

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

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Oxidoperoxido-molybdenum(VI) complexes containing acylpyrazolonate ligands were obtained by reaction of $[\text{Mo}(\text{O})(\text{O})_2(\text{H}_2\text{O})_n]$ with the corresponding acylpyrazolone compounds HQ^{R} . Complexes $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O})_2(\text{Q}^{\text{R}})]$ (R = 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^{R} in the presence of $\text{Ph}_4\text{P}^+\text{Cl}^-$. Alternatively, neutral complexes $[\text{Mo}(\text{O})(\text{O})_2(\text{Q}^{\text{R}})]_2$ (R = neopentyl, **9**; hexyl, **10**; cyclohexyl, **11**) were formed when two equivalents of HQ^{R} were used in the reaction. These complexes were isolated in good yields as yellow or yellow-orange crystalline solids and were spectroscopically (IR, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR), theoretically (DFT) and structurally characterised (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 PPh_3 as the oxygen-acceptor. Complexes $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O})_2(\text{Q}^{\text{R}})]$ were shown to be poor catalyst precursors in oxidation reactions, while the activity of $[\text{Mo}(\text{O})(\text{O})_2(\text{Q}^{\text{R}})]_2$ species is good in all the studied reactions and comparable to related oxidoperoxido-molybdenum(VI) complexes. Complex $[\text{Mo}(\text{O})_2(\text{Q}^{\text{C6}})]_2$, **12**, was obtained by treatment of **10** with one equivalent of PPh_3 , demonstrating that the first step in the epoxide deoxygenation mechanism was the oxygen atom transfer toward the phosphane.

Introduction

Acylpyrazolonate ligands are modified β -diketonates with a pyrazole ring fused to the chelating moiety, which can be straightforwardly obtained by treatment of the acylpyrazolone compound, HQ^{R} , with a base.¹ In general, their $\kappa^2(\text{O},\text{O}')$ -chelating ability towards transition metals is superior with respect to traditional β -diketonates. The presence of the pyrazole ring stabilizes the metal derivatives by creating a π conjugate system, when the heterocyclic ring is directly bonded to an aromatic substituent. This fact allows the formation of stable complexes that are compatible with high oxidation states and harsh reaction conditions.¹ For instance, some metal-acylpyrazolonates were shown to possess high catalytic activities in oxidation reactions with hydrogen peroxide (epoxidation and alcohol oxidation) when the metal was vanadium,^{2,3} or cerium.⁴ Concerning molybdenum compounds, acylpyrazolonate derivatives were known in low oxidation states⁵ and, in addition, dioxidomolybdenum(VI)

complexes of general formula $[\text{Mo}(\text{O})_2(\text{Q}^{\text{R}})]_2$ were synthesised,^{6,7} structurally characterised^{8,9} and their activity as catalysts in deoxygenation of epoxides and deoxydehydration of diols were recently described by us.¹⁰

Following our interest in oxido-¹¹ and oxidoperoxido-molybdenum chemistry,^{12,13} we here report the synthesis and characterization of novel oxidoperoxido-acylpyrazolonate complexes of molybdenum, $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O})_2(\text{Q}^{\text{R}})]$, **1-8**, and $[\text{Mo}(\text{O})(\text{O})_2(\text{Q}^{\text{R}})]_2$, **9-11**, (Q^{R} = acylpyrazolonate, see Schemes 1 and 2 below). The behaviour of some of these complexes as catalyst precursors in epoxidation of selected alkenes, oxidation of selected sulphides and deoxygenation of selected epoxide substrates are also here described.

Results and discussion

Synthesis and characterization of acylpyrazolonate-oxidoperoxidomolybdenum(VI) complexes

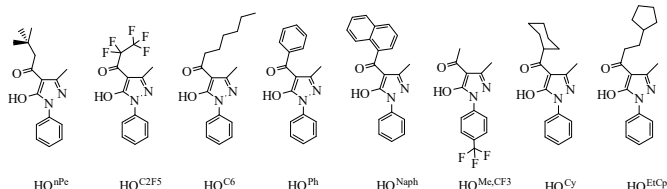
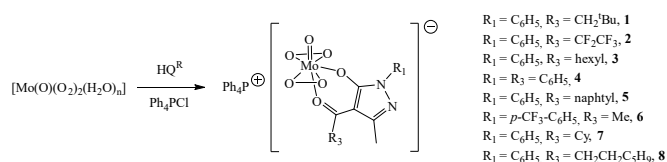
The treatment of a solution of $[\text{Mo}(\text{O})(\text{O})_2(\text{H}_2\text{O})_n]$ with one equivalent of acylpyrazolone compounds HQ^{R} , in the presence of $\text{Ph}_4\text{P}^+\text{Cl}^-$, produces complexes $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O})_2(\text{Q}^{\text{R}})]$ (R = 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

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Electronic Supplementary Information (ESI) available: Crystal data, comparison between selected experimental and theoretical structural parameters, DFT optimised structures and coordinates. See DOI: 10.1039/x0xx00000x

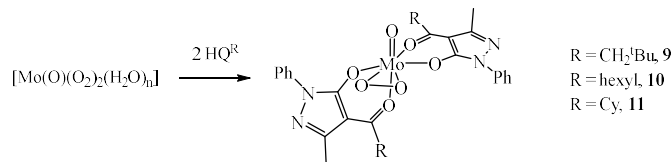


Scheme 1 Synthesis of complexes $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ (**1-8**) from the corresponding acylpyrazolone compounds HQ^{R}

1). The existence of several strong bands in the IR spectra (1675-1500 cm^{-1} range), attributed to $\nu(\text{CO})$, $\nu(\text{CN})$ and $\nu(\text{CC})$, confirmed the presence of the acylpyrazolonate ligands in these derivatives.¹ The $\nu(\text{CO})$ absorption in the free compounds HQ^{R} appears at a higher frequency (eg. at 1632 cm^{-1} for HQ^{C_6}) than in compounds $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ (1630-1600 cm^{-1} range; at 1618 cm^{-1} for **3**, which contains the Q^{C_6} ligand), in accordance with the ligand coordination to the molybdenum centre. Besides the acylpyrazolonate absorptions, the oxido group generates characteristic $\nu(\text{Mo}=\text{O})$ bands at around 950 cm^{-1} (960-940 cm^{-1} range), while the peroxido ligands display distinctive $\nu(\text{OO})$, $\nu_{\text{as}}[\text{Mo}(\text{OO})]$ and $\nu_{\text{s}}[\text{Mo}(\text{OO})]$ absorptions close to the expected ranges for this ligand: 870-850, 660-650 and 585-572 cm^{-1} , respectively.¹⁴

