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Molybdenum(VI) *cis*-dioxo complexes bearing (poly)pyrazolyl-methane and -borate ligands: syntheses, characterization and catalytic applications

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Reaction of $MoO_2Cl_2(THF)_2$ with mono- (L_1) and bi-dentate (L_2) pyrazole type ligands leads to octahedral complexes of formula $MoO_2Cl_2(L_1)_2$ and $MoO_2Cl_2(L_2)$ (**1**, L_1 = 3,5-Me_2pz; **2**, L_2 = $Me_2C(pz)_2$). The structure of **2** has been determined crystallographically. Reaction of $MoO_2X_2(THF)_2$ (X = Cl or Br) with tridentate ligands (L_3), *e.g.* tris(pyrazolyl)methane or tris(pyrazolyl)borate, leads to the replacement of both co-ordinated solvent molecules and one of the chloride ligands to give $[MoO_2X(L_3)]X$ (**3**, X = Cl, L_3 = $HC(pz)_3$; **4**, X = Br, L_3 = $HC(pz)_3$; **5**, X = Cl, L_3 = $HC(3,5\text{-}Me_2pz)_3$) and $MoO_2Cl\{(pz)_3BH\}$ **6**. Depending on the donor ability and the steric bulk of the ligand, rapid rotation is observed at room temperature in some cases. At lower temperatures the structures are less fluxional. Nevertheless, bidentate and tridentate pyrazolyl ligands produce distinctly different chemical shifts in the ^{95}Mo NMR spectra. The turnover frequencies of the described complexes in olefin epoxidation, with *t*-butyl hydroperoxide as oxidizing agent, are in the range of 150–460 [mol/(mol catalyst h)]. This activity is in the middle of the range observed for $MoO_2X_2L_2$ complexes with N–donor ligands.

Introduction

Several molybdenum(VI) complexes have proven to be useful catalysts for the epoxidation of olefins with hydroperoxides, *e.g.* *t*-butyl hydroperoxide (TBHP).[1] Recently, we have presented a study on the catalytic activity of $MoO_2X_2(L_2)$ complexes in which the ligands were mainly substituted 1,4-diazabutadienes. This study is now extended to include poly(pyrazolyl)-borate and -methane ligands.

Since Trofimenko[2] synthesized the poly(pyrazolyl)borate ligands, they have widely been used in inorganic and organometallic chemistry, especially with f and d transition elements.[3–7] Also, tris(pyrazolyl)borate and related tripodal ligands have had a significant impact on the modeling of the active centre of molybdenum enzymes.[8] The related neutral ligands, poly(pyrazolyl)methanes, have been studied much less, since the few metal complexes were first reported by Trofimenko in 1970.[9] Recently, an improved synthesis, that delivers good yields of highly pure ligands, was developed by Jameson and Castellano.[10] This procedure unlocks the coordination chemistry of poly(pyrazolyl)methane with various metals and enables comparison with related boron complexes. So far, this type of ligand was used more in the chemistry of low oxidation state metals like Sn^{II},[11] Pd^{II}[12] and Y^{III}.[13] In fact, to the best of our knowledge, there are no examples in the literature of molybdenum(VI) dioxo complexes bearing this type of ligand.

Moreover, these ligands are interesting due to the fact that their fluxional behaviour has been established,[13,14] especially in the case of the tridentate ligands. It would appear that the presence of a relatively weakly coordinating ligand in the complex positively influences the catalytic activity for epoxidation reactions.[1a] Thus, the use of these ligands in molybdenum(VI) dioxo complexes should, in principle, lead to good catalytic results. So far, related complexes have not widely been tested as far as their catalytic properties are concerned. The only exception is the oxidation of Ph_3P to Ph_3PO, catalysed by $MoO_2Cl\{(3,5\text{-}Me_2pz)_3BH\}$ (3,5-Me_2pz = 3,5-dimethylpyrazolyl) using Me_2SO as oxidizing agent and a catalyst : substrate ratio of 1 : 20.[15]

In this work we report the synthesis and characterization of several molybdenum(VI) dioxo complexes bearing poly(pyrazolyl)borate and poly(pyrazolyl)methane ligands. The complex $MoO_2Cl_2(3,5\text{-}Me_2pz)_2$ is also synthesized for comparison purposes. The fluxional behaviour of selected complexes is studied *via* temperature-dependent ^{1}H NMR and all the complexes are tested for their catalytic activity towards the epoxidation of cyclooctene with TBHP as oxidant under catalytic conditions.

