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Camphor-based β-hydroxyphosphoryl ligands and their complexes of the type $[MoO(O_2)_2L(H_2O)]$

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Homochiral hydroxyphosphoryl compounds, L, such as the novel camphor-based (1*R*)-*endo,endo*-3*S*-(diphenylphosphoryl)-2*R*-hydroxybornane, have been found to be prevented from behaving as bidentate ligands in the epoxidation catalysts $[MoO(O_2)_2L(H_2O)]$ by unexpectedly strong multiple-bond delocalisation producing near linear Mo–O–P angles.

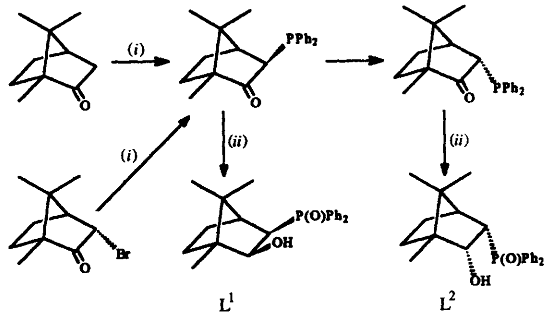
Molybdenum(VI) oxoperoxo complexes $[MoO(O_2)_2L_2]$ are well established systems for the oxidation of organic substrates, notably alkenes.[1] The use of chiral ligands can lead to these complexes producing enantiomerically enriched products from prochiral starting materials,[2] particularly when bidentate ligands of high rigidity are employed.[2,3] Chiral β-oxohydroxy ligands have been particularly successful in this respect.[4] We have recently shown that chiral phosphorylhydroxy compounds are very versatile ligands for high-oxidation-level transition metals, including molybdenum(VI).[5,6] We have therefore synthesized the new, chiral, camphor-based β-phosphorylhydroxy compounds L^1 and L^2 (Scheme 1) and examined their ligand behaviour towards the $MoO(O_2)_2$ fragment.

The known, slow *exo* ⟶ *endo* interconversion of the intermediate phosphinoketones in solution[7] allowed the isolation of both isomers from modifications of a single procedure. The products were obtained from the phosphinoketones by stereoselective reduction by $LiAlH_4$ to the hydroxyphosphines, followed by oxidation of the phosphine to the phosphine oxides with H_2O_2. The two isomers have quite distinct spectroscopic properties.*

Reaction of ethanolic solutions of L^1 or L^2 with $[MoO(O_2)_2(H_2O)_x]$ led to the isolation of yellow $[MoO(O_2)_2L(H_2O)]$ complexes.† The L^2 complex crystallised readily from the reaction mixture giving X-ray-quality plates. The L^1 analogue was recovered as a slightly impure yellow powder by concentration of the reaction mixture and precipitation with diethyl ether. The contaminant appeared to be the ketophosphoryl, probably produced at the H_2O_2 oxidation step.

The structure of $[MoO(O_2)_2L^2(H_2O)]$ is shown in Fig. 1.‡ The co-ordination about the Mo^{VI} is the expected distorted pentagonal bipyramid common to complexes of this type, with the peroxo groups and the P=O oxygen of L^2 occupying the equatorial sites. Surprisingly, the ligand is monodentate, with an unbound hydroxy group. The co-ordination site opposite the oxo group is occupied by a water molecule. A further water molecule (centred on the unique C_2 crystallographic axis) is incorporated in the crystal lattice forming hydrogen bonds to the bound waters of two adjacent complexes. The hydroxide group of co-ordinated L^2 is not hydrogen bonded to any other unit, and the failure of this ligand to co-ordinate in a bidentate mode was quite unexpected.

The Mo–O(P) bond length at 2.013(3) Å is, to our knowledge, the shortest reported (*cf.* 2.085[9] and 2.057 Å[10] in related



L^1 L^2

Scheme 1 (*i*) LiBu, PPh_2Cl, tetrahydrofuran (thf); (*ii*) $LiAlH_4$, then H_2O_2, thf

