Oxidoperoxidomolybdenum(VI) complexes with acylpyrazolonate ligands: synthesis, structure and catalytic properties

Emilio Begines,à Carlos J. Carraasco,à Francisco Montilla,à Eleuterio Álvarez,b Fabio Marchetti,c Ricardo Pettinari,c Claudio Pettinari,c & Agustín Galindo*à

Oxidoperoxido-molybdenum(VI) complexes containing acylpyrazolonate ligands were obtained by reaction of \([\text{Mo(O)(O}_2\text{H}_2\text{O})_2]\) with the corresponding acylpyrazalone compounds HQ\(_8\). Complexes \(\text{Ph}_2\text{P}[\text{Mo(O)(O}_2\text{H}_2\text{O})_2(Q^2)]\) \((Q = \text{neopentyl, 1; perfluoroethyl, 2; hexyl, 3; phenyl, 4; naphthyl, 5; methyl, 6; cyclohexyl, 7; ethylcyclopentyl, 8)}\) were obtained if the reaction was carried out with one equivalent of HQ\(_8\) in the presence of \(\text{Ph}_2\text{PCl}\). Alternatively, neutral complexes \([\text{Mo(O)(O}_2\text{H}_2\text{O})_2(Q^2)_2]\) \((Q = \text{neopentyl, 9; hexyl, 10; cyclohexyl, 11)}\) were formed when two equivalents of HQ\(_8\) were used in the reaction. These complexes were isolated in good yields as yellow or yellow-orange crystalline solids and were spectroscopically \((\text{IR, } ^1\text{H}, ^13\text{C}(^1\text{H}) \text{ and } ^3\text{P}(^1\text{H}))\) NMR, theoretically \((\text{DFT})\) and structurally characterised \((\text{X-ray for 1, 2, 9 and 10)}\). Compounds 1 and 9 were selected to investigate their catalytic behaviour in epoxidation of selected alkenes and oxidation of selected sulphides, while 10 and 11 were tested as catalyst precursors in the deoxygenation of selected epoxide substrates to alkenes, using \(\text{PPH}_3\) as the oxygen-acceptor. Complexes \(\text{Ph}_2\text{P}[\text{Mo(O)(O}_2\text{H}_2\text{O})_2(Q^2)]\) were shown to be poor catalyst precursors in oxidation reactions, while the activity of \([\text{Mo(O)(O)}_2\text{H}_2\text{O})_2(Q^2)_2]\) species is good in all the studied reactions and comparable to related oxidoperoxido-molybdenum(VI) complexes. Complex \([\text{Mo(O)(O}_2\text{H}_2\text{O})_2(Q^2)_2]\), 12, was obtained by treatment of 10 with one equivalent of \(\text{PPH}_3\), demonstrating that the first step in the epoxide deoxygenation mechanism was the oxygen atom transfer toward the phosphine.

Results and discussion

Synthesis and characterization of acylpyrazolonate-oxidoperoxidomolybdenum(VI) complexes

The treatment of a solution of \([\text{Mo(O)(O)}_2\text{H}_2\text{O})_2]\) with one equivalent of acylpyrazalone compounds HQ\(_8\), in the presence of \(\text{Ph}_2\text{PCl}\), produces complexes \(\text{Ph}_2\text{P}[\text{Mo(O)(O}_2\text{H}_2\text{O})_2(Q^2)]\) \((Q = \text{neopentyl, 1; perfluoroethyl, 2; hexyl, 3; phenyl, 4; naphthyl, 5; methyl, 6; cyclohexyl, 7; ethylcyclopentyl, 8)}\). They were isolated in good yields, after the appropriate work-up, as yellow crystalline solids (Scheme...
The existence of several strong bands in the IR spectra (1675-1500 cm⁻¹ range), attributed to ν(CO), ν(CN) and ν(CC), confirmed the presence of the acylpyrazolone ligands in these derivatives. The ν(CO) absorption in the free compounds HQ⁸ appears at a higher frequency (e.g., at 1632 cm⁻¹ for HQ⁸) than in compounds Ph₃P[Mo(O)(O₂)₂(Q)] (1630-1600 cm⁻¹ range; at 1618 cm⁻¹ for 3, which contains the Q⁶ ligand), in accordance with the ligand coordination to the molybdenum centre. Besides the acylpyrazolone absorptions, the oxido group generates characteristic ν(Mo=O) bands at around 950 cm⁻¹ (960-940 cm⁻¹ range), while the peroxido ligands display distinctive ν(OO), ν₂[Mo(OO)] and ν₁[Mo(OO)] absorptions close to the expected ranges for this ligand: 870-850, 660-650 and 585-572 cm⁻¹, respectively.¹⁴