Results and discussion

Synthesis

Preparation of the new complexes **1**–**5** (see Chart 1) is carried out by the stoichiometric combination of $MoO_2Cl_2(THF)_2$ with the appropriate ligand. Complex **6** was prepared by direct metathesis of $MoO_2Cl_2(THF)_2$ and $K[HB(pz)_3]$. An alternative synthesis using $MoO_2Cl_2(OPPh_3)_2$ also provides the compounds in good yields. All the reactions proceed in THF in good to almost quantitative yields. These complexes are soluble in co-ordinating solvents like THF and $NCCH_3$, moderately soluble in CH_2Cl_2 and insoluble in diethyl ether and *n*-hexane. All can be handled briefly in air. Complex **1** decomposes under these conditions within a few minutes whereas **2**–**6** decompose within a few hours, as indicated by the appearance of pyrazole or 3,5-dimethylpyrazole in the NMR spectra.

Infrared spectra

The infrared spectra of the compounds exhibit two strong ν(Mo=O) bands at 930–950 and 900–920 cm^{-1} characteristic

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Table 1 Selected catalytic and spectroscopic data for the complexes **1**–**6**

Compound	TOF [mol/(mol catalyst h)][a]	ν(Mo=O)/cm^{-1}	$\delta(^{95}Mo)$
1	240	943, 906	157
2	460	943, 916	144
3	270	953, 920	87
4	150	948, 918	158
5	300	946, 912	87
6	210	935, 905	80

[a] The TOF values were calculated for all examined complexes after 5 minutes reaction time and are defined as mol epoxide/[(mol catalyst × time (h)].

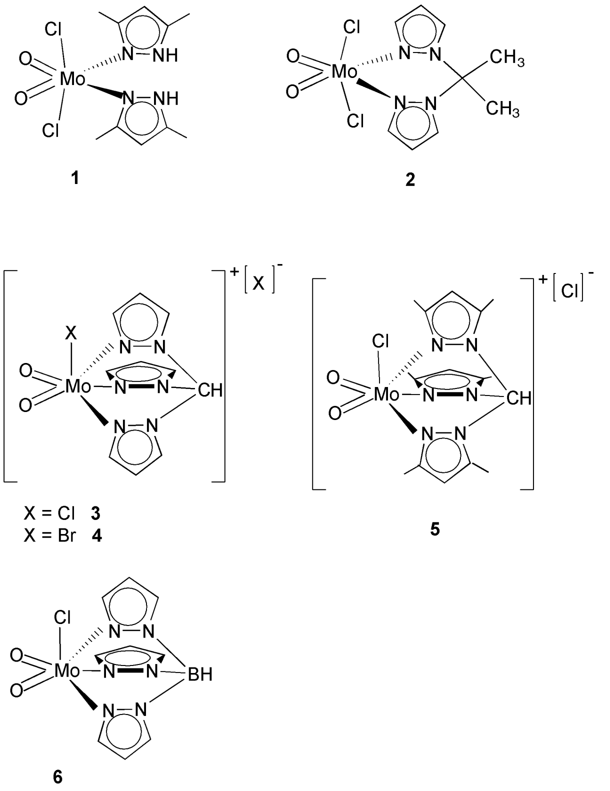

Chart 1

of the *cis*-$[MoO_2]^{2+}$ fragment asymmetric and symmetric vibrations respectively. Although there are no dramatic ligand dependent changes in **1**–**6** in the IR region for this moiety, there are distinctive differences (see Table 1), notably in the case of the borate derivative **6** where these bands are shifted to lower wavenumbers. This observation can easily be explained by considering the fact that complex **6** bears the only negatively charged tripod ligand of the examined series. It also shows the typical band for ν(B–H) at 2485 cm^{-1} indicating a stronger B–H bond as in the case of $MoO_2Cl\{(Me_2pz)_3BH\}$ where this band appears at 2550 cm^{-1}.[15]

NMR Spectra

The ^{1}H, ^{95}Mo and ^{11}B NMR spectra of compounds **1**–**6** were recorded in CD_2Cl_2 at room temperature. Temperature-dependent ^{1}H NMR spectra were also recorded for some of the complexes in order to study their fluxional behaviour. It has been observed previously that many poly(pyrazolyl)borate complexes show dynamic behaviour on the NMR timescale.[13,14] The fluxional behaviour of their neutral analogues poly(pyrazolyl)methanes was also investigated.

At ambient temperature, complex **1** presents two sets of resonances of relative intensity 1 : 6 (at δ 5.9 and 2.28, respectively), and a very broad peak at δ *ca.* 14 corresponding to the N–*H* of the pyrazole ring. The signal at δ 5.9 is due to the pyrazole ring protons, that at δ 2.28 to the methyl groups on the one and three position of the pyrazole rings. Apparently, a quick exchange of the hydrogen atom between the two nitrogens takes place. Therefore, the two different methyl groups become equivalent, as we only see their averaged resonance. Owing to the presence of the electron withdrawing Lewis-acidic molybdenum(VI) centre, the ligand signals are, in general, shifted to lower field in comparison to those of the free ligand (Table 2). The N–*H* proton can be observed as a very broad signal at *ca.* δ 14. Cooling the dissolved complex results in a freezing of the ligand exchange. The N–*H* proton resolves to a sharp singlet at δ 15.5 at −90 °C. The other two resonances do not change with temperature. Therefore, the exchange process seems to remain at low temperature, taking place less quickly than at higher temperatures.

