Journal of Molecular Catalysis A: Chemical 331 (2010) 117–124

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Highly soluble dichloro, dibromo and dimethyl dioxomolybdenum(VI)-bipyridine complexes as catalysts for the epoxidation of olefins

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ARTICLE INFO

Article history:
Received 27 May 2010
Received in revised form 29 July 2010
Accepted 5 August 2010
Available online 14 August 2010

Keywords:
Homogeneous catalysis
Molybdenum
Bipyridine complexes
Epoxidation
Ionic liquid

ABSTRACT

The reaction of solvent substituted $MoO_2X_2(S)_2$ (X = Cl, S = THF; X = Br, S = DMF) complexes with one equivalent of bidentate nitrogen donor ligands at room temperature leads within a few minutes to the quantitative formation of complexes of the type $[MoO_2X_2L_2]$ (L = 4,4′-bis-methoxycarbonyl-2,2′-bipyridine, 5,5′-bis-methoxycarbonyl-2,2′-bipyridine, 4,4′-bis-ethoxycarbonyl-2,2′-bipyridine, 5,5′-bis-ethoxycarbonyl-2,2′-bipyridine). Treatment of the complexes $[MoO_2Cl_2L_2]$ with Grignard reagents at low temperatures yields dimethylated complexes of the formula $[MoO_2(CH_3)_2L_2]$. $[MoO_2Br_2$(4,4′-bis-ethoxycarbonyl-2,2′-bipyridine)], $[MoO_2Br_2$(5,5′-bis-methoxycarbonyl-2,2′-bipyridine)] and $[MoO_2Br_2$(5,5′-bis-ethoxycarbonyl-2,2′-bipyridine)] have been exemplary examined by single crystal X-ray analysis. The complexes were applied as homogenous catalysts for the epoxidation of cyclooctene with *tert*-butyl hydroperoxide (TBHP) as oxidising agent under solvent-free conditions. The complexes containing L = Cl have been additionally investigated with room temperature ionic liquids (RTILs) as solvents. The catalytic activity of the $[MoO_2X_2L_2]$ complexes in olefin epoxidation with *tert*-butyl hydroperoxide is on average very good. The main advantage of the synthesised complexes in comparison to previously reported complexes is their high solubility. This good solubility is apparently the reason that the catalytic potential of the compounds can unfold. The turnover frequencies (TOFs) in RTILs are even higher, showing the performance of the catalysts under optimised conditions.

1. Introduction

Molybdenum(VI) complexes are applied as homogeneous catalysts in industrial processes for the epoxidation of propylene with alkyl hydroperoxides as oxygen source since many years [1]. Epoxides are important organic intermediates undergoing ring-opening reactions with a variety of reagents to yield mono- or bifunctional organic products [2,3]. In general, epoxides can be prepared by the reaction of olefins with hydrogen peroxide or alkyl hydroperoxides, catalyzed by transition metal complexes [1b,1c,4]. Among the variety of efficient catalysts known today for olefin epoxidation are several organometallic and inorganic oxides containing a metal in its highest oxidation state [5]. It is well known that complexes of the type $[MoO_2X_2(L)_n]$ (X = Cl, Br, CH_3; L = mono- or bidentate neutral N-ligand) are versatile catalyst precursors for the epoxidation of olefins in the presence of *tert*-butyl hydroperoxide (TBHP) [6–8]. Treatment of $[MoO_2X_2]$ species (X = halide, OR, $OSiR_3$) with Lewis bases (L or L_2), such as pyridine, 2,2-bipyridine, 1,10-phenanthroline and 4,4′-*tert*-butyl-2,2′-bipyridine, and with donor solvents such as acetonitrile and THF, leads to adducts of composition $[MoO_2X_2L_2]$ [5,9–11]. In the presence of TBHP as oxygen source some of these complexes have shown quite good catalytic activities. TBHP is one of the industrially preferred oxygen sources, partly because it is a mild and selective oxidant, not particularly corrosive or hazardous, and the byproduct of the reaction, *tert*-butyl alcohol, can be separated and recycled for use in other industrial processes [12]. Important properties, such as the solubility of the complex and the Lewis acidity of the metal centre can be fine-tuned by variation of both ligands X and L of the $[MoO_2X_2L_2]$ complexes.

Dioxomolybdenum(VI) halides and related compounds are useful precursors for the synthesis of other molybdenum complexes via oxygen or halogen/ligand abstraction or substitution [13–16]. The usual route to bromo complexes consists of reacting anhydrous $[MoO_2Br_2]$ with the appropriate ligand in aprotic solvents [17]. However, $[MoO_2Br_2]$ is not readily available [18,19] and has accordingly limited the coordination chemistry of this dibromodioxomolybdenum(VI) family. Another synthetic procedure is based on the reaction of aqueous solutions of molybdates in hydrobromic acid with neutral ligands [20]. However, the procedure has not been extended to the synthesis of related species. Thus, the number of

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1381-1169/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.molcata.2010.08.014

dioxomolybdenum(VI) bromide adducts that has been reported is low in comparison to those of $[MoO_2Cl_2]$ [17].

In this work the synthesis of well soluble compounds is described, since most of the $[MoO_2X_2(bipy)]$ compounds reported so far are only fairly soluble in most organic solvents. This low to moderate solubility appears to be responsible for the fact that $[MoO_2X_2L_2]$-type catalysts are usually regarded as inferior to other, related homogeneous epoxidation catalysts, such as CH_3ReO_3 (MTO) or $[CpMoO_2R]$ derivatives [5], although the $[MoO_2X_2L_2]$ compounds would be both cheaper and more easily accessible than the former compounds. Furthermore, the electronic contribution of the different functional groups in different positions at the bipyridine rings and the implications of these differences on the catalyst activity are examined.

2. Experimental

General: All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere with standard Schlenk techniques. $[MoO_2Cl_2]$, TBHP (5.5 M solution in decane, stored over molecular sieve) was purchased from Aldrich, 4,4′-dicarboxy-2,2′-bipyridine and 5,5′-dicarboxy-2,2′-bipyridine were purchased from HetCat and used as received. Solvents were dried by standard procedures, distilled, and kept under argon over molecular sieves (hexane, THF, and diethyl ether over Na/benzophenone ketyl, dichloromethane, chloroform over CaH_2, methanol and ethanol over Mg/I_2). $[MoO_2Br_2(DMF)_2]$ was prepared according to published procedures [21]. Elemental analyses were performed with a Flash EA 1112 series elemental analyzer. ^1H, ^{13}C and ^{95}Mo NMR spectra were measured in $CDCl_3$ with a 400 MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded with a PerkinElmer 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. X-ray structure determination [22] was carried out on an area detecting system (APEX II, κ-CCD) at the window of a rotating anode (Bruker AXS, FR591) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Raw data were corrected for Lorentz polarization, and, arising from the scaling procedure, for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimising $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography. Detailed information on the crystallographic data of compounds **6**, **7**, and **8** are provided in the supporting information.