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds **1-8** show signals corresponding to the acylpyrazolonate ligand in agreement with the proposed formulation $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$. These signals are those of the common Q skeleton together with the characteristic signals of the R substituents in Q^{R} ligands. Thus, for example, the 3-methyl group (C-1, see notation at Experimental) originated singlets in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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 $^{13}\text{C}\{^1\text{H}\}$ 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 $^{13}\text{C}\{^1\text{H}\}$ 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 Q^{R} -containing complexes reported in the literature.¹⁵

In a similar way, complexes $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ (R = neopentyl, **9**; hexyl, **10**; Cy, **11**) were obtained by the reaction of $[\text{Mo}(\text{O})(\text{O}_2)(\text{H}_2\text{O})_n]$ with two equivalents of HQ^{R} acylpyrazolone compounds, under the appropriate reaction conditions (Scheme 2). They were obtained as yellow-orange crystalline solids in good yields. Two set of resonances



Scheme 2 Synthesis of complexes $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ (**9-11**)

were found in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for the two non-equivalent Q^{R} groups in agreement with the proposed formulation $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$, which was further confirmed by X-ray crystallography. The NMR spectra of complexes **9-11** additionally showed small resonances for extra Q^{R} 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 $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{nPe}})]$, **1**, $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{C}_2\text{F}_5})]$, **2**, $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{nPe}})_2]$, **9**, and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{C}_6})_2]$, **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 acylpyrazolonate ligand with the two O-donor atoms occupying the remaining axial and equatorial positions. The $\text{Mo}=\text{O}$ 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 $[\text{Mo}(\text{O})(\text{O}_2)_2\text{L}_{\text{eq}}\text{L}_{\text{ax}}]^{0/n-}$ complexes.^{14,16,17} 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.^{14,16} The $\text{Mo}1-\text{O}2$ bond lengths of ca. 2.3 Å (Q^{R} ligand, for **1** and **2**) clearly reflect the *trans* influence of the oxido group.

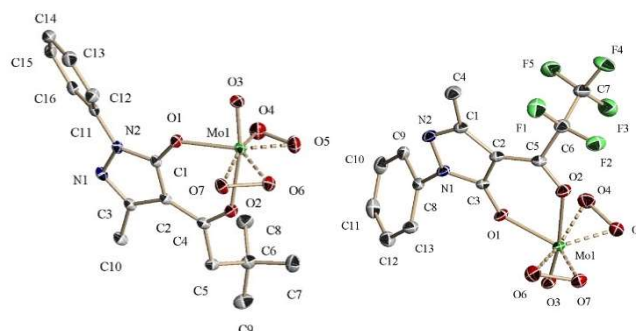


Fig. 1 Structures of the anions of $\text{PPh}_4[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{nPe}})]$, **1**, (left) and $\text{PPh}_4[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{C}_2\text{F}_5})]$, **2**, (right). ORTEP diagrams drawing at 30% probability level. Hydrogen atoms were omitted for clarity.

Table 1 Selected structural parameters of compounds $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{nPe}})]$, **1**, $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{CF}_5})]$, **2**, $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{nPe}})_2]$, **9**, and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{C}_6})_2]$, **10**.

Bond distances (Å) and angles (°)	1	2	9	10
Mo=O	1.686(1) 1.952(1)	1.680(1) 1.904(2)	1.684(2)	1.687(8)
Mo-O (peroxido)	1.918(1) 1.921(1) 1.951(1)	1.909(2) 1.942(2) 1.947(2)	1.908(2) 1.912(2)	1.885(8) 1.915(5)
Mo-O (Q ^R) (<i>trans</i> oxido)	2.278(1)	2.325(2)	2.150(2)	2.138(2)
Mo-O (Q ^R) (<i>trans</i> peroxido)	-	-	2.121(2)	2.138(2)
Mo-O (Q ^R) (<i>cis</i> oxido)	2.081(1)	2.063(1)	2.027(2) 2.028(2)	2.0380(19)
O-O	1.474(2) 1.4707(19)	1.447(2) 1.461(2)	1.4162(18)	1.424(6)
C=O	1.251(2)	1.236(3)	1.266(3) 1.277(3)	1.275(4)
C-O	1.296(2)	1.288(2)	1.289(3) 1.292(4)	1.299(4)
O=Mo-O (peroxido)	102.64(7) 102.21(6) 101.27(7)	102.84(7) 102.94(7) 101.23(8)	102.16(15) 100.73(13)	103.2(2) 102.4(3)
O=Mo-O (<i>trans</i>)	99.77(7) 169.37(6)	101.31(7) 171.30(6)	166.08(11) 98.20(11)	170.5(3)
O=Mo-O (<i>cis</i>)	88.99(6)	92.21(6)	89.96(11) 91.50(11)	103.4(2) 90.4(3)

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^R 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^R 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 bonds.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 d⁰-Mo(O)(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 $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ complexes

Acylpyrazolonate ligands are asymmetric in their standard $\kappa^2(O,O')$ -bidentate coordination to the metal centre and, consequently, two possible isomers can be considered for the $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ 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

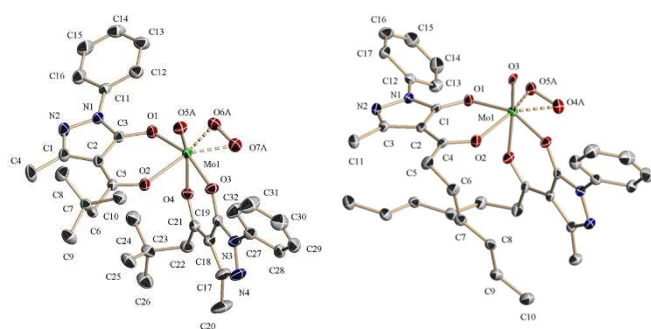
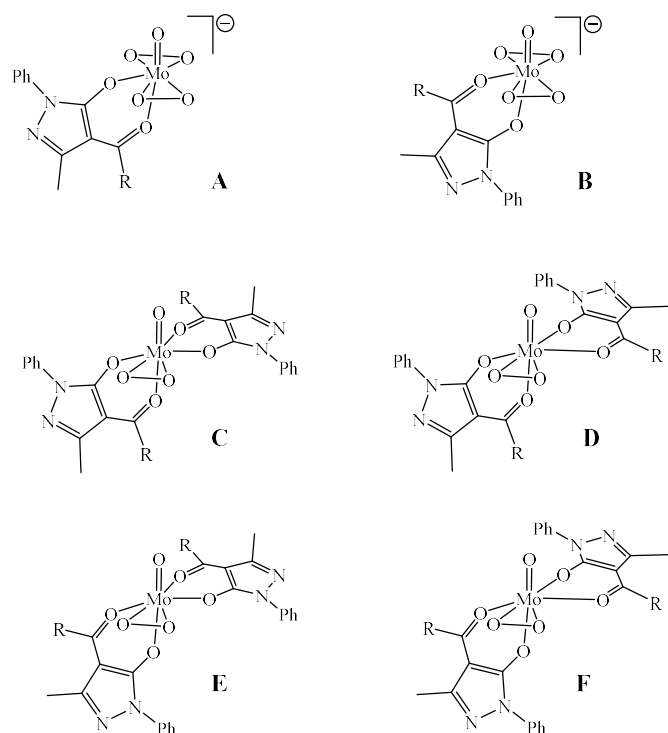