For complex **2** four resonances are present at ambient temperature with a relative intensity of 1 : 1 : 1 : 3 at δ 8.77 and 7.95 (H-3,5), 6.55 (H-4) and 2.25 (CH_3), respectively. These signals are slightly shifted to lower field when compared to those of the free ligand (Table 2). By lowering the temperature to −90 °C no significant dynamic behaviour is detected, only the signals at δ 8.77 and 7.95 resolve into doublets with a coupling constant of 2.22 Hz. The different behaviour of compounds **1** and **2** is certainly due to the absence of N–H bonds in **2** and also to the higher rigidity arising from the bidentate ligand system in **2**.

At ambient temperature complex **3** shows equivalent pyrazole rings with resonances at δ 9.17, 8.31 (3,5-H) and 6.62 (H-4); the C–H resonance is found at δ 10.83. Once again, the resonances are shifted to lower field in relation to those of the free ligand (see Table 2). At room temperature all three nitrogen atoms interacting with molybdenum are equivalent due to their rapid rotation. At −90 °C each type of hydrogen atom of the pyrazole ring shows two resonances in a 1 : 2 ratio. The coalescence temperature is −40 °C. Two of the three nitrogen donor atoms are located *trans* to the oxygens, in equatorial positions, whereas the other nitrogen atom is in axial position, *trans* to the chloride ligand. At ambient temperature all the pyrazole rings of the ligand are equivalent, while at low temperature the motion is hindered and the complex probably 'freezes' in C_s symmetry. This is analogous to the related compounds $MoO_2Cl[\{(3,5\text{-}Me_2pz)_3BH\}]$[15] or $MoO_2(CH_3)[\{(3,5\text{-}Me_2pz)_3BH\}]$,[16] where the pyrazole rings are in a facial arrangement. At room temperature, however, the axial and equatorial positions become equivalent due to rotation of the ligand. The bromine derivative **4** shows a very similar behaviour. The ^{1}H NMR signals are only slightly shifted in comparison to those of the Cl derivative **3**. However, it is clear from the observed resonances that the better donor capability of the bromine ligand is reflected in the observed chemical shifts (see Table 2).

In complex **5** two of the protons of each pyrazole ligand (in 3 and 5 positions) are replaced by methyl groups, thus generating a bulkier ligand. Accordingly, complex **5** shows two different types of resonances for the 3,5-dimethylpyrazole ring of the $HC(3,5\text{-}Me_2pz)_3$ ligand, even at ambient temperature. In this case the rotation of the ligand is slower than in complex **3** due to the steric hindrance caused by the presence of the methyl groups. Lowering the temperature to −90 °C does not produce significant changes in the ^{1}H NMR spectrum, as would be expected. The rigidity of the methylated ligand system has been noted.[17]

The borate complex **6** also shows a fluxional behaviour. Three proton signals can be observed for the pyrazole ligand (see Table 2), and another for the B–H. Even at −90 °C the system remains flexible. The signals broaden but do not split in a 1 : 2 ratio.

The compounds exhibit ^{95}Mo NMR resonances with chemical shifts close to the centre of the chemical shift range of this nucleus (see Table 1). Complexes **1** and **2** show their ^{95}Mo NMR chemical shifts at δ 157 and 144, respectively (see also Table 1).

Table 2 ^{1}H NMR chemical shifts of compounds **1**–**7** and the free ligands. All measurements were performed in methylene chloride at room temperature

Compound	N–H	CH_3/H-3	H-4	CH_3/H-5	B–H/C–H
1	14.0	2.28	5.93	2.28	
Ligand	12.1	2.22	5.75	2.22	
2		8.77	6.55	7.95	2.25
Ligand		7.54	6.28	7.48	2.28
3		9.17	6.62	8.31	10.83
Ligand		7.64	6.34	7.55	8.42
4		8.35	6.64	8.07	9.06
5		2.79/2.76 (1 : 2)	6.32/6.26 (1 : 2)	2.73; 2.79	2.70; 8.05
Ligand		2.16	5.90	1.98	8.08
6		7.67	6.06	7.23	8.0
Ligand		7.52	6.1	7.25	4.7

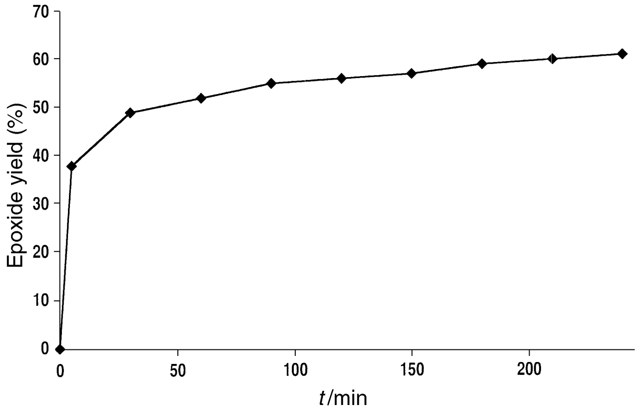

Fig. 1 Typical catalytic run in cyclooctene epoxidation with compound **2** as the catalyst. For details see text.