Warning: TBHP (in decane) is toxic, possibly mutagen and a strong oxidiser. It is a combustible liquid and is readily absorbed through the skin and must be stored below 8 °C.

2.1. Ligand synthesis

An appropriate amount of 2,2′-bipyridine ligand precursors (1.0 g, 4.5 mmol) in methanol (17 ml) was added to concentrated sulfuric acid (2 ml), which is placed into an ice bath. After refluxing overnight, the solution was poured into water (42 ml) forming a white slurry. The pH of the slurry was adjusted to 8 with 25% (w/v) ammonia solution. The product was then extracted with chloroform, dried over magnesium sulfate and evaporated to dryness.

4,4′-Bis-methoxycarbonyl-2,2′-bipyridine: Yield 0.76 g (2.8 mmol, 62%). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 8.94 (s, 2H, py-$H^{6,6'}$), 8.84 (d, $^3J_{H,H}$ = 5.1 Hz, 2H, py-$H^{3,3'}$), 7.88 (dd, $^3J_{H,H}$ = 5.1 Hz, 2H, py-$H^{5,5'}$), 3.98 (s, 6H, CH_3).

4,4′-Bis-ethoxycarbonyl-2,2′-bipyridine: Yield 0.95 g (3.2 mmol, 71%). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 8.93 (s, 2H, py-$H^{6,6'}$), 8.84 (d, $^3J_{H,H}$ = 4.9 Hz, 2H, py-$H^{3,3'}$), 7.89 (dd, $^3J_{H,H}$ = 4.9 Hz, 2H, py-$H^{5,5'}$), 4.44 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, CH_2), 1.42 (t, $^3J_{H,H}$ = 7.8 Hz, 6H, CH_3).

5,5′-Bis-methoxycarbonyl-2,2′-bipyridine: Yield 0.72 g (2.6 mmol, 58%). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 9.28 (d, $^3J_{H,H}$ = 1.66 Hz, 2H, py-$H^{3,3'}$), 8.57 (dd, $^3J_{H,H}$ = 8.35 Hz, 2H, py-$H^{6,6'}$), 8.43 (dd, $^3J_{H,H}$ = 8.26 Hz, 2H, py-$H^{4,4'}$), 3.98 (s, 6H, CH_3).

5,5′-Bis-ethoxycarbonyl-2,2′-bipyridine: Yield 0.90 g (3 mmol, 67%). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 9.28 (s, 2H, py-$H^{3,3'}$), 8.56 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, py-$H^{6,6'}$), 8.42 (dd, $^3J_{H,H}$ = 8.6 Hz, 2H, py-$H^{4,4'}$), 4.43 (q, $^3J_{H,H}$ = 7.3 Hz, 4H, CH_2), 1.42 (t, $^3J_{H,H}$ = 7.7 Hz, 6H, CH_3).

2.2. Complex synthesis

Synthesis of complexes 1–4: 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 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′-bis-methoxycarbonyl-2,2′-bipyridine)](1) $[MoO_2Cl_2(THF)_2]$ (0.96 mmol). Yield: 0.45 g (95%). Color: white. Selected IR (KBr): ν(cm^{-1}) = 1726(vs), 1563(s), 1435(s), 1020(w), 951(vs), (Mo=O_{sym}), 918(vs) (Mo=O_{asym}). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 9.72 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, py-$H^{6,6'}$), 8.90 (s, 2H, py-$H^{3,3'}$), 8.28 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, py-$H^{5,5'}$), 4.10 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.7 (C=O), 153.2 (py-$C^{4,4'}$), 150.3 (py-$C^{2,2'}$), 142.1 (py-$C^{6,6'}$), 126.8 (py-$C^{3,3'}$), 122.7 (py-$C^{5,5'}$), 54.0 (CH_3). Anal. Calc. For $C_{14}H_{12}Cl_2MoN_2O_6$ (471.10): C 35.69, H 2.57, N 5.95. Found C 34.88, H 2.65, N 5.70.

$[MoO_2Cl_2$(5,5′-bis-methoxycarbonyl-2,2′-bipyridine)](2) $[MoO_2Cl_2(THF)_2]$ (1.75 mmol). Yield: 0.77 g (94%). Color: white. Selected IR (KBr): ν(cm^{-1}) = 1730(vs), 1608(s), 1431(vs), 1045(s), 942(vs), (Mo=O_{sym}), 910(vs) (Mo=O_{asym}). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 10.14 (d, 2H, py-$H^{3,3'}$), 8.79 (dd, $^3J_{H,H}$ = 8.2 Hz, 2H, py-$H^{6,6'}$), 8.41 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, py-$H^{4,4'}$), 4.05(s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.3 (C=O), 153.5 (py-$C^{2,2'}$), 151.7 (py-$C^{6,6'}$), 142.0 (py-$C^{4,4'}$), 130.0 (py-$C^{5,5'}$), 123.2 (py-$C^{3,3'}$), 53.4 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C, ppm): δ = 201 ppm. Anal. Calc. For $C_{14}H_{12}Cl_2MoN_2O_6$ (471.10): C 35.69, H 2.57, N 5.95. Found C 36.16, H 2.88, N 5.67.

$[MoO_2Cl_2$(4,4′-bis-ethoxycarbonyl-2,2′-bipyridine)](3) $[MoO_2Cl_2(THF)_2]$ (1.01 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}). ^1H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 9.67 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, py-$H^{6,6'}$), 8.88 (s, 2H, py-$H^{3,3'}$), 8.27 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, py-$H^{5,5'}$), 4.55 (q, $^3J_{H,H}$ = 7.1 Hz, 4H, CH_2), 1.48 (t, $^3J_{H,H}$ = 7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.2 (C=O), 153.1 (py-$C^{4,4'}$), 150.3 (py-$C^{2,2'}$), 142.5 (py-$C^{6,6'}$), 126.8 (py-$C^{3,3'}$), 122.7 (py-$C^{5,5'}$), 63.4 (CH_2), 14.4 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 202 ppm. Anal. Calc. For $C_{16}H_{16}Cl_2MoN_2O_6$ (499.15): C 38.50, H 3.23, N 5.61. Found C 37.64, H 3.17, N 5.41.

