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Chiral phosphinoylalcohol complexes of monooxobis(peroxo)molybdenum(VI) and their use as asymmetric oxidants

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Abstract

Complexes of the type $[MoO(O_2)_2(L^*)(ROH)]$, where L^* = chiral β-phosphinoylalcohol, have been synthesised and used as stoichiometric oxidants for a number of unfunctionalised alkenes. In all of the complexes the chiral auxiliary is bound through the phosphinoyl oxygen as a monodentate ligand. The coordination about the metal atom in these pseudo-pentagonal bipyramidal molecules is completed by a solvent molecule (ethanol/water) lying opposite the axial Mo=O bond. Oxidation of small-chain non-functionalised alkenes occurs in variable yield to give epoxides with an enantiomeric excess of up to 40%. These compounds also behave as catalysts for the Bu^tOOH oxidations of alkenes, but with similar modest enantioselectivities. The modest enantioselectivities are explained on the basis of the mode of coordination of the chiral ligand, and it is argued that there may be inherent limits in the use of these systems in asymmetric oxidations.

Keywords: Chiral phosphinoylalcohol complexes; Molybdenum; Asymmetric oxidation

1. Introduction

Seven-coordinate molybdenum peroxo-complexes of the type $[MoO(O_2)_2(L)(L'')]$ and $[MoO(O_2)_2(L–L'')]$ [1] have been widely exploited as oxidants (oxygen-transfer agents) for organic substrates. In particular they are employed as catalysts for the epoxidation of alkenes [2]. Some examples act as both efficient catalysts for the Bu^tOOH oxidation of alkenes and (less efficiently) as stoichiometric oxidants in their own right [3]. Others preferentially oxidise alcohols before alkenes [4], and yet others are inherently unreactive towards alkenes in the absence of added oxidising agents [5]. For all of these reactions, there is considerable uncertainty over the oxygen transfer mechanism [6].

The presence of a chiral ligand converts the complexes above into potentially enantioselective oxidants. Of the asymmetric transformations studied to date, the alkene to epoxide conversion has

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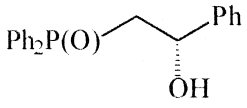
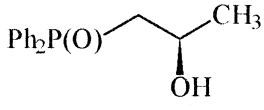
received most attention [3,4]. It has been established that bidentate chiral ligands give enantiomeric excesses of up to 50% e.e. in the epoxide products, whereas monodentate auxiliaries produce only small enantioselectivities ($< 10\%$ e.e.).

We are interested in developing new chiral compounds for employment as asymmetric oxidising agents and have previously shown heterobidentate systems containing the phosphinoyl group to be excellent ligands for hard Lewis acids [7,8]. The proliferation of catalytic systems based on complexes of high-valent metals reflects the potential of these ligands as asymmetric auxiliaries in such transformations. This paper details the synthesis and characterisation of complexes containing chiral phosphinoylalcohol ligands bound to the $MoO(O_2)_2$ core, and explores aspects of their use as oxidants for the production of epoxides from olefinic precursors.

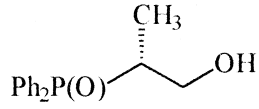
2. Experimental



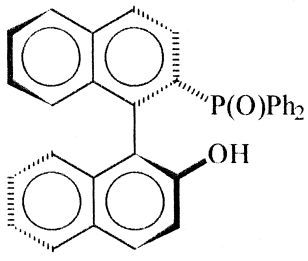
R-**I**



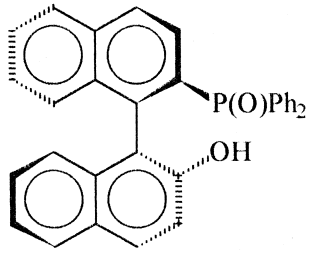
S-**II**



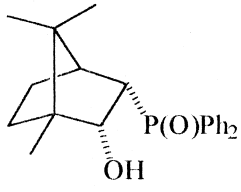
R-**III**



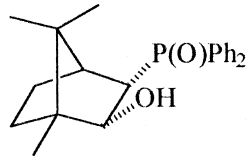
S-**IV**



R-**V**



R,R,S-**VI**



R,S,R-**VII**

The ligands **I**, **II**, **IV** and **V** were prepared as previously described [7,8]. All manipulations involving trivalent phosphorus compounds were performed under a nitrogen atmosphere using standard schlenk-line techniques. (2*S*)-2-chloropropanoic acid and (2*S*)-2-chloropropanol were prepared as described [9]. Microanalyses were carried out at the Glasgow University Chemistry Department Microanalytical Laboratory.