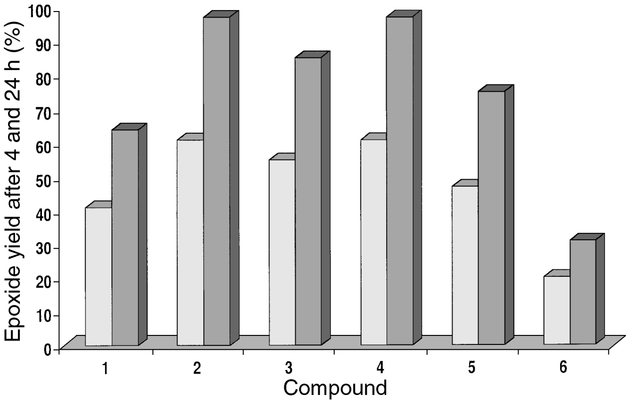

Fig. 2 Cyclooctene epoxide yields after 4 and 24 h, respectively. Compounds **1**–**6** have been used as catalysts. See text for more details.

These values are in accordance with those in the literature for octahedral MoO_2X_2L complexes, with L = bidentate Lewis base N donor ligand and X = Cl or Br.[1a,18] Complexes **3**, **5**, **6** display their ^{95}Mo NMR chemical shift between δ 80 and 90, in good agreement with values from the literature for oxohalogenomolybdenum(VI) complexes with tripodal N donor ligands.[15] The borate complex **6** is, as expected and consistent with the IR data, the most electron rich complex. However, the chemical shift difference between compounds **5** and **6** is rather small (7 ppm). For **3** and **4** the observed chemical shifts exhibit an inverse halogen dependence. Inverse halogen dependencies of chemical shifts have also been observed for other oxohalogenomolybdenum(VI) complexes.[1a,19]

Complexes 1–6 in oxidation catalysis

The complexes were tested for the catalytic epoxidation of cyclooctene with *t*-butyl hydroperoxide. The TBHP is used as a 5.5 M solution in n-decane, and after its addition homogeneous conditions are obtained. The applied temperature was 55 °C and the catalyst : substrate : oxidant ratio 1 : 100 : 200. Further details are given in the Experimental section. Blank reactions were performed. Without catalyst no significant epoxide formation (<5%) was observed under these conditions. Significant by-product formation, *e.g.* diol instead of epoxide, was never observed in the uncatalysed or catalysed runs.

In general, the compounds show an overall yield between 40 and 60% after 4 h. If the reaction time is increased to 24 h the yield increases significantly being almost quantitative in the cases of **2**–**5**. This indicates that the catalysts have a high stability under the reaction conditions and that the conversions after 4 h are mainly due to a relatively slow reaction and not to decomposition of the catalyst. In Fig. 1 a typical catalytic run is shown for compound **2**. Within the experimental limit defined by the time of the initial measurement there is no indication of an induction period and, therefore, the catalytically active species must be formed shortly after the addition of the peroxide. The coordinating ligands profoundly influence the product yield. The catalytic activities of compounds **1**–**6** are shown in Fig. 2, and the turnover frequencies (TOF) are given in Table 1.

Comparing the activity of compounds **3** and **4**, the bromine derivative shows a lower turnover frequency than the chlorine derivative (see Table 1). This is in good agreement with observations made from comparable complexes of formula $MoX_2O_2L_2$.[1a] However, after a longer reaction time (4 and 24 h, see Fig. 2) the difference is within the experimental error of these measurements. This might be due to the fact that both complexes appear to be stable under the catalytic conditions so that, finally, nearly quantitative epoxide yields are reached in both cases. The differences caused by the changes of the organic ligand are much more pronounced. In fact, compound **6**, bearing the most electron donating ligand $[HB(pz)_3]^-$, shows much lower activity than **3** and **5**. In fact, among compounds **3**–**6**, the latter is the only one that has a negatively charged ligand which, ultimately, increases the electron density at the metal centre, as can be seen from both IR and NMR data (see Table 1). The fact that the epoxide yield with complex **6** as catalyst precursor did not increase very much from 4 to 24 h reaction time indicates that an oxidation of the catalyst occurs, as is expected for a B–H bond under such conditions. It should be noted, in this context, that the complexes **3** and **6** have very similar structures and steric bulk around the Mo but have different charges. A comparison of their catalytic behaviour, however, is difficult to make due to the decomposition of **6**. Compound **1** has, according to our NMR examinations, two relatively weakly bound ligands and is also less stable than **2**–**5**. The chelate effect of the ligand in complex **2** obviously has a big influence on the catalyst stability and subsequently on the catalytic activity. This is even more conspicuous if one examines the bis(pyrazole) derivative of complex **1**: (i) this compound is too unstable to be isolated; (ii) it decomposes well below room temperature. The activity difference between compounds **3** and **5** is very small, despite the fact that the methylated ligand of **5** is more electron rich and bulkier than that of **3**. This means that the activity growth can be related to the electron density at the metal centre at least to a certain degree. Electron donating ligands decrease the activity somewhat. Also, steric hindrance might contribute to a lower activity, as it can make the co-ordination of the peroxide to the metal centre more difficult, and also hinders the approach of the olefin. However, with respect to compounds **3** and **5** this effect does not appear to be very pronounced. Although it cannot totally be ruled out that the catalytic activity is due to a significantly different species derived from the precursor complexes, it seems beyond reasonable doubt that the organic ligands remain, at least partially, attached to the metal in the catalytically active centre and determine its activity.