$[MoO_2Cl_2$(5,5′-bis-ethoxycarbonyl-2,2′-bipyridine)](4) $[MoO_2Cl_2(THF)_2]$ (1.00 mmol). Yield: 0.5 g (94%). Color: white. Selected IR (KBr): ν(cm^{-1}) = 1730(vs), 1607(s), 1471(w), 1059(w), 945(vs) (Mo=O_{sym}), 911(vs) (Mo=O_{asym}). ^1H NMR (400 MHz, CD_3NO_2, 20 °C, ppm): δ = 9.96 (s, 2H, py-$H^{3,3'}$), 8.88 (dd, $^3J_{H,H}$ = 8.6 Hz, 2H, py-$H^{6,6'}$), 8.73 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, py-$H^{4,4'}$),

4.51 (q, $^3J_{H,H}$ = 7.3 Hz, 4H, CH_2), 1.44 (t, $^3J_{H,H}$ = 7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, CD_3NO_2, 20 °C, ppm): δ = 164.9 (C=O), 154.7 (py-$C^{2,2'}$), 153.3 (py-$C^{6,6'}$), 143.8 (py-$C^{4,4'}$), 132.2 (py-$C^{5,5'}$), 126.1 (py-$C^{3,3'}$), 69.2 (CH_2), 14.6 (CH_3). ^{95}Mo NMR (26 MHz, CD_3NO_2, 20 °C): δ = 191 ppm. $C_{16}H_{16}Cl_2MoN_2O_6$ (499.15): calc. C 38.50, H 3.20, N 5.61; found C 38.65, H 3.27, N 5.18.

Synthesis of complexes 5–8: The complex $[MoO_2Br_2(DMF)_2]$ 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 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.

$[MoO_2Br_2$(4,4′-bis-methoxycarbonyl-2,2′-bipyridine)] (5)
$[MoO_2Br_2(DMF)_2]$ (0.46 mmol). Yield: 0.25 g (98%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1733(vs), 1619(w), 1486(w), 1073(w), 946(vs), (Mo=O_{sym}), 912(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 9.77 (d, $^3J_{H,H}$ = 6.2 Hz, 2H, py-$H^{6,6'}$), 8.90 (s, 2H, py-$H^{3,3'}$), 8.27 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, py-$H^{5,5'}$), 4.10 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.7 (C=O), 153.5 (py-$C^{4,4'}$), 150.5 (py-$C^{2,2'}$), 142.1 (py-$C^{6,6'}$), 126.8 (py-$C^{3,3'}$), 122.9 (py-$C^{5,5'}$), 54.0 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 249 ppm. Anal. Calc. For $C_{14}H_{12}Br_2MoN_2O_6$ (560.00): C 30.03, H 2.16, N 5.00. Found C 29.83, H 2.30, N 5.05.

$[MoO_2Br_2$(5,5′-bis-methoxycarbonyl-2,2′-bipyridine)](6)
$[MoO_2Br_2(DMF)_2]$ (0.60 mmol). Yield: 0.32 g (95%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1729(vs), 1607(s), 1429(s), 1058(w), 938(vs), (Mo=O_{sym}), 906(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 10.18 (d, 2H, py-$H^{3,3'}$), 8.80 (dd, $^3J_{H,H}$ = 8.3 Hz, 2H, py-$H^{6,6'}$), 8.42 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, py-$H^{4,4'}$), 4.05 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.3 (C=O), 153.7 (py-$C^{2,2'}$), 151.8 (py-$C^{6,6'}$), 142.1 (py-$C^{4,4'}$), 130.0 (py-$C^{5,5'}$), 123.4 (py-$C^{3,3'}$), 53.6 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 249 ppm. Anal. Calc. For $C_{14}H_{12}Br_2MoN_2O_6$ (560.00): C 30.03, H 2.16, N 5.00. Found C 29.74, H 2.34, N 4.98.

$[MoO_2Br_2$(4,4′-bis-ethoxycarbonyl-2,2′-bipyridine)](7)
$[MoO_2Br_2(DMF)_2]$ (0.40 mmol). Yield: 0.24 g (97%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1729(vs), 1616(w), 1461(w), 1093(w), 948(vs) (Mo=O_{sym}), 911(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 9.74 (d, $^3J_{H,H}$ = 5.7 Hz, 2H, py-$H^{6,6'}$), 8.88 (s, 2H, py-$H^{3,3'}$), 8.25 (d, $^3J_{H,H}$ = 5.8 Hz, 2H, py-$H^{5,5'}$), 4.55 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, CH_2), 1.49 (t, $^3J_{H,H}$ = 7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.5, (C=O), 153.8 (py-$C^{4,4'}$), 150.7 (py-$C^{2,2'}$), 142.8 (py-$C^{6,6'}$), 127.1 (py-$C^{3,3'}$), 123.2 (py-$C^{5,5'}$), 63.8 (CH_2), 14.8 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 253 ppm. Anal. Calc. For $C_{16}H_{16}Br_2MoN_2O_6$ (588.06): C 32.68, H 2.74, N 4.76. Found C 32.69, H 3.02, N 4.90.

$[MoO_2Br_2$(5,5′-bis-ethoxycarbonyl-2,2′-bipyridine)](8)
$[MoO_2Br_2(DMF)_2]$ (0.46 mmol). Yield: 0.25 g (91%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1723(vs), 1609(w), 1470(w), 1061(w), 943(vs), (Mo=O_{sym}), 911(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): δ = 10.16 (d, 2H, py-$H^{3,3'}$), 8.79 (dd, $^3J_{H,H}$ = 8.4 Hz, 2H, py-$H^{6,6'}$), 8.42 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, py-$H^{4,4'}$), 4.52 (q, $^3J_{H,H}$ = 7.1 Hz, 4H, CH_2), 1.47 (t, $^3J_{H,H}$ = 7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.2 (C=O), 154.1 (py-$C^{2,2'}$), 152.3 (py-$C^{6,6'}$), 142.3 (py-$C^{4,4'}$), 130.9 (py-$C^{5,5'}$), 123.7 (py-$C^{3,3'}$), 63.4 (CH_2), 14.8 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 246 ppm. $C_{16}H_{16}Br_2MoN_2O_6$ (588.06): calc. C 32.68, H 2.74, N 4.76; found C 32.06, H 2.73, N 4.54.