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* Found for L^1: C, 74.1; H, 8.0. Found for L^2: C, 74.7; H, 7.8. Calc. for $C_{22}H_{27}O_2P$: C, 74.55; H, 7.70%. Spectroscopic data: L^1, NMR ($CDCl_3$), ^1H, δ 5.00 (br, 1 H), 4.36 (t, 1 H), 3.02 (m, 1 H), 2.24 (m, 1 H), 2.03 (m, 1 H), 1.62 (t, 1 H), 1.37 (m, 2 H), 0.89 (s, 3 H), 0.87 (s, 3 H) and 0.83 (s, 3 H); ^{31}P, δ 33.8; IR (KBr) 3330 (OH), 1157, 1155 cm^{-1} (P=O); L^2, NMR ($CDCl_3$), ^1H, δ 4.03 (dd, 1 H), 3.62 (br, 1 H), 2.65 (dd, 1 H), 1.94 (dd, 1 H), 1.75 (m, 2 H), 1.31 (s, 3 H), 1.10 (m, 2 H), 0.95 (s, 3 H) and 0.76 (s, 3 H); ^{31}P, δ 38.0; IR (KBr) 3333, 3269 (OH), 1198, 1186 cm^{-1} (P=O).

† The oxide MoO_3 (0.200 g, 1.39 mmol) was suspended in 30% H_2O_2 (4 cm^3) and the mixture held at 45 °C for 4 h. After cooling, the solution was filtered into a solution of L^1 or L^2 (0.5 g, 1.4 mmol) in EtOH (10 cm^3). The complex $[MoO(O_2)_2L^2(H_2O)]\cdot 0.5H_2O$ was isolated as yellow crystals (77% yield) after leaving overnight (Found: C, 47.2; H, 5.3. Calc. for $C_{22}H_{30}MoO_{8.5}P$: C, 47.40; H, 5.45%). NMR $[(CD_3)_2CO]$: ^1H, δ 4.66 (t, 1 H), 3.82 (br, 1 H), 3.45 (br, 1 H), 2.17 (m, 2 H), 1.80 (t, 1 H), 1.57 (m, 1 H), 1.21 (m, 1 H), 0.91 (s, 3 H), 0.88 (s, 3 H) and 0.83 (s, 3 H); ^{31}P, δ 64.7; IR (KBr) 3486 (OH), 1142 (P=O), 970 (Mo=O), 876, 868 cm^{-1} (O–O). The complex $[MoO(O_2)_2L^1(H_2O)]$ was isolated as a yellow powder after concentration *in vacuo* at < 20 °C (90% yield): elemental analyses revealed variable hydration and/or lattice ethanol (Found: C, 46.7; H, 6.0. Calc. for $C_{24}H_{37}MoO_{10}P$: C, 47.05; H, 6.10%). NMR ($CDCl_3$): (methyls only) δ 0.94, 0.89, 0.79, 0.65 and 0.39; ^{31}P, δ 57.6; IR (KBr) 1119 (P=O), 974 (Mo=O), 875, 871 cm^{-1} (O–O).

‡ Crystal data: $C_{22}H_{30}MoO_{8.5}P$, $M = 557.37$, yellow plates, crystal dimensions 0.37 × 0.37 × 0.10 mm, orthorhombic, space group $P22_12_1$, $a = 8.0214(6)$, $b = 16.0189(7)$, $c = 18.5983(9)$ Å, $U = 2389.8(2)$ Å^3, $Z = 4$, $D_c = 1.549$ g cm^{-3}, Mo-Kα radiation (graphite monochromator), λ = 0.710 73 Å, $F(000) = 1148$, 3333 observed reflections collected on an Enraf-Nonius Turbo CAD4 diffractometer. The structure was solved by direct methods and subsequent electron-density difference synthesis and refined by full-matrix least squares based on F^2 (SHELXL 93[8]) using 3079 absorption (ψ scans)-corrected data. The O–H atoms were found from Fourier-difference maps; the C–H atoms were included in calculated positions (C–H = 0.96 Å). The final *R*1 and *wR*2 $[I > 2\sigma(I)]$ were 0.0280 and 0.0669 for 299 parameters using the weighting scheme $w = [\sigma^2(F_o^2) + (0.0404\ P)^2 + 0.4463\ P]^{-1}$, where $P = F_o^2/3 + 2F_c^2/3$. A water molecule of crystallisation was found, sited on the crystallographic two-fold axis (*i.e.* occupancy 0.5). One of the hydrogen atoms of the ligated water molecule [O(7)] was disordered (0.75:0.25). Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/286.