2.1. (1R),(2S),(3R)-exo,exo-1,7,7-trimethyl-3-(diphenylphosphinoyl)bicyclo[2.2.1]heptan-2-ol, ***VII***

To a stirred solution of (1*R*)-*endo*-3-bromocamphor (10 g, 43 mmol) in THF (150 ml) was added dropwise at −78° a solution of *n*-BuLi in hexane (20 ml, 20% excess, 2.5 M). After stirring for 1 h at −78°, a solution of diphenylchlorophosphine (8 ml, 44 mmol) in THF (20 ml) was added. The mixture was allowed to come to room temperature and stirred for 2 h before being added dropwise to lithium aluminium hydride (2.5 g) in THF (250 ml) at 0°. This mixture was stirred overnight at room temperature, and then hydrolysed with H_2O (3 ml), 12% aqueous sodium hydroxide (3 ml) and finally H_2O (a further 9 ml). After stirring at room temperature for 3 h the mixture was filtered in air, washed thoroughly with THF and the filtrate treated with 30% H_2O_2 (30 ml), left to stand overnight, and the excess hydrogen peroxide quenched with aqueous sodium sulfite. The volatiles were removed in vacuo, and the residue partitioned between water and diethyl ether (1:1, 500 ml). The organic phase was washed with water (3 × 100 ml) and dried over Na_2SO_4. The solvent was removed to a clear oil which was purified by dry-column chromatography. A 8 × 20-ml silica column was used, and the purified compound was obtained by gradient elution with 100 ml fractions over the range 4–20% THF in dichloromethane with 1% increments. The desired compound was obtained as a white solid ($R_f = 0.45$, 5% THF in DCM). Yield = 5 g. It was recrystallised from diethyl ether as fibrous needles. ^{31}P NMR ($CDCl_3$): δ 38.0. ^{1}H NMR ($CDCl_3$): δ 5.00 (br, 1H), 4.36 (t, 1H), 3.02 (m, 1H), 2.24 (m, 1H), 2.03 (m, 1H), 1.62 (t, 1H), 1.37 (m, 2H), 0.89 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H).

2.2. (1R), (2R), (3S)-endo,endo-1,7,7-trimethyl-3-(diphenylphosphinoyl)-bicyclo[2.2.1]heptan-2-ol, ***VI***

To a stirred solution of (1*R*)-camphor (10 g, 66 mmol) in THF (100 ml) at −78° was added butyllithium (36 ml, 2 M, 73 mmol). After 1 h, diphenylchlorophosphine (11.8 ml, 66 mmol) was added and the mixture was allowed to warm to room temperature. After stirring for 2 days, the solvent was removed and the residue stirred in ethanol (250 ml) at 0° whereupon a thick white solid precipitated. The solid was filtered in air, washed with cold ethanol and dried in vacuo. A solution of this phosphinoketone (12 g) in THF (250 ml) was added to lithium aluminium hydride (4 g) in THF (250 ml) with ice cooling. It was then stirred at room temperature for 12 h and worked up as above. Colourless crystals were formed from diethyl ether at −20°. Yield = 8 g (35% based on camphor). ^{31}P NMR ($CDCl_3$): δ 33.8. ^{1}H NMR ($CDCl_3$): δ 4.03 (dd, 1H), 3.62 (br, 1H), 2.65 (dd, 1H), 1.94 (dd, 1H), 1.75 (m, 2H), 1.31 (s, 3H), 1.10 (m, 2H), 0.95 (s, 3H), 0.76 (s, 3H).

2.3. (S)-chloropropyl tetrahydropyranyl ether

Solid *para*-toluenesulfonic acid monohydrate (75 mg, 1 mol%) was added to a solution of 2(*S*)-chloropropanol (3.5 g, 37 mmol) and 3,4-dihydropyran (6.75 ml, 74 mmol) in dichloromethane (75 ml) at 0°. After stirring at room temperature for 2 h, the mixture was shaken with aqueous sodium hydrogen carbonate then water and the organic phase dried over magnesium sulfate. Removal of the

solvent gave a yellow residue which was distilled (65–70°, 0.5 mm) to give the desired compound as a colourless liquid. Yield = 6.5 g (99%).