¹H and ¹³C(¹H) NMR spectra of compounds 1-8 show signals corresponding to the acylpyrazolone ligand in agreement with the proposed formulation Ph₃P[Mo(O)(O₂)₂(Q)]. These signals are those of the common Q skeleton together with the characteristic signals of the R substituents in Q⁸ ligands. Thus, for example, the 3-methyl group (C-1, see notation at Experimental) originated singlets in the ¹H and ¹³C(¹H) NMR spectra centred around 1.3-2.4 ppm and 15-18 ppm, respectively. The 1-phenyl group gave rise in the ¹H NMR to the typical pattern doublet:triplet:triplet, 2:2:1, in the 7-8 ppm range and in ¹³C(¹H) NMR to four signals in the range 115-140 ppm (ipso, C-6; ortho, C-7; meta, C-8; and para, C-9, carbon atoms, see notation at Experimental). In addition, the common Q ligand skeleton has three carbon atoms of the pyrazole ring along with the carbon atom of the acyl group, which gave singlets in the ¹³C(¹H) NMR spectra. Pyrazole carbon atoms appeared within the range 135-160 ppm (C-2, C-3 and C-4), while the signal of the acyl carbon atom, C-5, arose around 190-200 ppm (see notation at Experimental). These assignments are analogous to other related Q⁸-containing complexes reported in the literature.¹⁵

In a similar way, complexes [Mo(O)(O₂)₂(Q)] (R = neopentyl, 9; hexyl, 10; Cy, 11) were obtained by the reaction of [Mo(O)(O₂)₂(H₂O)] with two equivalents of HQ⁸ acylpyrazolone compounds, under the appropriate reaction conditions (Scheme 2). They were obtained as yellow-orange crystalline solids in good yields. Two set of resonances were found in the ¹H and ¹³C(¹H) NMR spectra for the two non-equivalent Q⁸ groups in agreement with the proposed formulation [Mo(O)(O₂)(Q⁸)], which was further confirmed by X-ray crystallography. The NMR spectra of complexes 9-11 additionally showed small resonances for extra Q⁸ groups that can be assigned to isomers of the main product. In fact, four isomers are possible for an octahedral oxido-peroxido complex with an asymmetric bidentate ligand. Although the X-ray structure of 9 and 10 correspond to only one isomer (isomer C, see Scheme 3 below), the computed energies for the other three isomers are comparable (see DFT discussion below). Consequently, the preferential formation this isomer, shown in Scheme 2, is ascribable to kinetic reasons.

The molecular structure of the complexes Ph₃P[Mo(O)(O₂)₂(Q)] (1, Ph₃P[Mo(O)(O₂)₂(Q)] (2, [Mo(O)(O₂)(Q)] (9), and [Mo(O)(O₂)(Q)] (10), were determined by X-ray methods and the results are shown in Figs. 1-2. Selected structural data are included in Table 1. Assuming that peroxido ligand occupies one coordination position, complexes 1 and 2 display a trigonal bipyramidal structure (bpt) with an axial oxido and two equatorial side-on peroxido ligands. The bpt coordination is completed by the acylpyrazolone ligand with the two O-donor atoms occupying the remaining axial and equatorial positions. The Mo=O oxido distance in 1 and 2 are close to the mean value of 1.68(2) Å (range 1.61-1.73 Å) found in mononuclear [Mo(O)(O₂)₂L]⁶⁻ complexes.³⁴,⁶,¹⁷ Concerning the peroxido ligands, they are side-on asymmetrically bonded to molybdenum (see Table 1) and the peroxido O-O bond lengths fit well with the mean value of 1.47(2) Å for the range 1.35-1.54 Å observed in these complexes.³⁴,¹⁶ The Mo1-O2 bond lengths of ca. 2.3 Å (Q⁸ ligand, for 1 and 2) clearly reflect the trans influence of the oxido group.
Complexes 9 and 10 have a distorted octahedral structure where two acylpyrazolonate ligands are coordinated to the metal centre through two oxygen atoms and the molybdenum six-coordination is completed by the presence of mutually cis oxido and peroxido groups. In both complexes, the O atoms from the carbonyl moiety of the acyl group of each Q\(^\text{cis}\) ligand (O2 and O4 atoms in 9 or O2 in 10) occupy the trans position with respect to the oxido (O5 for 9 and O3 for 10) and peroxido groups (O6-O7 for 9 and O4-O5 for 10). The oxygen atoms of the hydroxido groups of pyrazole in the two Q\(^\text{cis}\) ligands (O1 and O3 for 9 and O1 for 10) are arranged in mutually trans positions. The Mo=O bond distances, for both, are similar to those of 1 and 2 and within the known range for the Mo=O bond.\(^{16}\) The bond distances between the Mo centre and the oxygen atoms of the acylpyrazolonate ligands (range 2.02-2.15 Å) are similar as those found in other related complexes,\(^{10,16}\) but shorter than the Mo1-O2 bond lengths of ca. 2.3 Å of 1 and 2. The cis-oxido-peroxido-molybdenum moiety shows the characteristic O=Mo=O angles higher than 90° and the typical distortions from an ideal octahedron of a \(d^8\)-Mo(O2) system.\(^{18}\) Focusing the attention on the ligand Q skeleton, in all these complexes the C-O distance (from the hydroxido group) is slightly larger than the C=O distance (from the acyl group) and this fact suggests a small delocalization on the acylpyrazolonate ligand.