The complexes examined in this work display turnover frequencies which are within the range of the TOFs of $MoX_2O_2L_2$ complexes already described. The range of the TOFs of complexes of general formula $MoX_2O_2L_2$ is *ca.* 20–600 [mol/(mol catalyst h)], mainly depending on the ligand L.[1a] The most active complexes with ligands of the 1,4-diaza-1,3-butadiene type have TOFs up to 600 [mol/(mol catalyst h)].[1a] Complexes with bipyridine ligands show TOFs below 100 [mol/(mol catalyst h)].[1a] The solvent ligated complexes of formula $MoX_2O_2(Solv)_2$ (Solv) = THF, RCN, *etc.* display TOFs between *ca.* 100 and 200 [mol/(mol catalyst h)],[18] the alkylated derivatives $MoR_2O_2L_2$ (R = Me or Et) between 20 and 180 [mol/(mol catalyst h)].[20] The well known catalyst $MoO_2(acac)_2$ displays a TOF of 105 [mol/(mol catalyst h)], $Mo(CO)_6$ of *ca.* 75 [mol/(mol catalyst h)].[1a] Therefore the compounds examined in this work are medium active $Mo^{VI}O_2$ catalysts. However, they are of good stability and the yields obtained after 4 and 24 h are comparable with those obtained with other systems of higher TOFs. A comparison with other related systems, *e.g.* $MoCp^*O_2Cl$, described by Trost and Bergmann[21] (which can be regarded as analogous to the complexes **3**–**5**), and MoO_2L_4 and WO_2L_4, described by Herrmann *et al.*[22] is more difficult. Either no turnover frequencies are given in the original literature and/or the reactions have been performed under different conditions, *e.g.* at different temperatures. It is clear, however, that significantly more active epoxidation catalysts exist, *e.g.* molybdenum(VI) monoperoxo complexes of formula $MoO_2(O_2)L_2$[1f,23] or the extensively examined $Re(CH_3)O_3$[24] and its adducts of formula $Re(CH_3)O_3L$ and $Re(CH_3)O_3L_2$.[25] Nevertheless, these established systems have other disadvantages. While $Re(CH_3)O_3$ leads to significant diol formation, the last two complex types require a ligand excess of about 10 : 1 [L/L_2 : $Re(CH_3)O_3$] to be efficient epoxidation catalysts.

Crystal structure of $MoO_2Cl_2(C_9H_{12}N_4)$ 2

The crystal structure of compound **2** involves discrete molecules without short interatomic contacts. The molecular structure is shown in Fig. 3; selected bond lengths and angles are listed in Table 3. The molecule has nearly C_s symmetry in the solid state but it exhibits no real crystallographic symmetry. The co-ordination around the metal centre is best described as a distorted octahedron. All bond lengths and angles of the $MoO_2Cl_2N_2$ moiety do not vary significantly and are comparable to those observed in other structural fully characterized molybdenum compounds with the same core geometry.[26g] NMR and IR data are consistent with these observations. All crystallograpically characterised complexes with a 2,2-bis(pyrazolyl)propane ligand exhibit a very similar geometry in the organic building block. Distances and angles in the molecule are unexceptional and do not require further comment.