Fig. 2 Molecular structures of $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{nPe}})_2]$, **9**, (left) and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{C}_6})_2]$, **10**, (right). ORTEP diagrams drawing at 30% probability level. Hydrogen atoms were omitted for clarity.



Scheme 3 Possible isomers of $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]^-$ anions (A-B) and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]^-$ complexes (C-F)

frequently observed in the lengths of ligands that occupy the *trans* position with respect to a ligand with a strong *trans* influence.²⁰ 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

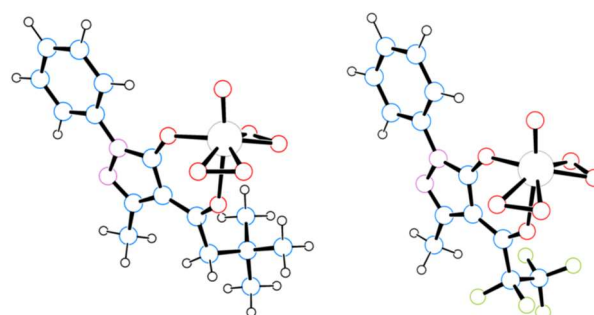
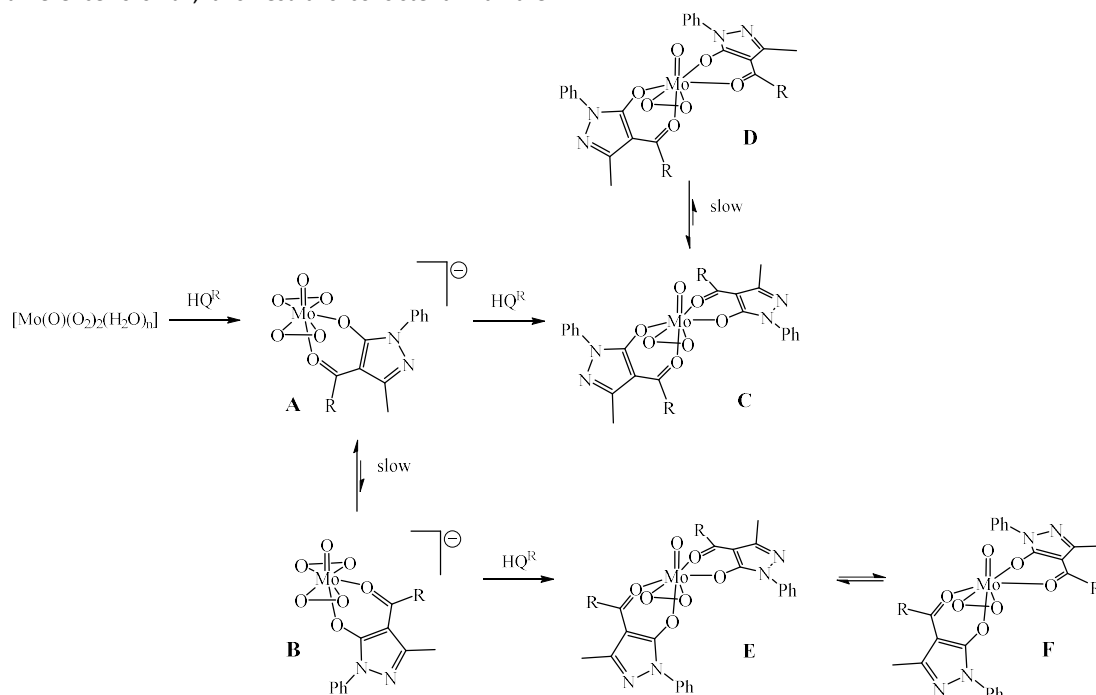


Fig. 3 Optimised structures (type **A**) of the anions of complexes $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{RPe}})]^-$, **1**, (left) and $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{CF3}})]^-$, **2**, (right).

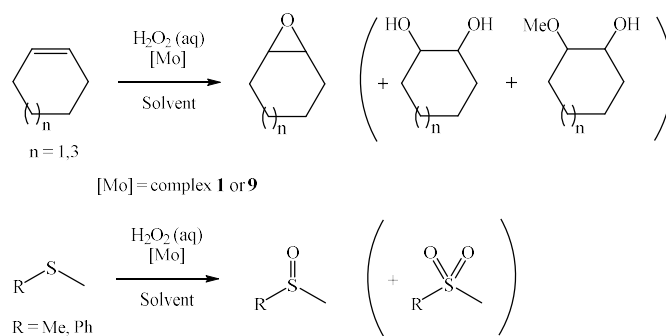
experimental structures found for complexes **1** and **2** that correspond to the most stable isomer **A**.

Concerning compounds $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$, 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 $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ complexes, we can suggest a mechanism for the preferential formation of isomer **C** (Scheme 4). The first step is the interaction of the parent $[\text{Mo}(\text{O})(\text{O}_2)(\text{H}_2\text{O})_n]$ with HQ^{R} with water substitution and formation of the anionic intermediate $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]^-$. The latter most likely has a type **A**



Scheme 4 Suggested mechanism of preferential formation of complex $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$, isomer **C**, with respect to their isomers **D-F**

structure (thermodynamic isomer), being the isomerisation to the intermediate with **B** structure a slow process. The interaction of $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$, **A**, with a second molecule of HQ^{R} would produce the isomer of type **C** $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ 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 $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ with HQ^{R} 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).