2.4. (R)-(diphenylphosphinoyl)propyl tetrahydropyranyl ether

To a solution of 2(*S*)-chloropropyl tetrahydropyranyl ether (5.15 g, 29 mmol) and diphenylphosphine (5.38 g, 29 mmol) in dimethyl sulfoxide (30 ml) under N_2 was added via syringe 50% aqueous KOH (4 ml, 35 mmol). The mixture was stirred at 50° for 12 h and then poured into H_2O (250 ml) and extracted into dichloromethane (3×100 ml). The organic phase was stirred with 20% aqueous hydrogen peroxide for 3 h, washed with aqueous sodium sulfite and dried over magnesium sulfate. The solvent was removed to give a white solid. Yield = 9 g (95%). ^{31}P NMR ($CDCl_3$): δ 33.84, 33.77. ^{1}H NMR ($CDCl_3$): δ 1.16 (dd, CH_3), 1.23 (dd, CH_3), 1.3–1.6 (m, CH_2C), 2.78 (m, C*H*P), 3.3–4.0 (m, CH_2O), 4.39 (t, C*H*O), 4.43 (t, C*H*O), 7.3–7.9 (aromatics).

2.5. (R)-(diphenylphosphinoyl)propanol, *III*

The tetrahydropyranyl derivative from above was dissolved in methanol (100 ml) and stirred with Dowex® 50 WX8-100 (15 g) in the protonated form for 24 h. The resin was filtered off, washed with methanol (2×50 ml) and the filtrate taken to dryness in vacuo to give a white solid. Yield = 5.5 g (82%). ^{31}P NMR ($CDCl_3$): δ 39.6. ^{1}H NMR ($CDCl_3$): 7.4–7.9 (m, 10H), 3.83 (m, 2H), 3.25 (br, 1H), 2.64 (m, 1H), 1.17 (dd, 3H).

2.6. $MoO(O_2)_2$(*I*)

Molybdenum trioxide (0.89 g, 6.2 mmol) was added in small portions to 30% aqueous hydrogen peroxide (3 ml) and the mixture warmed at 40° for 4 h before being filtered to give a clear yellow solution. This was added to a solution of **I** (2 g, 6.2 mmol) in methanol to give a gummy yellow solid. The mixture was taken to near dryness in vacuo at $< 10°$, azeotroped with ethanol (2×20 ml) and the sticky residue dissolved in the minimum amount of ethanol. An equal volume of diethyl ether was added to precipitate the complex as a free-flowing yellow solid which was recrystallised from chloroform at 4°. (Warming these solutions resulted in decomposition of the complex). Yield = 2.2 g (73%). *Anal.*: Calc. for $C_{20}H_{19}O_7PMo$: C, 48.20; H, 3.85%. Found: C, 48.1; H, 4.0%.

2.7. $[MoO(O_2)_2$(*II*)$]nH_2O \cdot xEtOH$

An analogous procedure to that described for the preparation of $MoO(O_2)_2$(**I**) was used, with ligand **I** being replaced by 2.5 g (9.6 mmol) of **II** and using 1.38 g (9.6 mmol) of MoO_3. A yellow solid was obtained with difficulty. Yield = 1.5 g. C.H.N. analyses for this compound were not reproducible and suggested, along with appropriate spectroscopic observations, appreciable and variable solvation.

2.8. $[MoO(O_2)_2$(*III*)$(H_2O)]$

Addition of **III** (1.1 g, 4.2 mmol) in methanol (7 ml) to the filtered solution of MoO_3 (0.6 g, 4.2 mmol) gave, on warming, a clear solution. This was concentrated in vacuo, azeotroped with ethanol and taken to small volume. It was then stirred in dry diethyl ether at 0° to give the *product* as a

free-flowing yellow powder. Yield = 1.1 g (58%). *Anal.*: Calc. for $C_{15}H_{19}O_8PMo$: C, 39.66; H, 4.22%. Found: C, 39.9; H, 4.1%.

*2.9. [MoO(O$_2$)$_2$(**IV**)(H$_2$O)]nH$_2$O · xROH*

An analogous procedure to that described for the preparation of MoO(O$_2$)$_2$(**III**)(H$_2$O) was used, replacing **III** by **IV**. An orange solid was obtained. Yield = 50%. Analyses were again not reproducible due to variable solvation.