Synthesis of complexes 9–11. A solution of $[MoO_2Cl_2(THF)_2]$ in THF (15 ml) was treated with one equiv. of ligands that were also dissolved in THF (10 ml). The colour of the solution changed immediately to yellow and the reaction mixture was stirred for further 30 min. To this solution, 2.1 equiv. CH_3MgBr were slowly added at −20 °C. The reaction mixture was allowed to warm-up to room temperature and was stirred for 2 h. The dark brown 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 removed in vacuo and the residue was recrystallised from CH_2Cl_2/Et_2O/hexane.

$[MoO_2(CH_3)_2$(4,4′-bis-methoxycarbonyl-2,2′-bipyridine)] (9)
$[MoO_2Cl_2(THF)_2]$ (0.53 mmol). Yield: 0.18 g (79%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1731(vs), 1612(w), 1441(w), 1064(w), 934(vs), (Mo=O_{sym}), 900(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 9.76 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, py-$H^{6,6'}$), 8.90 (s, 2H, py-$H^{3,3'}$), 8.11 (dd, $^3J_{H,H}$ = 5.6 Hz, 2H, py-$H^{5,5'}$), 4.08 (s, 6H, O-CH_3), 0.57 (s, 6H, Mo-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.7 (C=O), 153.5 (py-$C^{4,4'}$), 150.5 (py-$C^{2,2'}$), 142.1 (py-$C^{6,6'}$), 126.8 (py-$C^{3,3'}$), 122.9 (py-$C^{5,5'}$), 54.0 (CH_3), 22.4 (Mo-CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 449 ppm. Anal. Calc. For $C_{16}H_{18}MoN_2O_6$ (430.26): C 44.66, H 4.22, N 6.51. Found C 45.74, H 4.81, N 6.16.

$[MoO_2(CH_3)_2$(4,4′-bis-ethoxycarbonyl-2,2′-bipyridine)] (10)
$[MoO_2Cl_2(THF)_2]$ (1.02 mmol). Yield: 0.14 g (32%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1729(vs), 1613(w), 1467(w), 1099(w), 932(vs) (Mo=O_{sym}), 898(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 9.75 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, py-$H^{6,6'}$), 8.90 (s, 2H, py-$H^{3,3'}$), 8.10 (d, $^3J_{H,H}$ = 5.8 Hz, 2H, py-$H^{5,5'}$), 4.53 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, CH_2), 1.48 (t, $^3J_{H,H}$ = 7.9 Hz, 6H, CH_3), 0.57 (s, 6H, Mo-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.7 (C=O), 152.2 (py-$C^{4,4'}$), 149.9 (py-$C^{2,2'}$), 140.8 (py-$C^{6,6'}$), 125.1 (py-$C^{3,3'}$), 122.5 (py-$C^{5,5'}$), 63.2 (CH_2), 14.5 (CH_3), 22.3 (Mo-CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 449 ppm. Anal. Calc. For $C_{18}H_{22}MoN_2O_6$ (458.32): C 47.17, H 4.84, N 6.11. Found C 46.31, H 4.72, N 5.92.

$[MoO_2(CH_3)_2$(5,5′-bis-ethoxycarbonyl-2,2′-bipyridine)](11)
$[MoO_2Cl_2(THF)_2]$ (0.60 mmol). Yield: 0.14 g (51%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1725(vs), 1604(w), 1470(w), 1057(w), 932(vs), (Mo=O_{sym}), 900(vs) (Mo=O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 10.16 (d, $^3J_{H,H}$ = 1.2 Hz, 2H, py-$H^{3,3'}$), 8.69 (dd, $^3J_{H,H}$ = 8.4 Hz, 2 H, py-$H^{6,6'}$), 8.41 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, py-$H^{4,4'}$), 4.50 (q, $^3J_{H,H}$ = 7.1 Hz, 4H, CH_2), 1.45 (t, $^3J_{H,H}$ = 8.8 Hz, 6H, CH_3), 0.61 (s, 6H, Mo-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): δ = 163.5 (C=O), 152.6 (py-$C^{2,2'}$), 150.9 (py-$C^{6,6'}$), 140.0 (py-$C^{4,4'}$), 129.2 (py-$C^{5,5'}$), 122.8 (py-$C^{3,3'}$), 62.6 (CH_2), 14.5 (CH_3), 21.7 (Mo-CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 °C): δ = 461 ppm. $C_{18}H_{22}MoN_2O_6$ (458.32): calc. C 47.17, H 4.84, N 6.11; found C 46.01, H 4.95, N 5.35.

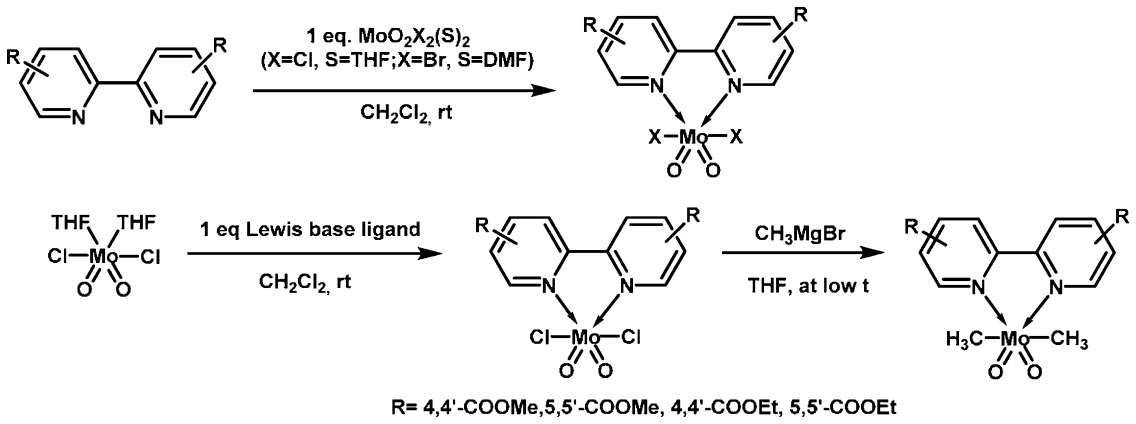
2.3. Synthesis of the ionic liquids

The RTILs [BMIM]PF_6, [C_8MIM]PF_6, [BMIM]NTf_2 and [BMIM]BF_4 were prepared and purified as described in the literature [23,27]. Their spectroscopic data are in accordance with the data reported previously.

2.4. Catalytic reactions

Without solvent: *Cis*-cyclooctene (7.3 mmol), mesitylene (2.00 g, internal standard), and 1 mol% of compounds **1–11** (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 under vigorous stirring. 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.