Scheme 5 Studied epoxidation and sulfoxidation reactions

Epoxidation and sulfoxidation reactions using $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ as catalyst precursors

Two oxidation reactions were selected to evaluate the catalytic behaviour of oxidoperoxido-acylpyrazolonate complexes, namely epoxidation of cyclohexene and cyclooctene and sulfoxidation 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 Cl_3CH or MeOH. For sulfoxidation, the oxidant:sulphide ratio was 1:1 and the reaction was performed at 0 or 25 °C for 1 h. Complexes $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{nPe}})_2]$, **1**, and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{nPe}})_2]$, **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 cyclohexane-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 oxidoperoxidomolybdenum 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 $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{nPe}})]$, **1**, and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{nPe}})_2]$, **9**, was investigated in the oxidation of selected sulphides (entries 5-9, Table

Table 2 Oxidation of several substrates with aqueous hydrogen peroxide catalysed by compounds $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{nPe}})]$, **1**, and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{nPe}})_2]$, **9**.^a

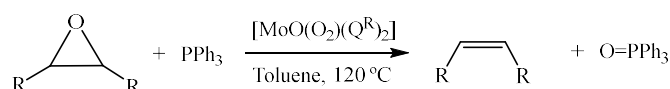
Entry	Catalyst precursor	Substrate	Conversion (%)	Selectivity to epoxide or sulfoxide (%)	Selectivity to diol or sulphone (%)
1	1	cC_8	0	0	0
2	9	cC_8	53	100	0
3	1	cC_6	44	18	33 (49) ^b
4	9	cC_6	60	0	16 (84) ^b
5 ^c	1	PhMeS	31	100	0
6 ^d	1	PhMeS	94	85	15
7 ^e	9	PhMeS	95	95	5
8 ^{e,f}	9	PhMeS	94	96	4
9 ^d	1	Ph_2S	71	71	29

^a [Mo] = 0.025 mmol, substrate: 1.0 mmol. Epoxidation: [substrate]/[oxidant] ratio: 1:1.5, T = 60 °C, t = 18 h, solvent = 1 ml Cl_3CH for cC_8 , 2 ml MeOH for cC_6 . Sulfoxidation: [substrate]/[oxidant] ratio: 1:1, solvent = 1 ml Cl_3CH . See experimental for other details. ^b In parenthesis: selectivity to β -methoxycyclohexanol. ^c T = 0 °C, t = 1 h. ^d T = 60 °C, t = 18 h. ^e T = 25 °C, t = 1 h. ^f Solvent: 1 ml of $[\text{C}_4\text{mim}]\text{PF}_6$. cC_8 = *cis*-cyclooctene, cC_6 = 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.¹³ 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 sulphoxidation than the anionic derivative, with high conversions and selectivities at 25 °C (*ca.* 95 %) in both Cl₃CH and the ionic liquid [C_{4mim}]⁺PF₆⁻ (entries 7 and 8, respectively; C_{4mim} = 1-n-butyl-3-methylimidazolium). These results are similar to those obtained by us with the catalyst [Mo(O)(O₂)(H₂O)_n].¹³ Conversely to that observed by us in other oxidodiperoxido-Mo-ionic liquid systems,^{12,21} 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^R)₂] complexes as catalysts and X-ray structure of [Mo(O)₂(Q^{C6})₂]

Oxido-molybdenum complexes are known for their abilities to catalyse oxygen atom transfer (OAT) reactions^{23,24} 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^R)₂] complexes in the deoxygenation of epoxides, using PPh₃ as oxygen acceptor, was also investigated (Scheme 6). Complexes [Mo(O)(O₂)(Q^{C6})₂], **10**, and [Mo(O)(O₂)(Q^{Cy})₂], **11**, were selected as representative catalyst



Scheme 6 Epoxide deoxygenation with PPh₃ catalyzed by [Mo(O)(O₂)(Q^R)₂] complexes

precursors and Ph₄P[Mo(O)(O₂)(Q^R)₂] derivatives were not tested due to their low catalytic activity. The selected reaction conditions were similar to those previously optimised for [Mo(O)₂(Q^R)₂] complexes,¹⁰ 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 cyclic epoxides (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^{C6})₂], **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)₂(Q^{C6})₂], previously described by us.¹⁰

Table 3 Deoxygenation of epoxides with PPh₃ using [Mo(O)(O₂)(Q^R)₂] catalyst precursors.^a

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

^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.

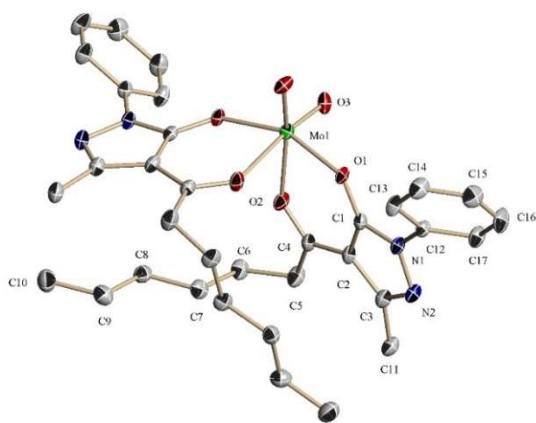


Fig. 4 Molecular structure of $[\text{Mo}(\text{O})_2(\text{Q}^{\text{C6}})_2]$, **12**. ORTEP diagram drawing at 30% probability level. Hydrogen atoms were omitted for clarity.

This result demonstrates that the first step in the epoxide deoxygenation reaction, using $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ complexes, is the OAT reaction of one of the oxygen atoms of complex **10** to the PPh_3 substrate. This would produce the $[\text{Mo}(\text{O})_2(\text{Q}^{\text{R}})_2]$ species that behaves as intermediate and that could be involved in a second OAT reaction in which the oxido group will undergo the second transfer to the PPh_3 phosphane. The formation of complex $[\text{Mo}(\text{O})_2(\text{Q}^{\text{C6}})_2]$, **12**, was confirmed by X-ray diffraction. Curiously, the structure of this complex (Fig. 4) is a polymorph of that previously described.¹⁰ Probably, the use of different crystallization solvents may explain the formation of these polymorphs that show structural differences in the hexyl group conformations (see Fig. S1). Other structural parameters are quite similar and does not require further comments (see Table S2).