*2.10. [MoO(O$_2$)$_2$(**V**)(H$_2$O)]nH$_2$O · xROH*

An analogous procedure to that described for the preparation of MoO(O$_2$)$_2$(**III**)(H$_2$O) was used, replacing **III** by **V**. Yield = 70%.

*2.11. [MoO(O$_2$)$_2$(**VI**)(H$_2$O)]0 · 5H$_2$O*

An analogous procedure to that described for the preparation of MoO(O$_2$)$_2$(**III**)(H$_2$O) was used, replacing **III** with **VI**. The *complex* crystallised from the reaction mixture on standing. Yield = 77%. *Anal.*: Calc. for $C_{22}H_{30}O_{8.5}PMo$: C, 47.40; H, 5.45%. Found: C, 47.2; H, 5.3%.

*2.12. [MoO(O$_2$)$_2$(**VII**)(H$_2$O)]H$_2$O · EtOH*

An analogous procedure to that described for the preparation of MoO(O$_2$)$_2$(**III**)(H$_2$O) was used, replacing **III** with VII. Yield = 90%. *Anal.*: Calc. for $C_{24}H_{37}O_{10}PMo$: C, 47.05; H, 6.10%. Found: C, 46.7; H, 6.0%. This complex did not give reproducible microanalyses because of variable solvation and a tendency to decompose by ligand oxidation.

2.13. Oxidation reactions

Unless stated otherwise, the oxidation reactions were all carried out following the procedure described. 10 mol equivalents of alkene was added to a solution of complex (50 mg) in 1 ml of nitromethane (with or without molecular sieves/magnesium sulfate) and the flask was stoppered. The reaction was allowed to proceed for 1–2 h, and the mixture was then extracted with hexane (2 ml). The hexane solution was then isolated for analysis by gas chromatography on a 25 m chiraldex column. Absolute configurations of the predominant enantiomer in the epoxide products were assigned by reference to the order of elution of *R* and *S* styrene oxide: the first-eluted enantiomer being *R* and the longest retained *S*.

2.14. Catalysed oxidations of hept-1-ene and 3,3-dimethylbut-1-ene

A solution of [MoO(O$_2$)$_2$(**VII**)] (100 mg) in dichloromethane (15 ml) was dried over $MgSO_4$ for 5 h. The alkene (20 mol equiv.) was added to the filtered solution, followed by Bu^{t}OOH (20 mol equiv. as a 5.5 molar solution in toluene). This was stirred overnight at ambient temperatures, filtered through silica, shaken with $Na_2S_2O_5$ solution and dried over $MgSO_4$. Vacuum removal of the solvent left a clear oil analysed, by NMR spectroscopy to be $>70\%$ epoxide. Enantiomeric excesses were determined by adding the chiral NMR shift reagent *R*-2,2,2-trifluoro-1-(9-anthryl)ethanol.