**DFT study of the possible isomers of Ph\(_2\)P[Mo(O)(O\(_2\))(Q\(^\text{cis}\))] and [Mo(O)(O\(_2\))(Q\(^\text{cis}\))] complexes**

Acylpyrazolonate ligands are asymmetric in their standard \(x\text{-}(O,O')\)-bidentate coordination to the metal centre and, consequently, two possible isomers can be considered for the Ph\(_2\)P[Mo(O)(O\(_2\))(Q\(^\text{cis}\))] complexes (A and B in Scheme 3, top). The two possible isomers of the anions of complexes 1 and 2 were analysed theoretically by using the Density Functional Theory (DFT) approach.\(^{19}\) Geometry optimisations were carried out without symmetry restrictions and the resulting optimised structures are shown in Fig. 3. All of them are stationary points on the potential energy surface (PES) as confirmed by the calculations of the frequencies. A comparison between the computed structural parameters for the isomer A of the anions of 1 and 2 and those experimentally found by X-ray diffraction was collected in Table S3 (see ESI). In general, a reasonable good agreement with experimental data was found. The Mo-O bond distances, trans with respect to the oxido group, are slightly overestimated (computed distances of ca. 1.705 Å). This is a feature

Table 1 Selected structural parameters of compounds Ph\(_2\)P[Mo(O)(O\(_2\))(Q\(^\text{cis}\))], 1, Ph\(_2\)P[Mo(O)(O\(_2\))(Q\(^\text{cis}\))] and [Mo(O)(O\(_2\))(Q\(^\text{cis}\))], 10.

<table>
<thead>
<tr>
<th>Bond distances (Å) and angles (°)</th>
<th>1</th>
<th>2</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo=O</td>
<td>1.686(1)</td>
<td>1.680(1)</td>
<td>1.684(2)</td>
<td>1.687(8)</td>
</tr>
<tr>
<td>Mo-O (peroxido)</td>
<td>1.951(1)</td>
<td>1.904(2)</td>
<td>1.908(2)</td>
<td>1.885(8)</td>
</tr>
<tr>
<td>Mo-O (Q(^\text{cis}))</td>
<td>2.278(1)</td>
<td>2.325(2)</td>
<td>2.150(2)</td>
<td>2.138(2)</td>
</tr>
<tr>
<td>Mo-O (Q(^\text{cis}))</td>
<td>-</td>
<td>-</td>
<td>2.121(2)</td>
<td>2.138(2)</td>
</tr>
<tr>
<td>O=Mo-O (cis oxido)</td>
<td>1.474(2)</td>
<td>1.447(2)</td>
<td>1.4162(18)</td>
<td>1.424(6)</td>
</tr>
<tr>
<td>C=O</td>
<td>1.251(2)</td>
<td>1.236(3)</td>
<td>1.266(3)</td>
<td>1.275(4)</td>
</tr>
<tr>
<td>C-O</td>
<td>1.296(2)</td>
<td>1.288(2)</td>
<td>1.289(3)</td>
<td>1.299(4)</td>
</tr>
<tr>
<td>O=Mo-O (peroxido)</td>
<td>102.64(7)</td>
<td>102.94(7)</td>
<td>102.16(15)</td>
<td>103.2(2)</td>
</tr>
<tr>
<td>O=Mo-O (trans)</td>
<td>101.27(7)</td>
<td>101.23(8)</td>
<td>100.73(13)</td>
<td>102.4(3)</td>
</tr>
<tr>
<td>O=Mo-O (cis)</td>
<td>99.77(7)</td>
<td>101.31(7)</td>
<td>98.20(11)</td>
<td>170.5(3)</td>
</tr>
<tr>
<td>O=Mo-O (cis)</td>
<td>169.37(6)</td>
<td>171.30(6)</td>
<td>166.08(11)</td>
<td>103.4(2)</td>
</tr>
<tr>
<td>C-O</td>
<td>88.99(6)</td>
<td>92.21(6)</td>
<td>89.96(11)</td>
<td>90.4(3)</td>
</tr>
</tbody>
</table>