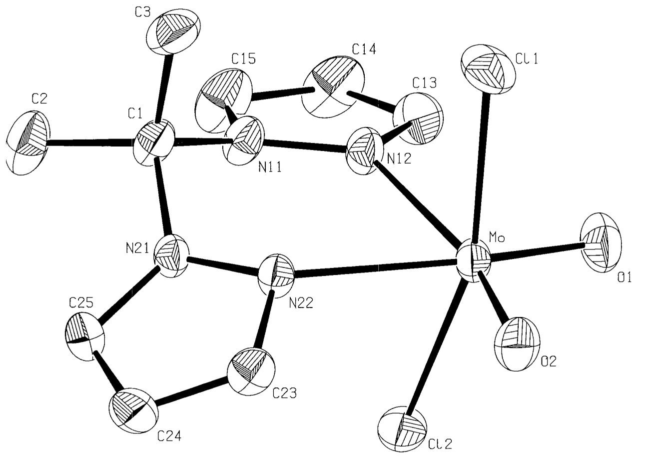

Fig. 3 PLATON[26f] plot of the solid state structure of complex **2**. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3 Selected interatomic distances (Å) and angles (deg) for compound **2**

Mo–Cl1	2.3570(7)	Mo–N12	2.301(2)
Mo–Cl2	2.3877(5)	Mo–N22	2.325(2)
Mo–O1	1.693(2)	N11–N12	1.362(3)
Mo–O2	1.690(2)	N21–N22	1.368(3)
Cl1–Mo–Cl2	163.36(2)	Cl2–Mo–N22	79.97(5)
Cl1–Mo–O1	95.76(6)	O1–Mo–O2	105.09(9)
Cl1–Mo–O2	95.22(6)	O1–Mo–N12	89.98(8)
Cl1–Mo–N12	83.85(5)	O1–Mo–N22	166.45(8)
Cl1–Mo–N22	88.12(5)	O2–Mo–N12	164.91(8)
Cl2–Mo–O1	93.37(6)	O2–Mo–N22	87.42(7)
Cl2–Mo–O2	95.80(6)	N12–Mo–N22	77.50(6)
Cl2–Mo–N12	82.26(5)		

Conclusion

Molybdenum(VI) *cis*-dioxo complexes bearing (poly)pyrazolylmethane and -borate ligands can readily be prepared by treating the appropriate ligands with solvent adducts of dihalogenodioxomolybdenum(VI). In the case of mono- and bi-dentate pyrazole derivatives, both solvent molecules co-ordinated to the starting material are replaced by the ligands, thus forming distorted octahedral complexes. Tridentate pyrazolyl derivatives, additionally replace one of the halogeno ligands. The co-ordination strength of the ligand depends on its electron donor capability and steric bulk. Weak donors, lacking substituents at the pyrazolyl moieties, rotate quickly about the Mo. Axial and equatorial positions are only distinguishable at lower temperatures. The described complexes can be utilized in the oxidation of olefins to epoxides without concomitant formation of diols. Tris(pyrazolyl)methane and its methylated derivatives form quite active and stable molybdenum(VI) catalysts. Different substituents at the pyrazole rings may, therefore, further improve the catalytic activity of these systems.

Experimental

All preparations and manipulations were carried out with standard Schlenk techniques under an oxygen free and water free nitrogen or argon atmosphere. Solvents were dried by standard procedures, distilled and kept under argon over 4 Å molecular sieves. Microanalyses and mass spectra were performed at the TUM (Garching) laboratories. IR spectra were measured on a Perkin-Elmer FTIR spectrometer, mass spectra with a Finnigan MAT 311 A and a MAT 90 spectrometer and ^1H (400.13), ^{13}C (100.62), ^{95}Mo (26.09) and ^{11}B NMR (128.37 MHz) on a Bruker Avance DPX-400. NMR spectra of the compounds recorded at 55 °C do not vary significantly from those at 25 °C and are therefore not commented upon. The starting material $MoO_2Cl_2(THF)_2$,[18] potassium hydrotris(1-pyrazolyl)borate,[2b] 2,2-di(1-pyrazolyl)propane,[27] tris(1-pyrazolyl)methane[10] and tris(3,5-dimethyl-1-pyrazolyl)-

methane[27] were prepared as described. All other chemicals mentioned were used as purchased from Aldrich.

Preparations

$MoO_2Cl_2(C_{10}H_{14}N_4)$ 1. To a solution of $MoO_2Cl_2(THF)_2$ (1307 mg, 3.81 mmol) in THF (15 mL), 3,5-dimethylpyrazole (732 mg, 7.62 mmol) is added at room temperature. The solution turns from colourless to yellow and then to orange within a few minutes. The mixture is allowed to react for 25 min. The volume is reduced to *ca.* 2 mL and 10 mL of diethyl ether are added under stirring. The solution is taken to dryness until a foamy orange solid is formed. The solid is washed twice with *n*-hexane and then dried. Yield: 1298 mg (87%). Calc. for $C_{10}H_{14}Cl_2MoN_4O_2$: C 30.87, H 3.63, N 14.40. Found: C 30.59, H 3.67, N 14.31%. IR (KBr, ν/cm^{-1}): 3118m, 1603vs, 1283s, 943vs (ν_{asym}(Mo=O)), 906s (ν_{sym}(Mo=O)), 902s, 713m, 572m. ^1H NMR: see Table 2. ^{13}C NMR (CD_2Cl_2, RT): δ 12.05 (CH_3–pz), 13.96 (CH_3–pz), 106.01 (4-C), 141.66 (3-C), 144.32 (5-C). ^{95}Mo NMR (CD_2Cl_2, RT): δ 156.8.