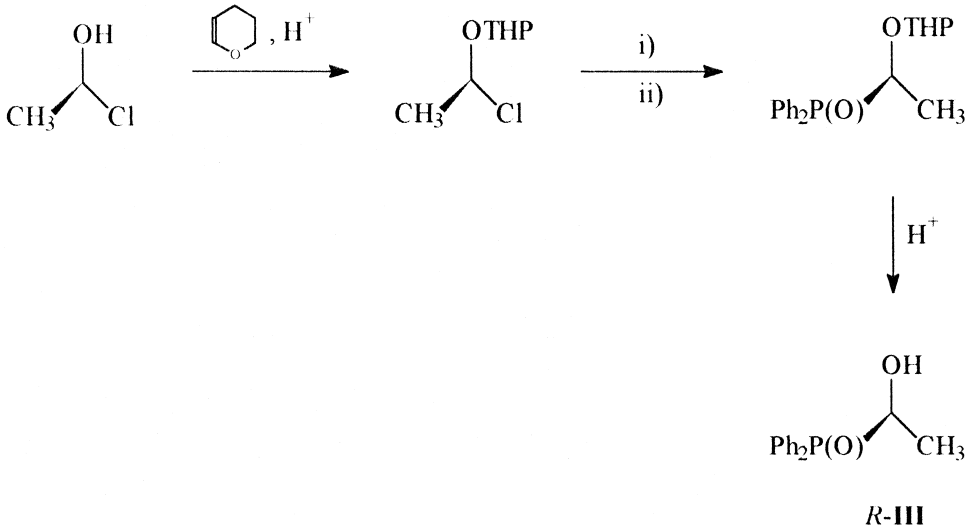
3. Results and discussion

3.1. Synthesis

All the ligands in this study are available in high optical purity using well-established procedures for their preparation. The two forms of the camphor derived ligand (**VI** and **VII**) are available from common starting materials as the intermediate phosphinoketone undergoes a slow inversion from the kinetic product (*exo*) to the thermodynamic product (*endo*) when left in solution [10]. Thus early reduction of the reaction mixture gives the *exo,exo*-phosphinoalcohol, whereas delayed reduction gives the *endo,endo* isomer. **VI** and **VII** were acquired from the oxidation of these phosphine derivatives. The two diastereoisomers have distinct physical and spectroscopic properties and their stereochemistry is readily defined by analysis of relevant J_{HH} and J_{HP} couplings in accord with similar systems [10]. The synthesis of the other ligands follow published routes except for **III** which was hitherto unknown, and whose preparation is outlined in Scheme 1.

The synthesis of the $[MoO(O_2)_2(\mathbf{L}^*)(S)]$ complexes was accomplished by the use of procedures developed by Mimoun et al. [11] albeit with minor modifications peculiar to each ligand as detailed in the experimental section. Within the series, $[MoO(O_2)_2(\mathbf{I})]$, $[MoO(O_2)_2(\mathbf{III})(H_2O)]$ and $[MoO(O_2)_2(\mathbf{VI})(H_2O)]0.5H_2O$ gave reproducible analytical data. For the remainder, variations in the degree of hydration/solvation were observed from batch to batch. The complexes containing the binaphthyl derived ligands had to be isolated quickly after their formation to prevent their decomposition to poorly-characterised red–brown compounds. A tendency for anionic molybdenum peroxo-complexes to oxidise alcohols has been reported [4,12] and the low thermal stability of some of these phosphinoyl–alcohol complexes might be ascribed to this.

Surprisingly, apart from $[MoO(O_2)_2(\mathbf{I})]$, it proved difficult to obtain the remaining complexes solvent-free. The application of dynamic vacuum and storage over phosphorus pentoxide were largely ineffectual, although such treatments were restricted by the thermal instability of the compounds. $[MoO(O_2)_2(\mathbf{I})]$ is unique in that it could be obtained free of coordinated and lattice solvent by a single recrystallisation from chloroform. The complexes were soluble in nitromethane, acetone and acetonitrile, with lower, but variable, solubility in chlorohydrocarbons.



Scheme 1. (i) Ph_2PH, 50% aq. KOH, DMSO; (ii) H_2O_2.

3.2. Infrared spectra

Salient infrared details are presented in Table 1. The ν(P=O) stretch for the uncoordinated phosphinoylalcohols was observed around 1160 cm^{-1}, shifted to lower energy by ~ 30 cm^{-1} with respect to like compounds without a neighbouring hydroxy group (Ph_3PO has this stretch at 1193 cm^{-1}). Such a shift is indicative of hydrogen bonding between the phosphinoyl oxygen and the alcohol hydrogen in these systems. Larger low-energy shifts were observed on coordination (Table 1) as the P=O double bond character is reduced (vide infra). It is should be noted that this assignment is ambiguous in several cases, since more than one strong band was observed in the ν(P=O) region; our assignments refer to the most intense absorbance within the narrow range.

Where the ν(OH) stretch was discernible, no shift in frequency was observed in the infrared spectra of the Mo(VI) complex with respect to the free ligand, indicating that the hydroxy oxygen remains uncoordinated in the complexes. Characteristic ν(Mo=O) and ν(O–O) stretches (the latter often observed as two peaks) were located around 970 and 870 cm^{-1}, respectively.

3.3. NMR spectra

Table 2 lists ^{31}P chemical shifts for ligands and complexes and Table 3 contains selected ^{1}H NMR data for some of the compounds. (Other parameters are listed in the experimental section). The ^{1}H NMR spectra of the complexes with hydrogens α to the P=O and OH groups reveal significant downfield shifts for the protons at the carbon α to the phosphinoyl function upon coordination (the greatest effects were observed for ligands **I** and **III**) but the protons α to the hydroxy group were largely unaffected. This pattern is indicative of a metal-bound P=O function but uncoordinated alcohol donors, i.e., the ligands are behaving as monodentate species by bonding to the metal through