With RTILs: *Cis*-cyclooctene (7.3 mmol), mesitylene (2.00 g, internal standard), and TBHP (11 mmol, 5.5 M in decane) were mixed in the reaction vessel under air at room temperature. The reaction is started under vigorous stirring by adding compounds **1–4** (7.3 μmol, 0.1 mol%), dissolved in RTIL (0.5 ml). The course



Scheme 1. Synthesis route for Mo(VI) complexes.

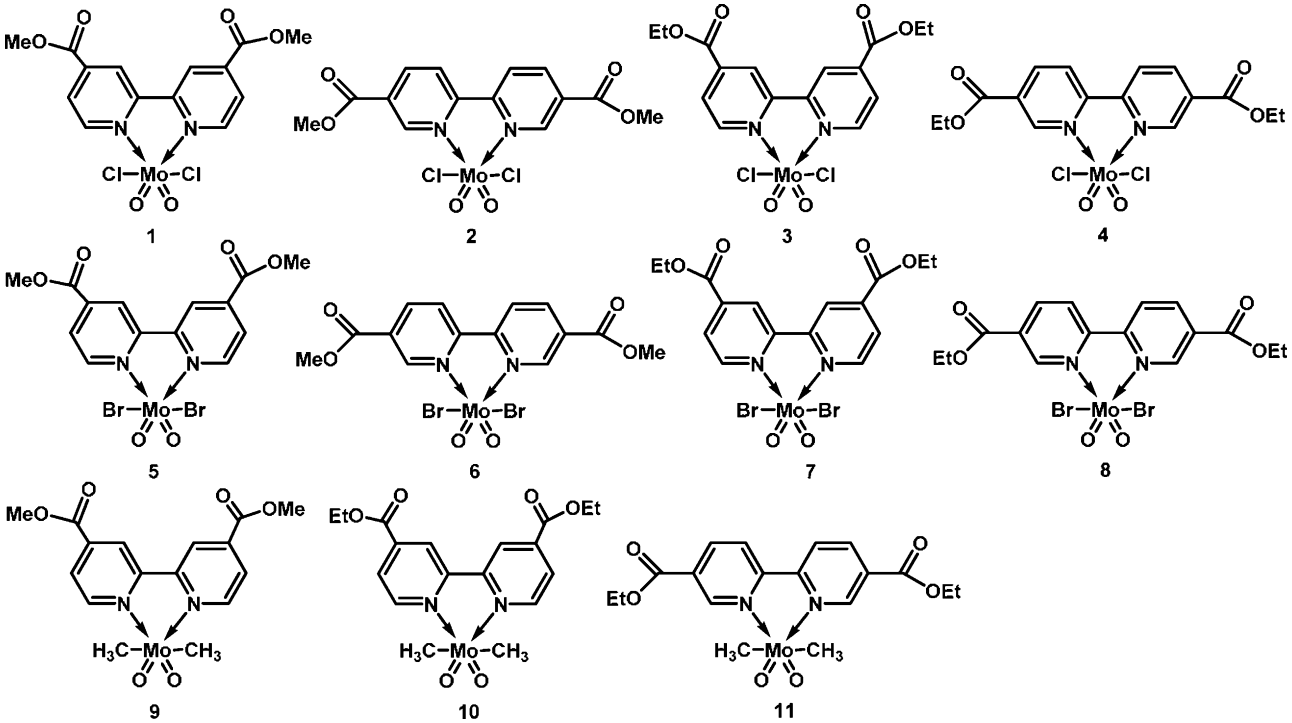
of the reaction was monitored by quantitative GC analysis. Two phases could be easily recognised and the samples were taken from the upper organic phase in regular time intervals. After diluting the samples with CH_2Cl_2 they were treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water 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.

3. Results and discussion

The synthesis of a series of dioxodichloromolybdenum(VI) bipyridine derived complexes has been described previously. In these cases the ligands had different functional groups at different positions on the bipyridine rings [24]. Among the complexes described previously is [MoO_2Cl_2(4,4′-bis-ethoxycarbonyl-2,2′-bipyridine)], which is also included in this paper as complex **4** for sake of comparison. For the present work the reaction of a variety of bipyridine derived ligands, which should lead to good complex solubility has been synthesised and applied. Scheme 1 shows the synthesis routes for the Mo(VI) complexes.

3.1. Synthesis and spectroscopic characterisation of complexes *1–11*

The dichlorodioxo molybdenum(VI) complexes **1–4** (Scheme 2) were obtained as white microcrystalline powders in yields between 94 and 98% by addition of 1 equiv. of the bidentate Lewis-base ligands to a solution of the adduct [$MoO_2Cl_2(THF)_2$] in CH_2Cl_2 at room temperature. The bromides are readily prepared from [$MoO_2Br_2(DMF)_2$] and the corresponding Lewis-base ligands for compounds **5–8** (Scheme 2) according to described procedures [25]. When synthesizing the complexes **9–11** [6a], the dichlorides do not need to be isolated prior to Grignard reagent addition. In some cases this isolation of the intermediates has negative effects on the overall yield of the final dialkyl products. Therefore, the whole process consists of dissolving [$MoO_2Cl_2(THF)_2$] in CH_2Cl_2,



Scheme 2. Structures of complexes **1–11**.

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 **1–11**.

Complex	υ(Mo=O) [cm^{-1}]			f(Mo=O)mdyn Å^{-1}	Decomp. temp.°C	δ (^{95}Mo) ppm	Deuterated solvent
	υ_{as}	υ_{s}	$\upsilon_{average}$				
1	918	951	935	7.00	275	Not determined	Not determined
2	910	942	926	6.88	290	201	$CDCl_3$
3	914	950	932	6.97	250	202	$CDCl_3$
4	911	945	928	6.91	275	191	CD_3NO_2
5	912	946	929	6.92	250	249	$CDCl_3$
6	906	938	922	6.82	275	249	$CDCl_3$
7	911	948	930	6.93	250	253	$CDCl_3$
8	911	943	927	6.89	275	246	$CDCl_3$
9	900	934	917	6.74	210	449	$CDCl_3$
10	898	932	915	6.71	200	449	$CDCl_3$
11	900	932	916	6.73	225	461	$CDCl_3$

treatment with the corresponding bidentate ligand and reaction of the *in situ* formed complex with the required amount of CH_3MgBr at low temperature. 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. The dichloromethane phase is dried and the residue recrystallised to give the alkyl complexes **9–11** (Scheme 2) in yields between 32 and 79%. All compounds are stable under laboratory atmosphere and can be handled in air.