Fig. 2 Molecular structures of [Mo(O)(O\(_2\))(Q\(^\text{cis}\))] and [Mo(O)(O\(_2\))(Q\(^\text{cis}\))], 9, (left) and [Mo(O)(O\(_2\))(Q\(^\text{cis}\))], 10, (right). ORTEP diagrams drawing at 30% probability level. Hydrogen atoms were omitted for clarity.
frequently observed in the lengths of ligands that occupy the trans position with respect to a ligand with a strong trans influence. From an energetic point of view, the isomer A is the most stable by ca. 3 kcal mol\(^{-1}\) (electronic energy) with respect to the isomer B. Although this energy difference is small, this result is consistent with the experimental structures found for complexes 1 and 2 that correspond to the most stable isomer A.

Concerning compounds [Mo(O)(O\(_2\))\(_2\)\(_2\)], the four possible isomers C-F (Scheme 3, bottom) of complexes 9 and 10 were also theoretically investigated at the same level of theory. All of the optimised structures (see Figs. S4 and S5, ESI) were stationary points and again the computed structural parameters for the C isomers compare well with those experimentally found by X-ray (Table S4). From an energetic point of view, the four isomers C-F have roughly the same energy with energy differences between them lower than 1 kcal mol\(^{-1}\) (electronic energy). Taking into account the computed energies and considering the C structure found in structurally characterised [Mo(O)(O\(_2\))\(_2\)\(_2\)] complexes, we can suggest a mechanism for the preferential formation of isomer C (Scheme 4).

The first step is the interaction of the parent [Mo(O)(O\(_2\))(H\(_2\)O\(_n\))] with HQ\(^{-}\) with water substitution and formation of the anionic intermediate [Mo(O)(O\(_2\))(Q\(_n\))\(_{-}\)]. The latter most likely has a type A structure found in structurally characterised [Mo(O)(O\(_2\))\(_2\)\(_2\)] complexes, we can suggest a mechanism for the preferential formation of isomer C (Scheme 4).
structure (thermodynamic isomer), being the isomerisation to the intermediate with B structure a slow process. The interaction of [Mo(O)(O2)(Q1)], A, with a second molecule of HQ3 would produce the isomer of type C [Mo(O)(O2)(Q1)] as the kinetic isomer. Small amounts of isomer D would appear through a slow isomerisation from C, while isomers E and F would be produced by reaction of the less stable isomer B of the intermediate [Mo(O)(O2)(Q1)] with HQ3 and subsequent isomerization, respectively. The isomerization from C to D was experimentally proved by heating a sample of complex 10 (isomer C) at 50 °C for 24 h (see Fig. S6, ESI).

Epoxidation and sulphoxidation reactions using PhP[Mo(O)(O2)(Q1)] and [Mo(O)(O2)(Q1)] as catalyst precursors