Table 1
Selected infrared details for the phosphinoyl ligands and complexes

Compound	ν(OH)[a]	ν(P=O)	ν(Mo=O)	ν(O-O)
I	3268	1159		
II	3371	1162		
III	3350	1160		
IV	3290	1157		
V	3278	1157		
VI	3330	1157		
VII	3333, 3269	1186		
$MoO(O_2)_2$(**I**)	3266	1126	974	874, 860
'$MoO(O_2)_2$(**II**)'[b]	obs	1127	969	877, 867
$MoO(O_2)_2$(**III**)(H_2O)	3282	1124	966	866
'$MoO(O_2)_2$(**IV**)'	3380	1119	970	870
'$MoO(O_2)_2$(**V**)'	obs	1124	974	868
$MoO(O_2)_2$(**VI**)(H_2O)[c]	3486	1142	970	876, 868
$MoO(O_2)_2$(**VII**)(H_2O)[d]	obs	1119	974	871

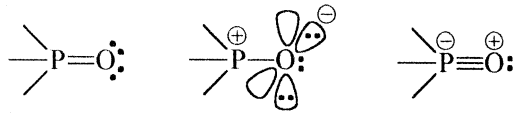
[a] In wavenumbers (cm^{-1}).
[b] Complexes in inverted commas are those that show inconsistent microanalyses.
[c] Sesquihydrate.
[d] Monohydrate monoethanolate.
obs = obscured.

Table 2
^{31}P NMR data for the ligands and complexes[a]

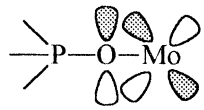
Compound	δ (ppm)
I	33.9
II	34.0
III	39.6
IV	30.9
V	31.0
VI	38.0
VII	33.8
$MoO(O_2)_2$(**I**)	56.0
'$MoO(O_2)_2$(**II**)'[b]	61.3
$MoO(O_2)_2$(**III**) (H_2O)	61.9
'$MoO(O_2)_2$(**IV**)'	60.4
'$MoO(O_2)_2$(**V**)'	57.9
$MoO(O_2)_2$(**VI**) (H_2O)[c]	58.0
$MoO(O_2)_2$(**VII**) (H_2O)[d]	57.6

[a] In $CDCl_3$.
[b] Complexes in inverted commas are those that gave inconsistent microanalyses.
[c] Sesquihydrate.
[d] Monohydrate monoethanolate.

the phosphinoyl oxygen only. This mode of coordination has been established previously for [$MoO(O_2)_2$(**VI**)(H_2O)] in the crystal [13].



1 **2** **3**



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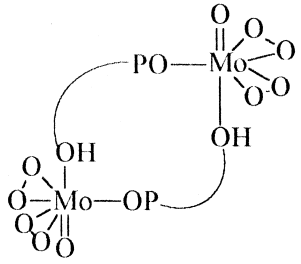
The monodentate nature of the ligands in solutions of these complexes is corroborated by ^{31}P NMR (Table 2), where large downfield shifts (> 20 ppm) were observed for the complexes relative to the

Table 3
Selected ^{1}H NMR details[a]

Compound	C*H*OH or CH_2OH	C*H*P(O) or CH_2P(O)	O*H*	CH_3
I	5.08 t	2.61 m		
$MoO(O_2)_2$(**I**)[b]	5.00 m	3.54 m		
III	3.84 m	2.64 m	3.25 br	1.17 dd
$MoO(O_2)_2$(**III**)(H_2O)	3.78 br	3.23 br	3.05 br	1.11 dd
VI	4.36 t	3.03 m		0.89, 0.87, 0.83
$MoO(O_2)_2$(**VI**)(H_2O)[c]	4.69 t	3.33 br		0.93, 0.87, 0.85

[a] In $CDCl_3$.
[b] In d_6-acetone.
[c] Sesquihydrate.

free ligands. Such shifts are mimicked in related $MoO_5(OPR_3)$ systems [14]. These large shifts for a centre not directly bound to the metal can be explained by considering the resonance structures **1** to **3**. Although the schematic in **1** is often used to denote the bonding in the phosphinoyl function, resonance structures **2** and **3** can be considered as more accurately defining the nature of the bonding in the phosphorus to oxygen link. In the phosphonium type, **2**, the oxygen has two orthogonal p orbitals (both filled) for π donation to appropriate acceptor orbitals on the d^0 molybdenum(VI) centre. One such interaction is shown in **4**. The result is $p\pi$–$d\pi$ delocalisation of electron density over the Mo–O–P link. To maximise this π stabilisation, this link should approximate to linearity (previously shown to be the case) and it is easy to visualise the depletion of electron density at the phosphorus centre, thus explaining the large ^{31}P shifts. With the Mo–O–P link at $\sim 180°$ it is not possible for the alcohol oxygen to approach the metal, hence the ligands remain monodentate. The stabilisation associated with chelate formation would appear to be insufficient to compensate for the loss of the π bonding contribution that would necessarily result if a chelate were formed. This conclusion is an extension of ideas noted previously by Burford et al. [15].