FT-IR spectroscopic data for complexes **1–11** are in consistence with other Lewis-base adducts of bis(halogeno)dioxomolybdenum described before [25]. The symmetric and asymmetric IR stretching vibrations for the *cis*-dioxo unit of the complexes are in the expected range between 900 and 950 cm^{-1} (Table 1). The corresponding force constants of the Mo=O bonds can be derived from the υ(Mo=O) values. The M=O vibrations of the complexes are always shifted to higher wave numbers compared to their precursor, $[MoO_2X_2]$. This is an indication for comparatively strong metal–Lewis-base ligand interactions. Additionally, this trend is reflected in the calculated force constants (see Table 1). A comparison of the observed IR-values for the complexes **9–11** (Table 1) indicates that the replacement of a halide by a methyl group weakens the equatorial metal–ligand bonds. The observed stretching vibrations as well as the calculated force constants (Table 1) show for both complex series, **1**, **5**, **9**; **2**, **6**, **10**; **3**, **7**, **11**, that there is a slight increase of Mo=O bond strength in the order $-CH_3 < Br < Cl$, in accordance with the inductive effects of these three ligands. The differences appear to be significant (the tendency is same in all three series of compounds), but not particularly pronounced.

The ^{1}H NMR spectra of complexes **1–11** were measured at room temperature using $CDCl_3$ as solvent. In general, the spectroscopic data for these complexes are in good agreement with those obtained for previously described MoO_2X_2–Lewis-base adducts [25]. Except for compounds **9–11** the protons are solely situated in the Lewis base. The chemical shift of the ligand protons is reported in the supporting information and compared to the chemical shifts observed for the protons of the free ligand. As stated above, the important feature of the most of the dioxomolybdenum(VI) complexes studied previously is that they are of low to moderate solubility in most common organic solvents [24]. However, the complexes synthesised in this work are generally of better solubility. The chemical shifts of the $-CH_3$ ligands of compounds **9–11** appear in the range between 0.57 and 0.61 ppm in ^{1}H NMR spectroscopy, in agreement with the values as previously reported for similar complexes [6c].

The differences in the ^{95}Mo NMR shifts [25] between the different bipyridine ligated complexes is comparatively small, only a few ppm in each case with the same ligand X (X = Cl, Br, $-CH_3$). The difference in the chemical shift between Cl and Br is ≈50 ppm, between Br and $-CH_3$ ligands it is nearly 200 ppm. Complexes of the composition $[MoO_2Cl_2L_2]$ generally display their ^{95}Mo NMR signals between 160 and 220 ppm, whereas the bromine derivatives show their ^{95}Mo signals between 170 and 280 ppm. The methyl complexes of formula $[MoO_2(CH_3)_2L_2]$ described in the literature display ^{95}Mo NMR shifts between 370 and 520 ppm. Methyl complexes with N-bidentate heterocyclic aromatic ligands display their signals in the low-field region of this range between 370 and 450 ppm [6c]. The obtained ^{95}Mo NMR spectra for the complexes synthesised are summarised in Table 1; the $[MoO_2Cl_2L_2]$ complexes show their signals around 200 ppm, the $[MoO_2Br_2L_2]$ complexes exhibit their signals between 246 and 253 ppm and the $[MoO_2(CH_3)_2L_2]$ complexes display their signals in the range between 449 and 461 ppm, which is in consistence with the literature reported results summarised above [6c].

Thermogravimetric analyses (TGA) were performed for all compounds (see Table 1). The onset of the first decomposition temperature for the compounds range between 200 and 290 °C. The synthesised dimethyldioxomolybdenum(VI) complexes are less stable than the dihalogenodioxomolybdenum(VI) complexes. In the case of methoxycarbonyl groups placed in the 4,4′-positions on the bipy-ring the decomposition temperature increases in the order **9** < **5** < **1**. Related to ethoxycarbonyls – regardless of the position of the functional groups located on the bipy-ring – both bromo and chloro molybdenum(VI) complexes have similar stability whereas in the case of complexes with methoxycarbonyl groups, dichlorodioxomolybdenum(VI) complexes are more stable than dibromodioxomolybdenum (VI) complexes. From the mass loss of the first decomposition step it can be concluded that in all cases one ligand X is lost first, triggering the follow-up decomposition of the whole molecule.

3.2. Crystal structures of complexes *6–8*

Single crystals of compounds **6–8** were obtained and examined by X-ray crystallography (see Fig. 1, S1, S2, and S3).

All obtained structures exhibit the central molybdenum atom, situated in a distorted octahedron formed by two trans-located bromo, two cis-oriented oxo ligands, and two nitrogen atoms of the chelating bipyridine ligand. The distortion of the octahedron results from the displacement of the molybdenum atom away from the centre towards the two oxo ligands. The Mo–O bond lengths in these complexes range from 1.688(2) to 1.704(2) Å, the lengths of the Mo–Br bonds are found within the range of 2.5155(5)–2.5306(5) Å, and the Mo–N bond lengths vary between 2.321(2) and 2.350(2) Å. All these values are expected for the respective Mo–E bond lengths [26].

3.3. DFT calculation of formation energies

Density functional calculations were carried out to get more information of the thermodynamic behaviour of the complexes.