Conclusions

Complexes $\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ (R = neopentyl, **1**; perfluoroethyl, **2**; hexyl, **3**; phenyl, **4**; naphthyl, **5**; methyl, **6**; cyclohexyl, **7**; ethylcyclopentyl, **8**) and $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ (R = neopentyl, **9**; hexyl, **10**; cyclohexyl, **11**) were synthesised and characterised spectroscopically, theoretically and structurally (**1**, **2**, **9** and **10**). The epoxidation of selected alkenes and oxidation of selected sulphides with aqueous hydrogen peroxide was investigated using these acylpyrazolonate-oxidoperoxido molybdenum(VI) complexes as catalyst precursors. Low activity were noticed for anionic compounds, while better results in epoxidation and sulphoxidation were observed for neutral complexes (for example, conversion and selectivity of 95 % in sulphoxidation of

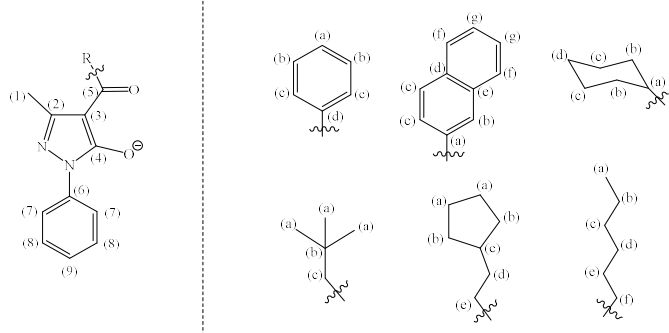
methylphenylsulphide using **9** as catalyst precursor). The selective and efficient deoxygenation of styrene oxide and *trans*-stilbene oxide substrates, employing PPh_3 and using complexes $[\text{Mo}(\text{O})(\text{O}_2)(\text{Q}^{\text{R}})_2]$ as catalysts, was demonstrated. The first step in the epoxide deoxygenation mechanism was the oxygen atom transfer to the phosphane. This was demonstrated through the stoichiometric reaction of **10** with one equivalent of PPh_3 , carried out on a preparative scale, which afforded complex $[\text{Mo}(\text{O})_2(\text{Q}^{\text{Cv}})_2]$, **12**.

Experimental

General. All preparations and other operations were carried out under dry aerobic conditions. Solvents were dried using standard procedures. Ph_4PCl and MoO_3 were purchased from Aldrich and they were used as supplied. Acylpyrazolonones HQ^{R} compounds^{1,29} and $[\text{Mo}(\text{O})(\text{O}_2)(\text{H}_2\text{O})_n]$ 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 $^{13}\text{C}\{^1\text{H}\}$ NMR shifts were referenced to the residual signals of deuterated solvents, while $^{31}\text{P}\{^1\text{H}\}$ 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 of Sevilla.

Syntheses

$\text{Ph}_4\text{P}[\text{Mo}(\text{O})(\text{O}_2)_2(\text{Q}^{\text{R}})]$ complexes (1-8**):** Complex **1** was prepared as follows: over a solution of compound HQ^{NPe} (67 mg, 0.25 mmol) in ethanol (5 ml) was added dropwise a solution of Ph_4PCl (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 $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{H}_2\text{O})_n]$. 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 HQ^{R} compound. For the notation of ^1H and ^{13}C signals, see the following scheme:



Ph₄P[Mo(O)(O₂)₂(Q^{nPe})], 1: IR (cm⁻¹, KBr): 3419 (br), 3055 (m), 2951 (m), 1611 (vs), 1596 (s), 1524 (vs), 1487 (s), 1441 (vs), 1401 (m), 1364 (m), 1316 (m), 1272 (w), 1231 (w), 1189 (w), 1167 (w), 1157 (w), 1109 (vs), 1079 (s), 1029 (w), 997 (m), 951 (vs), 973 (m), 863 (vs), 811(w), 762 (s), 724(vs), 691 (vs), 655 (s), 609(w), 581 (m), 528 (vs), 456 (brw). ¹H NMR (CDCl₃, 300 Hz): δ = 0.94 (s, 9H, CH-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{¹H} 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), 138.8 (s, C-6), 147.8 (s, C-2), 194.4 (s, C-5). ³¹P{¹H} NMR (CDCl₃): δ = 23.0 (s, PPh₄). C₄₀H₃₉MoN₂O₇P: calcd. C 61.07, H 5.00, N 3.56; found C 61.73, H 5.27, N 3.65 %.

Ph₄P[Mo(O)(O₂)₂(Q^{CF5})], 2: Yield: 37 % (8 mg). IR (cm⁻¹, KBr): 3444 (br), 3062 (w), 1631 (vs), 1596 (m), 1528 (m), 1488 (m), 1438 (s), 1384 (w), 1344 (w), 1319 (m), 1226 (m), 1205 (m), 1183 (vs), 1109 (s), 1065 (m), 1042 (w), 1019 (w), 997 (w), 960 (s), 904 (w), 867 (s), 760 (w), 750 (w), 724 (s), 689 (m), 658 (m), 629 (w), 586 (m), 527 (s). ¹H NMR (CDCl₃, 300 Hz): δ = 2.36 (s, 3H, CH-1), 7.20 (t, J = 7.5, 1H, CH-9), 7.36 (t, J = 7.5, 2H, CH-8), 7.59-7.66 (m, 8H, CH meta PPh), 7.76 (td, 8H, CH ortho PPh), 7.84-7.89 (m, 4H, CH para PPh), 8.00 (d, J = 7.5, 2H, CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 16.6 (s, C-1), 116.9 (s, C-7), 118.1 (s, C-8), 121.4 (s, C-9), 125.9 (s, C-4), 128.7 (s, C para PPh), 130.7 (s, C ortho PPh), 134.4 (s, 8CH, C meta PPh), 135.7 (s, C ipso PPh), 137.9 (s, C-6), 147.7 (s, C-2), 164.8 (s, C-3), 214.9 (s, C-5), CF₂CF₃ not observed. ³¹P{¹H} NMR (CDCl₃): δ = 23.1 (s, PPh₄). C₃₇H₂₈F₅MoN₂O₇P: calcd. C 53.25, H 3.38, N 3.36; found C 53.96, H 3.32, N 3.26 %.