$MoO_2Cl_2(C_9H_{12}N_4)$ 2. To a solution of $MoO_2Cl_2(THF)_2$ (686 mg, 2 mmol) in THF (10 mL) 2,2-di(1-pyrazolyl)propane (350 mg, 2 mmol) is added at room temperature. The solution turns yellow. After reacting for 15 min, it is filtered into another Schlenk tube. Then the volume is reduced to *ca.* 2 mL by oil pump vacuum. Diethyl ether is then added (10 mL) and the formation of a fine white precipitate occurs. The remaining solution is filtered off. After taking the residue to dryness a yellowish oil is obtained. This oil is dissolved in CH_3CN (10 mL) and diethyl ether (10 mL) added, leading to the formation of a white precipitate, which is then isolated by filtration and drying of the filtrate. Yield: 393 mg (52.5%). Calc. for $C_9H_{12}Cl_2MoN_4O_2$: C 28.82, H 3.22, N 14.94. Found: C 29.17, H 2.96, N 14.80%. IR (KBr, ν/(cm^{-1}): 3144s, 1510s, 1442s, 1308s, 943vs (ν_{asym}(Mo=O)), 916s (ν_{sym}(Mo=O)), 902s, 713m, 572m. ^1H NMR: see Table 2. ^{13}C NMR (CD_2Cl_2, RT): δ 30.24, 108.8, 132.82, 150.25. ^{95}Mo NMR (CD_2Cl_2, RT): δ 144. CI-MS: *m/z* (%) = 358(0.34) [$M^+ - CH_3$; ^{95}Mo, ^{35}Cl], 197 (7.24) [$M^+ - (CH_3)_2C(pz)_2$].

$MoO_2Cl_2(C_{10}H_{10}N_6)$ 3. To a solution of $MoO_2Cl_2(THF)_2$ (765 mg, 2.23 mmol) in THF (10 mL) tris(1-pyrazolyl)methane (477 mg, 2.23 mmol) is added at room temperature and allowed to react for 30 min. The yellow solution obtained is then filtered into another Schlenk and concentrated under oil pump vacuum to *ca.* 2 mL. To this solution 10 mL of diethyl ether are added with the subsequent formation of a slightly yellow precipitate; the solution is filtered into another Schlenk and the precipitate taken to dryness. To the solution more diethyl ether is added to precipitate the complex. The solution is filtered off and the precipitate taken to dryness and washed twice with diethyl ether. Yield: 561 mg (61%). Calc. for $C_{10}H_{10}Cl_2MoN_6O_2$: C 29.08, H 2.44, N 20.34. Found: C 28.82, H 2.31, N 20.07%. IR (KBr, ν/cm^{-1}): 3102s (N–H), 1409vs, 1067s, 953vs (ν_{asym}(Mo=O)), 920s (ν_{sym}(Mo=O)), 860s, 783vs, 603s. ^1H NMR: see Table 2. ^{95}Mo NMR (CD_2Cl_2, RT): δ 86.8.

$MoO_2Br_2(C_{10}H_{10}N_6)$ 4. To a solution of $MoO_2Br_2(THF)_2$ (811 mg, 1.88 mmol) in 40 mL of THF at 70 °C tris(1-pyrazolyl)methane (400 mg, 1.88 mmol) is added and the mixture allowed to react for 15 min. The solution obtained is filtered into another Schlenk and concentrated to *ca.* 2 mL. *n*-Hexane (5 mL) is then added leading to the formation of a bright yellow precipitate. This precipitate is taken to dryness, washed three times with n-hexane and finally with diethyl ether and taken to dryness again. Yield: 658 mg (70%). Calc. for $C_{10}H_{10}Br_2MoN_6O_2$: C 23.93, H 2.01, N 16.74. Found: C 23.77, H 2.15, N 16.59%. IR (KBr, ν/cm^{-1}): 3105m, 2947m, 1508s, 1408vs, 1098s, 1064s, 948vs (ν_{asym}(Mo=O)), 918vs (ν_{sym}(Mo=O)), 774vs, 604s. ^1H NMR: see Table 2. ^{13}C NMR (CD_2Cl_2, RT): δ 73.05, 107.56, 132.75, 145.11. ^{95}Mo NMR (CD_2Cl_2, RT): δ 157.79.