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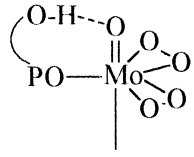


6

$MoO(O_2)_2$(**I**) differs from the other molybdenum (VI) complexes described as it is the only complex that is readily obtained free of bound solvent. It would therefore seem probable either that the complex contains a bidentate ligand, has a vacant site, or is a dimer of the type **5**. The $^{31}P\{^1H\}$ NMR spectrum of the complex consists of a singlet in both $CDCl_3$ and d_6-acetone. The ^1H spectra are different in the two solvents, however. In $(CD_3)_2CO$, the spectrum consists of three multiplets for each distinct C–H and a singlet for the hydroxyl proton, whereas in $CDCl_3$ (in which the solvent-free compound is only sparingly soluble) the pattern is more complex with five separate broadened signals. There is thus more than one species present in $CDCl_3$, but the nature of the mixture remains uncertain. It may be that a chelate complex is present, but, equally, hydrogen-bonded species such as **6** may exist in deuterochloroform. The fact that the ^{31}P NMR spectra showed only a single, well-shifted resonance would suggest that the roughly linear Mo-O-P link remains intact thus precluding the possible formation of a chelate. The H-bonded complex **6** is thus the more likely structure, with the simple ^1H NMR spectrum in d_6-acetone indicating the break-up of the weakly associated complex in this solvent.

The less well-defined complex of **VII** also gave a ^1H NMR spectrum indicative of more than one species in solution, even though only one singlet was observed in the ^{31}P NMR spectrum. This complex was, however, unstable in solution, decomposing through autooxidation to form the phosphinoylketone. [2] ^1H NMR spectra were not helpful for the solution characterisation of complexes

[2] A ν(CO) stretch at 1740 cm^{-1} was occasionally observed in the infrared spectrum of the isolated solid.

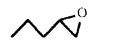
of **IV** and **V**, as only a mass of aromatic resonances were seen. The low solubility of $MoO(O_2)_2$(**II**) precluded any analysis by ^1H NMR spectroscopy.

3.4. Oxidation reactions

All the complexes prepared performed as stoichiometric oxidants for unfunctionalised alkenes. Results on pro-chiral examples are shown in Table 4. In addition, the cyclic olefins *cis*-cyclooctene and *cis*-cyclohexene were oxidised quantitatively to the *meso* epoxides *cis*-cyclooctene oxide and *cis*-cyclohexene oxide, respectively. Conversions for the non-cyclic alkenes tested ranged from high (> 80%), e.g., 3,3-dimethylbut-1-ene, to low or zero (*trans*-pent-2-ene). As might be expected from the monodentate coordination of the chiral phosphinoylalcohol ligands, the observed enantioselectivities were small (< 10% e.e.) except in the case of the binaphthyl derivatives where the highest e.e.'s of up to 39% were realised. It is interesting to note that the binaphthyl derivative $MoO(O_2)_2$(**V**) gave higher enantioselectivities for each of the prochiral substrates than $MoO(O_2)_2$(**IV**). These differences were caused by purity variations resulting from difficulties in getting the complexes solvent free. The optical yield of the epoxides did not appear to be affected by the choice of solvent, giving equivalent results when performed in dichloromethane or nitromethane. Similarly, pre-treating the nitromethane solutions of the oxidant with magnesium sulphate or activated molecular sieves (powdered or pelleted) before the addition of the alkene had no influence on the observed enantioselectivities, suggesting that any traces of moisture present had no influence.