Two oxidation reactions were selected to evaluate the catalytic behaviour of oxidoperoxido-acylpyrazolonate complexes, namely epoxidation of cyclohexene and cyclooctene and sulphoxidation of methylphenylsulphide and diphenylsulphide (Scheme 5). In all cases, 30 % aqueous hydrogen peroxide was used as the terminal oxidant, with the rest of the reaction conditions being those previously optimised for us for these reactions with related oxidoperoxido-Mo-systems.12,21 For epoxidation, a 1.5:1 oxidant:olefin ratio was employed, carrying out the reaction at 60 °C for 18 h in ClCH or MeOH. For sulphoxidation, the oxidant:sulphide ratio was 1:1 and the reaction was performed at 0 or 25 °C for 1 h. Complexes PhP[Mo(O)(O2)(Q1)], 1, and [Mo(O)(O2)(Q1)], 9, were selected as representative catalyst precursors. The results obtained are shown in Table 2, where other specific experimental details of the reaction conditions are included as footnote. Firstly, the activity in epoxidation was evaluated (entries 1-4 in Table 2). Complex 1 showed null activity in the oxidation of cis-cyclooctene (entry 1) and medium-low in the case of cyclohexene (entry 3). In the latter case, the epoxide selectivity is quite low (18 %) when the reaction was carried out in MeOH with formation of both cyclohexene-1,2-diol and β-methoxycyclohexanol (33 and 49 %, respectively). In both cases, the conversions are lower than those described by our group for other oxidoperoxido-rodenium complexes,12,21 lower than those reported for related rhenium complexes22 and lower than those observed for complex 9 (entries 2 and 4). In this case, the cis-cyclooctene oxidation provides comparable values to those previously obtained with other similar Mo-catalysts, even with better epoxide selectivity (entry 2).12,21 For the epoxidation of cyclohexene (entry 4) the conversion is comparable to the previous substrate (60 %) with good selectivity to β-methoxycyclohexanol (84 %) obtained by epoxide methanolysis. Secondly, the activity of PhP[Mo(O)(O2)(Q1)], 1, and [Mo(O)(O2)(Q1)], 9, was investigated in the oxidation of selected sulphides (entries 5-9, Table

### Table 2 Oxidation of several substrates with aqueous hydrogen peroxide catalyst by compounds PhP[Mo(O)(O2)(Q1)], 1, and [Mo(O)(O2)(Q1)], 9.8

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst precursor</th>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Selectivity to epoxide or sulphoxide (%)</th>
<th>Selectivity to diol or sulphone (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>cC8</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>cC8</td>
<td>53</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>cC6</td>
<td>44</td>
<td>18</td>
<td>33 (49)</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>cC6</td>
<td>60</td>
<td>0</td>
<td>16 (84)</td>
</tr>
<tr>
<td>5c</td>
<td>1</td>
<td>PhMeS</td>
<td>31</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>6d</td>
<td>1</td>
<td>PhMeS</td>
<td>94</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>7e</td>
<td>9</td>
<td>PhMeS</td>
<td>95</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>8f</td>
<td>9</td>
<td>PhMeS</td>
<td>94</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>9d</td>
<td>1</td>
<td>Ph2S</td>
<td>71</td>
<td>71</td>
<td>29</td>
</tr>
</tbody>
</table>

---

8 [Mo] = 0.025 mmol, substrate: 1.0 mmol. Epoxidation: [substrate]/[oxidant] ratio: 1:1.5, T = 60 °C, t = 18 h, solvent = 1 ml ClCH for cC5, 2 ml MeOH for cC6. Sulphoxidation: [substrate]/[oxidant] ratio: 1:1, solvent = 1 ml ClCH. See experimental for other details. In parenthesis: selectivity to β-methoxycyclohexanol. T = 0 °C, t = 1 h. T = 60 °C, t = 18 h. T = 25 °C, t = 1 h. Solvent: 1 ml of [Cmim]PF6, cC5 = cis-cyclooctene, cC6 = cyclohexene.
2. Again, the use of 1 in the reaction carried out at 0 °C leads to low conversions (entry 5), which are lower than those obtained for us with other related oxidodiperoxido-molybdenum catalysts. An increase in the conversion was only observed when the temperature was increased to 60 °C (94 %), with a concomitant decrease in the sulphoxide selectivity (85 %, entry 6). Complex 9 is much more active in sulphonoxidation than the anionic derivative, with high conversions and selectivities at 25 °C (ca. 95 %) in both Cl2CH and the ionic liquid [C4mim]PF6 entries 7 and 8, respectively; C4mim = 1-n-butyl-3-methylimidazolium. These results are similar to those obtained by us with the catalyst [Mo(O)(O2)(H2)2]13 Conversely to that observed by us in other oxidodiperoxido-Mo-ionic liquid systems, attempts to recycle the ionic liquid + catalyst mixture were not successful in this case since complete leaching of the molybdenum catalyst was observed.