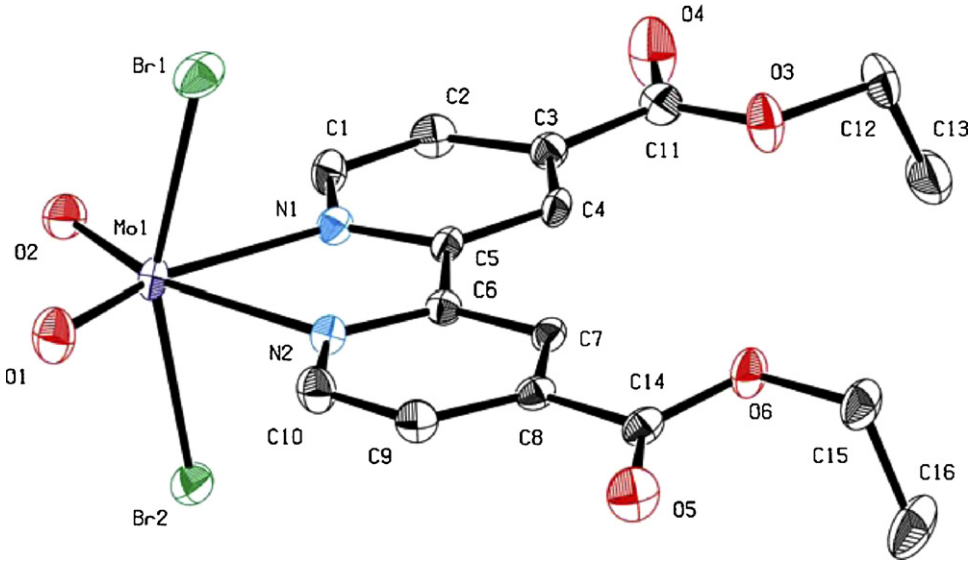


Fig. 1. ORTEP style plot of compound **7** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Mo1–Br1 2.5269(4), Mo1–Br2 2.5197(4), Mo1–O1 1.700(2), Mo1–O2 1.696(2), Mo1–N1 2.328(2), Mo1–N2 2.321(2); Br1–Mo1–Br2 159.22(1), Br1–Mo1–O1 96.80(7), Br1–Mo1–O2 95.75(6), Br1–Mo1–N1 81.14(5), Br1–Mo1–N2 80.13(5), Br2–Mo1–O1 95.82(7), Br2–Mo1–O2 96.38(6), Br2–Mo1–N1 81.74(5), Br2–Mo1–N2 82.73(5), O1–Mo1–O2 106.65(10), O1–Mo1–N1 161.93(9), O1–Mo1–N2 93.27(9), O2–Mo1–N1 91.42(8), O2–Mo1–N2 160.03(8), N1–Mo1–N2 68.67(7).

They show overall similar thermodynamic values. Reaction enthalpies for the formation of the complexes out of solvent-free $[MoO_2X_2]$ range between −14 and −17 kcal/mol for X = –CH_3, between −20 and −23 kcal/mol for X = Cl and between −23 and −26 for X = Br. Entropic considerations come more strongly into account when looking at the complete ligand exchange of the $[MoO_2X_2(THF)_2]$ complexes with the relevant bidentate bipy ligand. The free energy of these substitutions vary from −10 kcal/mol to −16 kcal/mol for all substituents X (–CH_3, Cl, Br) of the Mo centre. It can also be seen that substituents in the 4,4′-position lead to complexes that are more stable (ca. 2 kcal/mol) in comparison to the corresponding 5,5′-substituted compounds. The difference between –OMe and –OEt as bipy functionalised group is negligible. All the thermodynamic data are summarised in the Supporting Information.

3.4. Catalytic epoxidation of cis-cyclooctene

The epoxidation of cyclooctene using TBHP as oxidant in the presence of complexes **1–11** at 55 °C yields cyclooctene oxide as the only product. Two series of experiments with different molar ratio of catalyst:substrate:oxidant (1:100:150 and 1:1000:1500) were undertaken in order to compare the catalytic potential of the systems. The details of the catalytic reactions are given in the experimental section. Control experiments confirm that epoxidation does not take place in the absence of catalyst. The time-dependent curves obtained for compounds **1–11** are typical for $[MoO_2X_2L_2]$-type complexes used as epoxidation catalysts with TBHP [6,25]. Initially the reaction is fast, indicating that the active oxidising species are formed rapidly after addition of the peroxide to the reaction medium. Progressively, the reaction rate decreases, when the reaction is nearly complete, due to an increasing lack of substrate (Fig. 2). All examined compounds show high catalytic activity. Only complexes **5** and **6** show an induction period. Compounds **5** and **6** dissolve very slowly after addition of TBHP leading to a slow reaction in the beginning, whereas the other complexes dissolve immediately. After the catalyst has totally dissolved, the reaction is fast in all cases. The activities of the examined catalysts are in the range of 1600–2000 h^{-1} (Table 2) and yields 95% within 30 min. These results differ from literature data where the

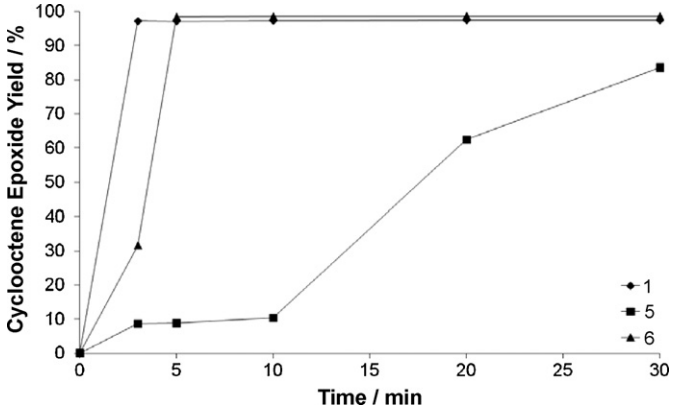


Fig. 2. Time-dependent yield of cyclooctene oxide in the presence compounds **1**, **5** and **6** as catalysts at 55 °C with 1 mol% catalyst concentration between 0 and 30 min. The curve for compound **1** is typical for the remaining compounds **2–4**, **7–11**.

halide complexes, particularly the –Cl compounds, were found to be significantly more active (for cyclooctene epoxidation) than the methyl derivatives under reaction conditions identical to those used in the present work [6c,25,26]. In the light of the results presented here it can be assumed that these lower activities of the

Table 2
The TOF values for $[MoX_2O_2L_2]$ type complexes **1–11** using cyclooctene as substrate. The TOFs of all complexes have been calculated at the time interval of highest conversion.

Compound	TOF [h^{-1}]
1	1950
2	1940
3	1880
4	1910
5	310
6	2010
7	1600
8	1970
9	1960
10	1900
11	1950

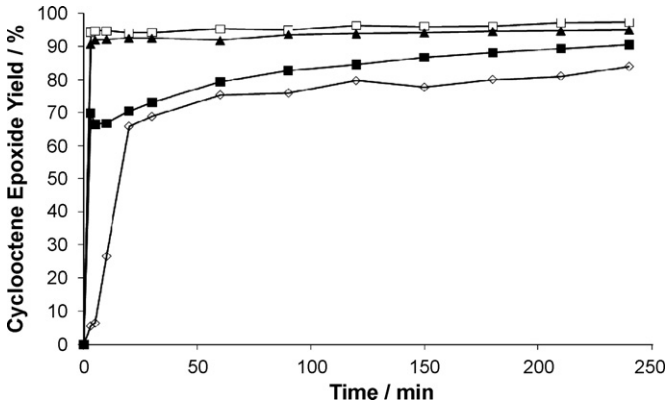


Fig. 3. Time-dependent yield of cyclooctene oxide with compound **8** as catalyst (□: catalyst:substrate:oxidant ratio 1:100:150 at 55 °C; ▲: catalyst:substrate:oxidant ratio 1:1000:1500 at 55 °C; ■: 2nd run catalyst:substrate:oxidant ratio 1:100:150 at 55 °C; ◊: catalyst:substrate:oxidant ratio 1:100:150 at r.t.).