Ph₄P[Mo(O)(O₂)₂(Q^{CF6})], 3: Yield: 61 % (123 mg). ATR-IR (cm⁻¹): 3060 (w), 2960 (w), 2922 (w), 1618 (s), 1597 (m), 1585 (m), 1520 (m), 1495 (m), 1484 (w), 1463 (w), 1455 (w), 1437 (s), 1403 (w), 1387 (w), 1315 (w), 1227 (w), 1187 (w), 1161 (w), 1107 (s), 1076 (m), 1026 (w), 996 (m), 951 (s), 910 (w), 872 (w), 855 (s), 760 (m), 752 (m), 722 (s), 691 (s), 657 (m), 647 (m), 629 (w), 614 (w), 579 (m), 525 (vs), 492 (w), 458 (w), 445 (w). ¹H NMR (CDCl₃, 300 Hz): δ = 0.82 (t, J = 7, 3H, CH-a), 1.21 (m, 6H, CH-b, CH-c, CH-d), 1.46 (m, 2H, CH-e), 2.37 (s, 3H, CH-1), 2.43 (t, J = 7.5, 2H, CH-f), 7.09 (t, J = 7.5, 1H, CH-9), 7.27 (m, 2H, CH-8), 7.56-7.62 (m, 8H, CH meta PPh), 7.70-7.75 (m, 8H, CH ortho PPh), 7.79-7.84 (m, 4H, CH para PPh), 8.00 (d, J = 7.5, 2H, CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 14.0 (s, C-a), 16.8 (s, C-1), 22.5 (s, C-b),

25.2 (s, C-c), 29.1 (s, C-d), 31.5 (s, C-e), 39.6 (s, C-f), 104.7 (s, C-3), 116.9 (s, C-7), 118.1 (s, C-8), 121.1 (s, C-9), 125.0 (s, C-4), 128.5 (s, C para PPh), 130.7 (s, C ortho PPh), 134.4 (s, C meta PPh), 135.6 (s, C ipso PPh), 138.8 (s, C-6), 147.8 (s, C-2), 194.9 (s, C-5). ³¹P{¹H} NMR (CDCl₃): δ = 22.9 (s, PPh₄). C₄₂H₄₃MoN₂O₇P: calcd. C, 61.27; H, 5.52; N, 3.49; found: C, 61.33; H, 5.22; N, 3.44 %.

Ph₄P[Mo(O)(O₂)₂(Q^{Ph})], 4: Yield: 76 % (152 mg). ATR-IR (cm⁻¹): 3056 (w), 1605 (m), 1523 (w), 1482 (m), 1435 (m), 1369 (w), 1107 (m), 1082 (w), 953 (m), 862 (m), 783 (w), 757 (w), 722 (s), 688 (s), 653 (m), 618 (w), 581 (m), 525 (vs), 438 (w). ¹H NMR (CDCl₃, 300 Hz): δ = 1.80 (s, 3H, CH-1), 7.16 (t, J = 7.5, 1H, CH-9), 7.26 (t, J = 7.5, 2H, CH-8), 7.32-7.38 (m, 5H, CH-a, CH-b, CH-c), 7.56-7.64 (m, 8H, CH meta PPh), 7.69-7.76 (m, 8H, CH ortho PPh), 7.79-7.84 (m, 4H, CH para PPh), 8.06 (d, J = 7.5, 2H, CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 16.2 (s, C-1), 105.1 (s, C-3), 116.9 (s, C-7), 118.1 (s, C-4), 121.2 (s, C-8), 125.3 (s, C-a), 127.5 (s, C-b), 128.2 (s, C-c), 128.6 (s, C-9), 130.3 (s, C para PPh), 130.6 (s, C ortho PPh), 134.3 (s, C meta PPh), 135.6 (s, C ipso PPh), 138.7 (s, C-d), 139.4 (s, C-6), 148.7 (s, C-2), 190.2 (s, C-5). ³¹P{¹H} NMR (CDCl₃): δ = 23.0 (s, PPh₄). C₄₁H₃₃MoN₂O₇P: calcd. C, 61.89; H, 4.56; N, 3.52; found: C, 60.67; H, 4.43; N, 3.51 %.

Ph₄P[Mo(O)(O₂)₂(Q^{Naph})], 5: Yield: 55 % (116 mg). ATR-IR (cm⁻¹): 3056 (w), 1600 (w), 1574 (w), 1525 (w), 1482 (w), 1433 (m), 1163 (s), 1106 (m), 1022 (w), 997 (w), 948 (m), 862 (m), 842 (w), 754 (m), 723 (s), 707 (m), 687 (s), 652 (m), 626 (w), 614 (w), 580 (m), 524 (vs), 451 (w), 408 (w). ¹H NMR (CDCl₃, 300 Hz): δ = 1.33 (s, 3H, CH-1), 7.11 (t, J = 7.5, 1H, CH-9), 7.2-7.3 (m, 6H, CH-8, CH-g, CH-f), 7.50-7.57 (m, 8H, CH meta PPh), 7.64-7.81 (m, 14H, CH-7, CH ortho PPh, CH para PPh), 7.92 (d, J = 7.5, 1H, CH-b), 8.06 (d, J = 7.8, 2H, CH-c). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 15.2 (s, C-1), 106.6 (s, C-3), 116.8 (s, C-7), 118.0 (s, C-8), 121.1 (s, C-9), 124.3 (s, C-c), 125.3 (s, C-b), 126.0 (s, C-4), 126.7 (s, C-f), 127.6 (s, C-g), 128.6 (s, C para PPh), 129.2 (s, C-e), 130.4 (s, C-d), 130.6 (s, C ortho PPh), 133.1 (s, C-a), 134.3 (s, C meta PPh), 135.5 (s, C ipso PPh), 138.6 (s, C-6), 149.3 (s, C-2), 190.2 (s, C-5). ³¹P{¹H} NMR (CDCl₃): δ = 23.0 (s, PPh₄). C₄₅H₃₅MoN₂O₇P: calcd. C, 63.91; H, 4.53; N, 3.31; found: C, 63.32; H, 4.21; N, 3.47 %.

Ph₄P[Mo(O)(O₂)₂(Q^{Me,CF3})], 6: Yield: 56 % (113 mg). ATR-IR (cm⁻¹): 3063 (w), 1622 (m), 1611 (m), 1586 (w), 1530 (m), 1496 (m), 1480 (m), 1435 (m), 1423 (m), 1384 (w), 1321 (s), 1156 (m), 1106 (s), 1087 (m), 1068 (s), 1012 (w), 997 (w), 972 (w), 952 (m), 869 (w), 858 (m), 779 (w), 755 (m), 722 (s), 690 (m), 679 (w), 650 (s), 615 (w), 578 (m), 524 (vs), 453 (w), 439 (m), 404 (w). ¹H NMR (CDCl₃, 300 Hz): δ = 2.17 (s, 3H, CH₃-CO), 2.36 (s, 3H, CH-1), 7.53 (d, J = 7.5, 2H, CH-8), 7.56-7.63 (m, 8H, CH meta PPh), 7.71-7.76 (m, 8H, CH ortho PPh), 7.82-7.87 (m, 4H, CH para PPh), 8.21 (d, J = 7.5, 2H, CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 16.8 (s, C-1), 27.7 (s, CH₃-CO), 105.3 (s, C-3), 116.8 (s, C-7), 118.0 (s, C-8), 120.4 (s, C-9), 122.4 (s, CF₃), 125.7 (s, C-4), 130.7 (s, C ortho PPh), 134.3 (s, C meta PPh), 135.7 (s, C para PPh), 141.5 (s, C ipso PPh), 149.1 (s, C-2), 162.3 (s, C-6), 192.1 (s, C-5). ³¹P{¹H} NMR (CDCl₃): δ = 23.0 (s, PPh₄). C₃₇H₃₀F₃MoN₂O₇P: calcd. C, 55.65; H, 3.79; N, 3.51; found: C, 55.94; H, 3.76; N, 3.58 %.