Deoxygenation of epoxides using [Mo(O)(O2)(Q)n] complexes as catalysts and X-ray structure of [Mo(O)(O2){C6H5}]+

Oxido-molybdenum complexes are known for their abilities to catalyse oxygen atom transfer (OAT) reactions25,26 and other related organic transformations.25,26 However, studies of the reaction of deoxygenation of epoxides to olefins are not common.27,28 For this reason, the catalytic activity of [Mo(O)(O2)(Q)n] complexes in the deoxygenation of epoxides, using PPh3 as oxygen acceptor, was also investigated (Scheme 6). Complexes [Mo(O)(O2)(Q)n], 10, and [Mo(O)(O2)(Q′n)]11, were selected as representative catalyst precursors and Ph4P[Mo(O)(O2)(Q′n)] derivatives were not tested due to their low catalytic activity. The selected reaction conditions were similar to those previously optimised for [Mo(O)(O2)(Q′n)] complexes, namely 18 h of reaction at 120 °C in toluene as solvent. As shown Table 3, the best results are obtained for the deoxygenation of stilbene and styrene oxides with complete conversion and a selectivity to the corresponding olefin for both 10 and 11 catalyst precursors (entries 1-4). In the case of cycloepoxides (entries 5-8) or for the linear epoxide oct-1-ene (entries 9-10), the conversion values were somewhat lower, detecting only in the case of cyclohexene oxide a selectivity of 100 % to the corresponding olefin. Analysis of the 31P(1H) NMR reaction showed in all cases the complete consumption of the phosphane PPh3 to O=PPh3.

In order to investigate the epoxide deoxygenation mechanism, the stoichiometric reaction of complex [Mo(O)(O2)(Q′6)], 10, with one equivalent of PPh3 was carried out on a preparative scale. From the resulting orange reaction solution, it was possible to isolate yellow crystals of complex 12, which were spectroscopically and structurally characterised. The IR spectrum and 1H and 13C(1H) NMR spectra were analogous to those of dioxidomolybdenum complex [Mo(O)(O2)(Q′6)], previously described by us.23

Table 3 Deoxygenation of epoxides with PPh3 using [Mo(O)(O2)(Q′n)] catalyst precursors.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst precursor</th>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Selectivity to alkene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>trans-stilbene oxide</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>trans-stilbene oxide</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>styrene oxide</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>styrene oxide</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>cyclooctene oxide</td>
<td>83</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>cyclooctene oxide</td>
<td>80</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>cyclohexene oxide</td>
<td>49</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>11</td>
<td>cyclohexene oxide</td>
<td>57</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>oct-1-ene oxide</td>
<td>85</td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>oct-1-ene oxide</td>
<td>79</td>
<td>57</td>
</tr>
</tbody>
</table>

a. [Mo] = 0.025 mmol, substrate = 0.5 mmol, [substrate]/{PPh3} ratio: 1:1, solvent 2.0 ml toluene, T = 120 °C, t = 18 h. See experimental for other details.
This journal is © The Royal Society of Chemistry 20xx

ARTICLE

Conclusions

The selective and efficient deoxygenation of styrene oxide and trans-stilbene oxide substrates, employing PPh₃ and using complexes [Mo(O)(O₂)(Q₆)₂] as catalysts, was demonstrated. The first step in the epoxide deoxygenation mechanism was the oxygen atom transfer to the phosphane. This was demonstrated through the stoichiometric reaction of 10 with one equivalent of PPh₃, carried out on a preparative scale, which afforded complex [Mo(O)(O₂)(Q₆)₂], 12.

Experimental

General. All preparations and other operations were carried out under dry aerobic conditions. Solvents were dried using standard procedures. Ph₅PCl and MoO₃ were purchased from Aldrich and they were used as supplied. Acylpyrazolones HQ₆ compounds¹,²⁹ and [Mo(O)(O₂)(H₂O)₃]³⁰ were prepared as previously reported. Infrared spectra were recorded on Perkin-Elmer FT-IR Spectrum Two spectrophotometer (KBr pellet or Nujol emulsion in NaCl plates or using the ATR technique). NMR spectra were run on Bruker AMX-300 or Avance III spectrometers at the Centro de Investigaciones, Tecnología e Innovación (CITIUS) of the University of Sevilla. ¹H and ¹³C NMR shifts were referenced to the residual signals of deuterated solvents, while ³¹P(¹H) shifts were referenced to external 85 % phosphoric acid. The gas chromatograms (GC) were obtained using a Varian Chromatogram CP-3800 with nitrogen as the carrier gas. The chromatogram used a Varian automatic injector, model CP-8410, flame ionisation detector (FID), and a Varian column, model CP-8741. Microanalyses (C, H, N) were carried out by CITIUS at the Universidad de Sevilla.