$-CH_3$ complexes are mainly due to solubility problems. Furthermore, in some cases the TOFs have been calculated differently (not at the steepest slope of the olefin epoxide formation curves), the reported numbers can therefore be regarded as 'lower limits' not as realistic turnover frequencies.

When changing the catalyst:substrate:oxidant ratio from 1:100:150 to 1:1000:1500, the activities lower except for complex **8**. In the latter case the TOF increases slightly from 1970 to 2310 h^{-1}. It appears that optimal activities for the system have been reached when applying a 1:100:150 catalyst:substrate:oxidant ratio. Lowering the reaction temperature to 25 °C also lowers the activity. In the case of compound 3, the TOF decreases from ca. 1884 h^{-1} (at 55 °C) to ca. 230 h^{-1} (at 25 °C) (Fig. 3).

A further set of experiments was performed to explore the stability of the complexes under catalytic conditions. After 24 h reaction time, when the product yield reaches ≈100%, more substrate and TBHP were added to the reaction mixture. The catalyst was still active and the reaction reaches more than 90% product yield within 4 h, albeit somewhat slower in catalysing the reaction (Fig. 3). This is most probably caused by the excess of *tert*-butyl alcohol present in the reaction mixture hindering the reaction process. This phenomenon is already known from related complexes and has been ascribed to an adduct formation of the catalyst with the byproduct *t*-BuOH, rather than a catalyst decomposition [6b].

3.5. Catalytic epoxidation of cis-cyclooctene with RTILs as solvents

The chloride-containing complexes are investigated additionally in RTILs ([BMIM]PF_6, [C_8MIM]PF_6, [BMIM]NTf_2 and [BMIM]BF_4) (BMIM = 1-butyl-3-methylimidazolium, C_8MIM = 1-octyl-3-methylimidazolium) as solvents. In contrast to the catalysis without an additional solvent this catalysis was performed at room temperature and with a catalyst:substrate:oxidant ratio from 1:1000:1500. The catalyst was dissolved in the RTIL and this solution was added to the reaction solution. Since the catalytically active Mo(VI) species are water-sensitive, the activity of the system depends on the water-content of the ionic liquid. [BMIM]NTf_2 has the lowest water-content of all the investigated RTILs [27], leading to the highest activity in this solvent. The TOFs in [BMIM]NTf_2 are considerably higher than the TOF under solvent-free conditions (see Table 3).

A reduction of the concentration of compound **2** to 0.05 mol% in [BMIM]NTf_2 even leads to a TOF of 10,080 h^{-1}. Another advantage of the performance in RTILs is the possibility to reuse the catalyst. After the reaction a phase separation ionic liquid/product takes place and the product can be easily removed quantitatively via a cannula. Additionally, oil pump vacuum allows the removal of *t*-BuOH from the RTIL phase. Since both starting reagents and epoxide are not present in the RTIL it can be concluded that the conversion of cyclooctene is achieved by a biphasic reaction and not by a homogeneous reaction. Addition of substrate and oxidising agent restarts the reaction. This catalytic procedure was repeated three times without any loss of activity and consequently without any leaching effects. Fig. 4 shows the kinetics of the compounds **1–4** in [BMIM]NTf_2.

Table 3
TOF values [h^{-1}] for [$MoO_2Cl_2L_2$] type complexes **1–4**, using cyclooctene as substrate and a RTILs as solvent. The TOFs of all complexes have been calculated for the time interval of highest conversion (c = 0.1 mol%).

Compound	[BMIM]NTf_2	[BMIM]BF_4	[BMIM]PF_6	[C_8MIM]PF_6
1	5390	280	1360	5390
2	8090	30	320	7110
3	7910	250	2490	5240
4	3430	660	430	2990

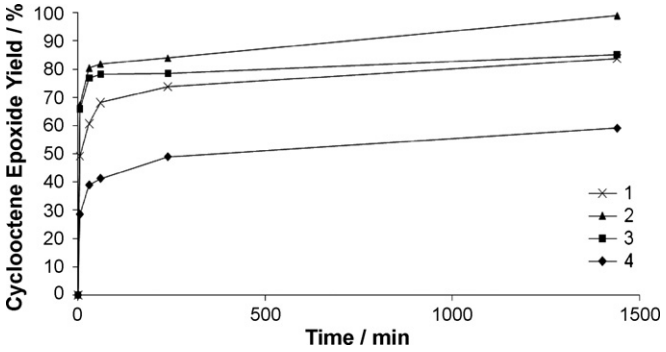


Fig. 4. Time-dependent yield of cyclooctene oxide in the presence of [$MoO_2Cl_2L_2$] and compounds **1–4** as catalysts at room temperature with 0.1 mol% catalyst concentration and [BMIM]NTf_2 as solvent.

4. Conclusion

The dioxomolybdenum(VI) complexes [$MoO_2X_2L_2$] (X = Cl, Br, $-CH_3$; L = 4,4′-bis-methoxycarbonyl-2,2′-bipyridine, 5,5′-bis-methoxycarbonyl-2,2-bipyridine, 4,4′-bis-ethoxycarbonyl-2,2′-bipyridine, 5,5′-bis-ethoxycarbonyl-2,2′-bipyridine) are very active and highly selective catalysts for the homogeneous epoxidation of cyclooctene using *tert*-butyl hydroperoxide (TBHP). Cyclooctene oxide is obtained quantitatively within 1 h and the reaction solution containing the catalyst can be reused. Catalytic results show that the reaction is selective to the desired epoxide and no diol formation is observed. It is important to note that almost all of the complexes described here are highly soluble in organic solvents in contrast to many of the previously reported related complexes. This shows that the ligand L is obviously more important for the solubility than the ligand X and R.

The major advantage of using RTILs as solvents is the formation of a biphasic system, which can be easily separated. After product removal the catalysts can be reused for additional cycles without observable loss of activity. Furthermore, no leaching of the catalyst can be observed. In [BMIM]NTf_2 the reactions yields the best results, correlating well with other reported Mo systems [28], because of the low water-content of this particular RTIL.

4.1. Additional information

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the

Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-776729 (**6**), CCDC-776730 (**7**), and CCDC-776731 (**8**). 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).

Acknowledgements

A.G. thanks the Elitenetzwerk Bayern NanoCat for a Ph.D. grant and for financial support. D.B. is thankful to the Bayerische Forschungsstiftung for a Ph.D. grant. The authors are acknowledged to Dr. Mirza Cokoja and Dr. Bettina Bechlars for helpful discussions and proofreading of the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.08.014.

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