Table 4 Summary of data for crystal structure analysis of compound **2**

Formula	$C_9H_{12}Cl_2MoN_4O_2$
Formula weight	375.05
Crystal system	Orthorhombic
Space group	*Pbca* (no. 61)
a/Å	12.0163(2)
b/Å	15.8867(4)
c/Å	14.4079(3)
V/Å^3	2750.5(1)
Z	8
μ/mm^{-1}	1.341
λ/Å	0.71073
T/K	173
No. reflections collected	24230
No. independent reflections/(R_{int})	2519/0.039
No. observed reflections ($I > 2\sigma I$)	2275
$R1$, $wR2$ indices ($I > 2\sigma I$)	0.0243, 0.0585
$R1$, $wR2$ indices (all data)	0.0277, 0.0602

$MoO_2Cl_2(C_{16}H_{22}N_6)$ 5. To a solution of $MoO_2Cl_2(THF)_2$ (314 mg, 0.918 mmol) in THF (10 mL), tris(3,5-dimethyl-1-pyrazolyl)methane (277 mg, 0.918 mmol) is added at room temperature. The colourless solution becomes orange and after *ca.* 10 min a yellow precipitate forms. The mixture is allowed to react for 15 min. The volume is reduced to *ca.* 3 mL and the remaining solution filtered off. The precipitate is washed twice with diethyl ether and taken to dryness. Yield: 421 mg (92%). Calc. for $C_{16}H_{22}Cl_2MoN_6O_2$: C 38.66, H 4.42, N 16.90. Found: C 37.91, H 4.40, N 16.91%. IR (KBr, ν/cm^{-1}): 3132s, 1564vs, 1457s, 1262s, 1046vs, 946vs (ν_{asym}(Mo=O)), 912s (ν_{sym}(Mo=O)), 705vs. ^1H NMR: see Table 2. ^{95}Mo NMR (CD_2Cl_2, RT): δ 87.4.

$MoO_2Cl(BC_9H_{10}N_6)$ 6. To a solution of $MoO_2Cl_2(THF)_2$ (820 mg, 2.39 mmol) in 10 mL of THF, potassium hydrotris(1-pyrazolyl)borate (602 mg, 2.39 mmol) is added at room temperature and allowed to react for 90 min. The colourless solution turns to orange. The volume is reduced to *ca.* 2 mL and 10 mL of diethyl ether were added, leading to the formation of a yellow precipitate. The solution is filtered off and the precipitate taken to dryness, washed twice with diethyl ether and recrystallized from CH_2Cl_2. Yield: 690 mg (77%). Calc. for $C_9H_{10}ClMoN_6O_2$: C 28.69, H 2.65, N 22.30. Found: C 27.93, H 2.60, N 22.01%. IR (KBr,ν/cm^{-1}): 3120 (N–H), 2485 (B–H), 935vs (ν_{asym}(Mo=O)), 905vs (ν_{sym}(Mo=O)), 774vs, 604s. ^1H NMR: see Table 2. ^{11}B NMR (CD_2Cl_2, RT): δ −4.3. ^{95}Mo NMR (CD_2Cl_2, RT): δ 80.3.

Catalytic reactions with compounds 1–6 as catalysts

800 mg (7.3 mmol) *cis*-cyclooctene, 800 mg n-dibutyl ether (internal standard), 1 mol% (73 µmol) **1**–**6** (as catalyst, added as a solid) and 2 ml 5.5 M *t*-butyl hydroperoxide in n-decane are added to a thermostated reaction vessel and stirred for 4 h at 55 °C. The course of the reaction is monitored by quantitative GC analysis. Samples are taken every thirty minutes, diluted with dichloromethane, and chilled in an ice-bath. For the destruction of hydroperoxide and removal of water, a catalytic amount of manganese dioxide and magnesium sulfate are added. After the gas evolution ceases, the resulting slurry is filtered over a filter equipped Pasteur pipette and the filtrate injected in the GC column. The conversion of cyclooctene and formation of cyclooctene oxide are calculated from a calibration curve ($r^2 = 0.999$) recorded prior to the reaction course.

Structure determination of complex 2

Details of the X-ray experiment, data reduction, and final structure refinement are summarized in Table 4. Crystals of complex **2** were grown by slow evaporation of a saturated solution of it in a mixture of diethyl ether, acetonitrile and dichloromethane. Preliminary examination and data collection were carried out on a Nonius Kappa CCD system area-detector diffractometer at the window of a rotating anode generator (NONIUS FR591; 50 kV; 60 mA; 3.0 kW) using graphite monochromated Mo-Kα radiation. Data collection was controlled by the Collect software package.[26a] Collected images were processed using Denzo.[26b] The unit cell parameters were obtained by full-matrix least-squares refinements of 42799 reflections.[26b] The structure was solved by a combination of direct methods and Fourier-difference syntheses.[26c] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the Fourier difference map and refined freely with individual isotropic thermal displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL 97.[26d] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref. 26(*e*). All other calculations (including ORTEP graphics) were done with the program PLATON.[26f] Calculations were performed on a PC workstation (Intel Pentium II) running LINUX.

CCDC reference number 154166.

See http://www.rsc.org/suppdata/dt/b0/b009202i/ for crystallographic data in CIF or other electronic format.

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