Syntheses

Ph₅PCl[Mo(O)(O₂)(Q₆)] complexes (1-8): Complex 1 was prepared as follows: over a solution of compound HQ₆ (67 mg, 0.25 mmol) in ethanol (5 ml) was added dropwise a solution of Ph₅PCl (93 mg, 0.25 mmol) in ethanol (5 ml). The mixture was stirred for 30 min at room temperature. Then, over the resulting solution was added dropwise 1 ml of an aqueous 0.25 M solution of complex [Mo(O)(O₂)(H₂O)₃]. The mixture was further stirred for 1 h at room temperature. The resulting solution was cooled to 4 °C. After 48 h yellow-orange crystals of complex 1 were obtained. Yield: 68 % (132 mg). Complexes 2-8 were prepared following the same experimental procedure but using the appropriate HQ₆ compound. For the notation of ¹H and ¹³C signals, see the following scheme:

This article is protected by copyright. All rights reserved.
Ph₃P[Mo(O)[O₂]₃(C₄H₉)₆], 1: IR (cm⁻¹, KBr): 3419 (br), 3055 (m), 1611 (vs), 1596 (s), 1524 (vs), 1487 (s), 1441 (vs), 1401 (m), 1364 (m), 1316 (m), 1272 (w), 1231 (w), 1189 (m), 1167 (w), 1157 (w), 1109 (vs), 1079 (s), 1029 (w), 997 (m), 951 (vs), 973 (m), 863 (vs), 811 (w), 762 (s), 724 (vs), 695 (m), 655 (s), 609 (w), 581 (m), 528 (vs), 456 (brw). ¹H NMR (CDCl₃, 300 Hz): δ = 0.94 (s, 9H, C₃H₉-A), 2.36 (s, 2H, CH-c'), 2.41 (s, 3H, CH-1), 7.08 (t, 1H, J = 7 Hz, CH-9), 7.25 (t, 2H, J = 7 Hz, CH-8), 7.58 (m, 8H, CH meta PPh), 7.73 (m, 8H, CH ortho PPh), 7.83 (m, 4H, CH para PPh), 8.0 (d, 2H, J = 7 Hz, CH-7). ¹³C(H) NMR (CDCl₃, 75.47 Hz): δ = 17.6 (s, C-1), 30.1 (s, C-a), 32.5 (s, C-b), 49.7 (s, C-c), 106.5 (s, C-3), 116.9 (s, C-7), 118.1 (s, C-8), 121.0 (s, C-9), 125.1 (s, C-4), 128.5 (s, C para PPh), 130.7 (s, C ortho PPh), 134.4 (s, C meta PPh), 135.7 (s, C ipso PPh), 138.4 (s, C para PPh), 139.4 (s, C meta PPh), 139.7 (s, C ipso PPh), 139.7 (s, C meta PPh), 141.2 (s, C meta PPh), 142.5 (s, C meta PPh), 143.3 (s, C meta PPh), 145.6 (s, C ipso PPh), 145.8 (s, C meta PPh), 148.7 (s, C-2), 149.4 (s, C-5). ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%. ³¹P(H) NMR (CDCl₃): δ = 23.0 (s, PPh₃) C₂H₅Mo₃O₇P₂: calc. C 61.07, H 4.56; found: C 61.33, H 4.43; N, 3.51%.
**PhMo[Mo(O)(O)]$_2$(Q)\(_2\), 7:** Yield: 68 % (136 mg). ATR-IR (cm\(^{-1}\)): 3470 (w), 2920 (w), 2845 (w), 1609 (m), 1584 (w), 1517 (m), 1485 (m), 1454 (w), 1433 (m), 1392 (w), 1160 (w), 1106 (m), 1078 (m), 1029 (w), 997 (w), 979 (w), 944 (m), 983 (w), 869 (m), 853 (m), 814 (w), 789 (w), 753 (m), 718 (s), 687 (s), 653 (m), 625 (w), 616 (w), 580 (m), 524 (vs), 464 (m), 447 (w). \(^1\)H NMR (CDCl$_3$, 300 Hz): \(\delta = 1.06-1.75\) (several m, 11H, C\(_{9H\alpha\gamma\beta\delta\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon\zeta\epsilon�
immediately cooled to 0 °C (ice bath) and the products were extracted with diethyl ether (6x3 ml). The resulting solution was dried (anhydrous MgSO\textsubscript{4}) and analysed by GC, using 50 μl of n-octane as internal standard.

