. Kühn, M. Groarke, É. Bencze, E. Herdtweck, A. Prazeres, A.M. Santos, M.J. Calhorda, C.C. Romão, I.S. Gonçalves, A.D. Lopes, M. Pillinger, Chem. Eur. J. 8 (2002) 2370;
(c) M. Groarke, I.S. Gonçalves, W.A. Herrmann, F.E. Kühn, J. Organomet. Chem. 649 (2002) 108;
(d) A.M. Al-Ajlouni, A.A. Valente, C.D. Nunes, M. Pillinger, T.M. Santos, J. Zhao, C.C. Romão, I.S. Gonçlaves, F.E. Kühn, Eur. J. Inorg. Chem. (2005) 1716;
(e) L.F. Veiros, A. Prazeres, P.J. Costa, C.C. Romão, F.E. Kühn, M.J. Calhorda, Dalton Trans. (2006) 1383.
[19] F.E. Kühn, A.M. Santos, P.W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I.V. Yudanov, C.D. Valentin, N. Rösch, Chem. Eur. J. 5 (1999) 3603.
[20] W.R. Thiel, J. Eppinger, Chem. Eur. J. 3 (1997) 696.
[21] A. Al-Ajlouni, A.A. Valente, C.D. Nunes, M. Pillinger, A.M. Santos, J. Zhao, C.C. Romão, I.S. Gonçalves, F.E. Kühn, Eur. J. Inorg. Chem. (2005) 1716.
[22] A. Togni, L.M. Venanzi, Angew. Chem., Int. Ed. Engl. 33 (1994) 497.
[23] F. Fache, E. Schulz, M.L. Tommasino, M. Lemaire, Chem. Rev. 100 (2000) 2159.
[24] A.K. Ghosh, P. Mathivanan, J. Cappiello, Tetrahedron: Asymmetry 9 (1998) 1.
[25] A. Günyar, M.-D. Zhou, M. Drees, P.N.W. Baxter, G. Bassioni, E. Herdtweck, F.E. Kühn, J. Chem. Soc., Dalton Trans. (2000) 1746.
[26] M.-D. Zhou, K.R. Jain, A. Günyar, P.N.W. Baxter, E. Herdtweck, F.E. Kühn, Eur. J. Inorg. Chem. (2009) 2907.
[27] J. Zhao, K.R. Jain, E. Herdtweck, F.E. Kühn, Dalton Trans. (2007) 5567.
[28] A.M. Al-Ajlouni, A. Günyar, M.-D. Zhou, P.N.W. Baxter, F.E. Kühn, Eur. J. Inorg. Chem. (2009) 1019.
[29] (a) C. Hiort, P. Lincoln, B. Nordén, J. Am. Chem. Soc. 115 (1993) 3448;
(b) P.N.W. Baxter, J.A. Connor, J.D. Wallis, D.C. Povey, A.K. Powell, J. Chem. Soc., Perkin Trans. 1 (1992) 1601;
(c) P.G. Hoertz, A. Staniszewski, A. Marton, G.T. Higgins, C.D. Incarvito, A.L. Rheingold, J.G. Meyer, J. Am. Chem. Soc. 128 (2006) 8234;
(d) C. Janiak, S. Deblon, H.-P. Wu, M.J. Kolm, P. Klufers, H. Piotrowski, P. Mayer, Eur. J. Inorg. Chem. (1999) 1507.