It is of interest in view of the ability of some peroxomolybdenum complexes to oxidise alcohols that not only were our complexes isolable, but they also preferentially oxidised alkenes rather than the (uncoordinated) alcohol part of their ligands. The latter reaction might have been expected to proceed

Table 4
Oxidation of alkenes by $MoO(O_2)_2$(**L**)

	Percentage conversion to epoxide product and % *e.e.* (configuration)				
					
L					
I	72, <2(*S*)	92, 8(*R*)	67, 4(*S*)	15, 4(*S*)	-
II	55, 0	63, 4(*S*)	39, <2(*R*)	28, 3(*S*)	-
III	77, <2(*R*)	91, 6(*S*)	80, <2(*R*)	50, 8(*S*)	
IV	39, 9(*R*)	64, 25(*S*)	70, 10(*S*)	36, 15(*S*)	
V	47, 23(*S*)	58, 39(*R*)	23, 38(*R*)	22, 20(*R*)	
VI	80, 8(*S*)	89, 2(*R*)	77, 5(*S*)	49, 5(*S*)	10, 15(*S*)
VII	35, 3(*R*)	55, <2(*S*)	56, 6(*R*)	31, 5(*R*)	

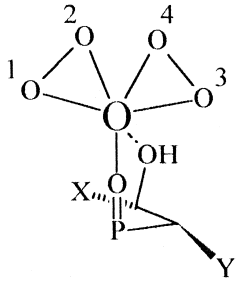


Fig. 1. Schematic to show the lack of C_2 symmetry in $MoO(O_2)_2(L)$ when L itself has no C_2 symmetry. Viewed down the Mo=O bond.

by either an intramolecular or intermolecular route. This in part might be the result of employing a ten-fold excess of alkene, but it seems more likely that the reported requirement for an anionic complex to achieve alcohol oxidation is of critical importance [12].

It is perplexing that the greatest chiral induction was seen with the less-well-characterised $MoO(O_2)_2$(**V**) system. The reasons for this remain obscure, but the binaphthyl structural motif is renowned for inducing high enantioselectivity in other systems even when monodentate coordination is all that is possible. It is noteworthy that other poorly-characterised compounds of a similar nature have proved to be peculiarly effective enantioselective oxidants [6].

The operation of compound $MoO(O_2)_2$(**VII**) was investigated in a catalytic role in the Bu^tOOH oxidations of hept-1-ene and 3,3-dimethylbut-1-ene. The oxidations proceeded to $>70\%$ epoxide, but with the same (within experimental error) small e.e. values produced in the stoichiometric reactions (Table 4). (In a preliminary investigation, the same compound catalysed the oxidation of *p*-tolylmethyl sulfide to form quantitative yields of the sulfoxide, but with only 8% e.e.).

The mechanism of oxygen-transfer in these systems remains debatable. The possible reaction pathways for the catalysed reactions are summarised by Thiele and Priermeier [5]. A critical question concerns the coordination or otherwise of the alkene to the metal ion prior to oxidation. This appears unnecessary at least when the molybdenum complexes act as a catalyst [5], but many authors favour a mechanism involving coordination of the alkene at an equatorial site [6]. We do not subscribe to this latter view for two reasons. First, for all known structures, the Mo–L bond in the equatorial position is shorter (ergo, stronger) than the axial bond. It is thus unlikely that such a bond would be broken to form a weak Mo(VI)-alkene function for which no known isolable species exist. Secondly, the very fact that in other systems bidentate chiral auxiliaries show large enantioselectivities with respect to monodentate derivatives [16] supports the notion that both donors of the former remain bound during the oxidation. That said, the several efforts to elucidate the intimate mechanism have produced conflicting arguments, and it seems quite probable that two or more mechanisms may be active and the dominance of one or the other may depend critically on the choice of reaction conditions.

It is, however, pertinent to note that although the exact mechanism of the oxygen transfer remains polemical, it seems likely that, in the absence of adventitious secondary reactions (e.g., leading to kinetic resolution), these systems will be innately limited. We first note the lack of C_2 symmetry in the complexes (Fig. 1), a feature that appears helpful in promoting enantioselectivity [17]. Whether or not the alkene coordinates to the metal ion, it seems logical that in order to generate enantioselectivity, the peroxo oxygens nearest the chiral ligand (O_1 and O_3 in the figure) are likely to be the ones transferred. It is clear that the environment of $O_1 \neq O_3$ [3] but, if rates of transfer are comparable, O_1

[3] Indeed, $O_2 \neq O_4$.

may give a single enantiomer of the epoxide whereas O_3 may not, or may even give the opposite enantiomer.

Acknowledgements

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