**General procedure for sulfoxidation reactions.** The reactor (a 50 ml vial equipped with a Young valve and a magnetic stirrer flea) was charged with the corresponding solid catalyst (0.025 mmol, 1 or 11), chloroform (2 ml) or \text{[C\text{mmim}]PF\textsubscript{6}} (1 ml), 30 % aqueous hydrogen peroxide (1 mmol per each mmol of sulphide) and the corresponding sulphide (PhMeS or Ph\textsubscript{2}S, 1 mmol), in the aforementioned order. The reactor was sealed and cooled to 0 °C (or 25 °C), maintaining constant stirring (600 rpm) in a thermostatted bath for the duration of the reaction. Upon completion, the mixture was treated with diethyl ether (10 ml) and filtered with 0.45 μm nylon syringe filter. The resulting solution was analysed by GC, using 50 μl of dodecane as internal standard.

**General procedure for epoxide deoxygenations.** The reactor (a 50 ml vial equipped with a Young valve and a magnetic stirrer flea) was charged with the corresponding solid catalyst (0.025 mmol, 10 or 11), PPh\textsubscript{3} (131 mg, 0.55 mmol), toluene (2 ml) and the corresponding olefin oxide (0.5 mmol), in the aforementioned order. The reactor was sealed and heated at 120 °C, maintaining constant stirring (600 rpm) in a thermostatted oil bath for the duration of the reaction (18 h). Upon completion, the mixture was cooled to 0 °C (ice bath) and analysed by \textsuperscript{31}P\textsuperscript{(H)} NMR. Then, the solution was evaporated to dryness, the resulting residue extracted with ethanol (10 ml) and filtered with 0.45 μm nylon syringe filter to remove the undissolved triphenylphosphane oxide. The resulting solution was analysed by GC, using 50 μl of dodecane as internal standard.

**Computational details**

The electronic structure and geometries of the isomers of the anions of complexes 1 and 2 were computed using density functional theory at the B3LYP level.\textsuperscript{31} The Mo atom was described with the LANL2DZ basis set\textsuperscript{32} while the 6-311++G** basis set was used for the C, O, N and H atoms. The optimised geometries of all the compounds were characterised as energy minima by a nonexistence of imaginary frequencies (Nimag = 0) in the diagonalisation of the analytically computed Hessian (vibrational frequencies calculations). The DFT calculations were performed using the Gaussian 09 suite of programmes.\textsuperscript{33} For coordinates of the optimised compounds, see Table S4 (ESI).

**X-ray crystallography**

A summary of the crystallographic data and structure refinement results for compounds 1-2, 9-10 and 12 is given in Table S2 (ESI). Crystals of suitable size for X-ray diffraction analysis were coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream (T = 213 K) to the goniometer head. Data collection was performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation λ(Mo Kα) = 0.71073 Å, by means of ω and ϕ scans with a width of 0.50 degree. The data were reduced (SAINT)\textsuperscript{34} and corrected for absorption effects by the multi-scan method (SADABS).\textsuperscript{35} The structures were solved by direct methods (SIR-2002)\textsuperscript{36} and refined against all F\textsuperscript{2} data by full-matrix least-squares techniques (SHELXL-2016/6)\textsuperscript{37} minimizing w(F\textsuperscript{2}−F\textsuperscript{2})\textsuperscript{2}. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. The crystal structures of complexes 9 and 10 show the oxido and peroxido groups disordered over two sets of atomic sites where both groups alternate with each other. While in complex 9 both disordered groups are located over general positions with refined occupancy coefficients in a 7:3 ratio, in 10 both groups are located around a C\textsubscript{2} axis that passes through the Mo atom and generates by symmetry the whole complex (only half complex appears in the asymmetric unit). For this reason, both disordered groups have identical occupancy. Some geometric restraints (DFIX instructions), the ADP restraint SIMU and the rigid bond restraint DELU were used to make the geometric and ADP values of the disordered atoms more reasonable.

CCDC 1580360 - 1580364 (for 1, 2, 9, 10 and 12, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This research was supported by the Junta de Andalucía (Proyecto de Excelencia, FQM-7079) and by the Universities of Sevilla (VI Plan Propio) and Camerino. We thank to the Centro de Servicios de Informática y Redes de Comunicaciones (CSIRC), Universidad de Granada, for providing the computing time.

**Notes and references**

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Functionalized model complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 

Selected examples of oxidodiperoxidomolybdenum(VI) complexes: (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Hartmann, 