Ph₄P[Mo(O)(O₂)₂(Q^{Cy})], 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), 1313 (w), 1160 (w), 1106 (m), 1078 (m), 1029 (w), 997 (w), 979 (w), 944 (m), 893 (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). ¹H NMR (CDCl₃, 300 Hz): δ = 1.06-1.75 (several m, 11H, C₆H₁₁-CO), 2.39 (s, 3H, CH-1), 7.09 (t, J = 7.5, 1H, CH-9), 7.27 (t, J = 7.5, 2H, CH-8), 7.55-7.62 (m, 8H, CH meta PPh), 7.69-7.76 (m, 8H, CH ortho PPh), 7.79-7.84 (m, 4H, CH para PPh), 7.99 (d, J = 7.5, 2H, CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 16.6 (s, C-1), 18.4 (s, C-b), 25.7 (s, C-c), 28.7 (s, C-d), 46.0 (s, C-a), 104.0 (s, C-3), 116.9 (s, C-7), 118.0 (s, C-8), 121.1 (s, C-9), 125.0 (s, C-4), 128.5 (s, C para PPh), 130.7 (s, C ortho PPh), 134.3 (s, C meta PPh), 135.6 (s, C ipso PPh), 138.8 (s, C-6), 147.4 (s, C-2), 197.8 (s, C-5). ³¹P{¹H} NMR (CDCl₃): δ = 23.0 (s, PPh₄). C₄₁H₃₉MoN₂O₇P: calcd. C, 61.66; H, 4.92; N, 3.51; found: C, 61.51; H, 5.21; N, 3.36 %.

Ph₄P[Mo(O)(O₂)₂(Q^{EtCp})], 8: Yield: 39 % (80 mg). ATR-IR (cm⁻¹): 3062 (w), 1618 (w), 1584 (w), 1522 (w), 1482 (w), 1435 (m), 1393 (w), 1339 (w), 1314 (w), 1186 (w), 1164 (w), 1106 (s), 1073 (w), 1025 (w), 995 (m), 976 (s), 871 (s), 751 (m), 721 (s), 688 (s), 652 (m), 603 (m), 559 (m), 523 (vs), 448 (w). ¹H NMR (CDCl₃, 300 Hz): δ = 0.94-1.10 (m, 2H, CH-d), 1.39-1.57 (m, 5H, CH-a, CH-c), 1.60-1.74 (m, 4H, CH-b), 2.38 (s, 3H, CH-1), 2.45 (t, J = 7.5, 2H, CH-e), 7.10 (t, J = 7.5, 1H, CH-9), 7.27 (t, J = 7.5, 2H, CH-8), 7.55-7.62 (m, 8H, CH meta PPh), 7.69-7.76 (m, 8H, CH ortho PPh), 7.79-7.84 (m, 4H, CH para PPh), 8.00 (d, J = 7.5, 2H, CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 16.8 (s, C-1), 25.0 (s, C-a), 31.1 (s, C-c), 32.4 (s, C-b), 38.9 (s, C-d), 40.2 (s, C-e), 104.7 (s, C-3), 116.9 (s, C-7), 118.0 (s, C-8), 121.1 (s, C-9), 125.0 (s, C-4), 128.5 (s, C para PPh), 130.6 (s, C ortho PPh), 134.3 (s, C meta PPh), 135.6 (s, C ipso PPh), 138.8 (s, C-6), 147.8 (s, C-2), 195.0 (s, C-5). ³¹P{¹H} NMR (CDCl₃): δ = 23.0 (s, PPh₄). C₄₂H₄₁MoN₂O₇P: calcd. C, 62.07; H, 5.08; N, 3.45; found: C, 62.19; H, 5.14; N, 3.39 %.

[Mo(O)(O₂)(Q^R)₂] complexes (9-11): Over a solution of compound HQ^R (1 mmol) in methanol (10 ml) was added dropwise 0.5 mmol of an aqueous 0.25 M solution of complex [Mo(O)(O₂)₂(H₂O)_n]. After 2h of stirring at room temperature, a yellow-orange solid was formed. It was isolated by filtration, washed with acetone and dried. From the solution a further crop was obtained. The solid fractions were recrystallised from diethyl ether or methanol.

[Mo(O)(O₂)(Q^{NPe})₂], 9: Yield: 72 % (251 mg). IR (cm⁻¹, KBr): 3419 (br), 2957 (m), 1604 (s), 1560 (vs), 1536 (vs), 1486 (s), 1442 (s), 1412 (s), 1376 (s), 1354 (m), 1275 (m), 1226 (m), 1078 (s), 1066 (s), 1009 (m), 952 (s), 951 (s), 912 (m), 814 (m), 754 (s), 689 (m), 656 (m), 636 (m), 612 (w), 562 (m), 505 (w), 472 (m). ¹H NMR (CDCl₃, 300 Hz): δ = 0.87 (s, 9H, CH-a), 1.04 (s, 9H, CH-a), 2.33 (AB system, J_{ap} = 14, 2H, CH-c), 2.50 (s, 3H, CH-1), 2.54 (s, 3H, CH-1), 2.91 (AB system, J_{ap} = 14, 2H, CH-c), 7.37 (m, 2H, CH-9), 7.53 (m, 4H, CH-8), 8.11 (m, 4H, CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 16.9 (s, C-1), 17.3 (s, C-1), 29.8 (s, C-a), 30.0 (s, C-a), 32.7 (s, C-b), 33.3 (s, C-b), 49.0 (s, C-c), 108.9 (s, C-3), 109.9 (s, C-3), 121.5 (s, C-7), 121.6 (s, C-7), 126.7 (s, C-9), 127.1 (s, C-9), 128.9 (s, C-4), 128.7 (s, C-4), 129.0 (s, C-8), 129.2 (s, C-8), 137.2

(s, C-6), 137.6 (s, C-6), 148.8 (s, C-2), 148.9 (s, C-2), 194.5 (s, C-5), 195.8 (s, C-5). C₃₂H₃₈MoN₄O₇: calcd. C 55.98, H 5.58, N 8.16; found C 56.88, H 5.60, N 8.03 %.

[Mo(O)(O₂)(Q^{C6})₂], 10: Yield: 68 % (433 mg). IR (cm⁻¹, KBr): 3462 (br), 2928 (s), 1608 (vs), 1561 (vs), 1532 (vs), 1490 (vs), 1444 (vs), 1419 (s), 1384 (s), 1354 (m), 1129 (m), 1077 (s), 1061 (s), 1037 (m), 1011 (m), 987 (m), 954 (s), 930 (s), 847 (m), 764 (s), 742 (m), 690 (m), 657 (m), 612 (w), 627 (m), 560 (m), 462 (m). ¹H NMR (CDCl₃, 300 Hz): δ = 0.82 (m, 6H, 2 x CH-a), 1.25 (m, 12H, 2 x (CH-b, CH-c, CH-d)), 1.60 (m, 4H, 2 x CH-e), 2.47 (s, 3H, CH-1), 2.55 (s, 3H, CH-1), 2.88 (t, J = 7, 4H, 2 x CH-f), 7.37 (m, 2H, 2 x CH-9), 7.54 (m, 4H, 2 x CH-8), 8.11 (dd, J = 7.5, 4H, 2 x CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 13.9 (s, C-1), 15.3 (s, C-1), 16.3 (s, C-a), 16.6 (s, C-a), 22.4 (s, C-b), 22.6 (s, C-b), 25.2 (s, C-c), 25.5 (s, C-c), 28.8 (s, C-d), 28.9 (s, C-d), 31.5 (s, C-e), 31.6 (s, C-e), 37.5 (s, C-f), 37.7 (s, C-f), 107.2 (s, C-3), 108.3 (s, C-3), 121.6 (s, C-7), 121.7 (s, C-7), 126.7 (s, C-9), 127.1 (s, C-9), 129.1 (s, C-8), 129.2 (s, C-8), 137.3 (s, C-4), 137.6 (s, C-4), 148.7 (s, C-6), 148.8 (s, C-6), 161.1 (s, C-2), 161.5 (s, C-2), 194.9 (s, C-5), 196.4 (s, C-5). C₃₄H₄₂MoN₄O₇: calcd. C 57.14, H 5.92, N 7.84; found C 57.42, H 5.95, N 7.68 %.

[Mo(O)(O₂)(Q^{Cy})₂], 11: Yield: 38 % (132 mg). IR (cm⁻¹, KBr): 3457 (br), 2932 (s), 2855 (s), 1608 (vs), 1560 (vs), 1533 (vs), 1490 (vs), 1443 (vs), 1418 (s), 1377 (s), 1360 (m), 1081 (s), 1070 (m), 1035 (m), 1009 (m), 984 (m), 952 (s), 930 (s), 850 (m), 818 (m), 757 (s), 689 (m), 658 (m), 629 (m), 558 (m), 461 (m). ¹H NMR (CDCl₃, 300 Hz): δ = 1.02-2.12 (several m, 20H, 2 x (CH-b, CH-c, CH-d)), 2.30 and 2.57 (s, 6H, 2 x CH-1), 2.65-3.40 (m, 2H, 2 x CH-a), 7.10-7.70 (m, 6H, 2 x (CH-9, CH-8)), 7.80-8.20 (m, 2H, 2 x CH-7). ¹³C{¹H} NMR (CDCl₃, 75.47 Hz): δ = 16.2 (s, C-1), 16.3 (s, C-1), 25.4, 25.6, 25.7, 25.8 (s, 2 x (C-d, C-c)), 28.8, 29.6 (s, 2 x C-b), 45.1, 45.6 (s, 2 x C-a), 106.2 (s, C-3), 107.1 (s, C-3), 120.1, 121.8 (s, 2 x C-7), 126.7, 127.1 (s, 2 x C-9), 129.0, 129.2 (s, 2 x C-8), 136.9, 137.3 (s, 2 x C-6), 148.2 (s, C-2), 149.0 (s, C-2), 161.3 (s, C-4), 161.9 (s, C-4), 197.5 (s, C-5), 199.5 (s, C-5). C₃₄H₃₈MoN₄O₇: calcd. C 57.47, H 5.39, N 7.88; found C 57.69, H 5.21, N 7.45 %.

[Mo(O)₂(Q^{Me})₂], 12: Over a solution of [Mo(O)(O₂)(Q^{C6})₂], **10**, (72 mg, 0.1 mmol) in Et₂O (15 ml), PPh₃ (26 mg, 0.1 mmol) was added. The mixture was stirred for 2h, during this time, the resulting yellow solution darkens to orange, and then the solution was cooled to -20 °C. After 24 hours yellow crystals were obtained, which were collected by filtration and dried under vacuum. Yield: 54 % (37 mg). The spectroscopic data of **12** (IR and ¹H and ¹³C{¹H} NMR) were similar to those previously described by us.¹⁰

Catalytic assays

General procedure for olefin epoxidations. 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 **9**), methanol (2 ml) or CHCl₃ (1 ml), 30 % aqueous hydrogen peroxide (170 μl, 1.5 mmol) and the corresponding olefin (1 mmol), in the aforementioned order. The reactor was sealed and heated at 60 °C, maintaining constant stirring (600 rpm) in a thermostatted oil bath for the duration of the reaction (18 h). Upon completion, the reactor was

immediately cooled to 0 °C (ice bath) and the products were extracted with diethyl ether (6x3 ml). The resulting solution was dried (anhydrous MgSO₄) 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 **9**), chloroform (2 ml) or [C₄mim]PF₆ (1 ml), 30 % aqueous hydrogen peroxide (1 mmol per each mmol of sulphide) and the corresponding sulphide (PhMeS or Ph₂S, 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**), PPh₃ (131 mg, 0.5 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 ³¹P{¹H} 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.³¹ The Mo atom was described with the LANL2DZ basis set³² 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.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)³⁴ and corrected for absorption effects by the multi-scan method (SADABS).³⁵ The structures were solved by direct methods (SIR-2002)³⁶ and refined against all F² data by full-matrix least-squares techniques (SHELXL-2016/6)³⁷ minimizing w[F_o²-F_c²]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 C₂ 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 instruction), 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.

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