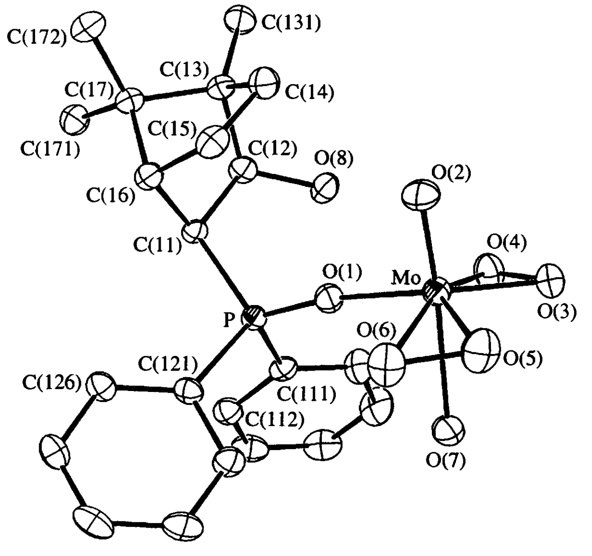

Fig. 1 Crystal structure of $[MoO(O_2)_2L^2(H_2O)]$ with thermal ellipsoids shown at the 30% probability level. Selected distances (Å) and angles (°): Mo–O(1) 2.013(3), Mo–O(2) 1.659(3), Mo–O(3) 1.930(3), Mo–O(4) 1.938(3), Mo–O(5) 1.909(4), Mo–O(6) 1.943(3), Mo–O(7) 2.386(3), O(1)–P 1.517(3), O(3)–O(4) 1.468(5) and O(5)–O(6) 1.465(5); P–O(1)–Mo 171.0(2), O(1)–Mo–O(7) 81.08(12), O(1)–Mo–O(2) 95.64(14), O(1)–Mo–O(6) 88.77(13), O(1)–Mo–O(4) 87.57(13), O(6)–Mo–O(5) 44.70(14), O(3)–Mo–O(4) 44.60(14), O(2)–Mo–O(6) 102.1(2), O(2)–Mo–O(7) 175.22(13) and O(2)–Mo–O(4) 103.5(2)

Table 1 The ^{31}P NMR data for complexes of the type $[MoO(O_2)_2L(H_2O)]$ recorded in $CDCl_3$

P-Containing ligand	δ		
	Ligand	Complex	Δδ/ppm
R-$Ph_2P(O)CH_2CHPh(OH)$[5]	33.9	56.0	22.1
S-$Ph_2P(O)CH_2CHMe(OH)$[5]	34.0	55.8	21.8
S-$Ph_2P(O)CHMeCH_2(OH)$[5]	39.6	61.9	22.3
S-L′*[6]	30.9	59.0	28.1
L^2	38.0	61.0	23.0
L^1	33.8	57.6	23.8

* L′ = 2-Diphenylphosphoryl-2′-hydroxy-1,1′-dinaphthalene.

complexes), suggesting appreciable M–O double-bond character. This is supported by the almost linear P–O–Mo angle (171.0°). Burford *et al.*[11] have discussed the relation between bond lengths and angles and the extent of p_π–d_π type conjugate bonding in phosphine oxide complexes. They proposed that relatively extensive M=O=P bonding occurred in compounds where the P–O–M linkages approached linearity. It should be noted, however, that although a P–O–M bond linearity similar to that in our structure is observed in $[MoO(O_2)_2\{P(NMe_3)_3O\}(H_2O)]$,[10] the coincident shortening of the Mo–O(P) bond was not apparent there.

The inability to isolate the desired $[MoO(O_2)_2L^2]$ containing bidentate L^2 was unexpected.[12] Molecular models reveal no adverse steric or geometric constraints on chelate formation if a P–O–Mo angle of approximately 120–140° were adopted. Such chelate-ring formation would necessarily disrupt the near linear P–O–Mo linkage, however, and reduce the π bonding at the metal. Since the isolation of monodentate $[MoO(O_2)_2L^2(H_2O)]$ is not the consequence of steric hindrance, and is not encouraged by the formation of favourable hydrogen bonds (the non-co-ordinated OH function of the ligand is distant from all possible sources of intra- and inter-molecular hydrogen bonds), the π-bonding effect must dominate in this system. The ^1H NMR spectrum of $[MoO(O_2)_2L^2(H_2O)]$ allows unambiguous detection of the co-ordinated water, and confirms that bidentate co-ordination does not occur in solution either.

The ^{31}P NMR spectrum of $[MoO(O_2)_2L^2(H_2O)]$ reveals an extremely large chemical shift from that of the uncomplexed hydroxyphosphoryl compound. This shift of 23 ppm is comparable to that caused by protonation at the phosphoryl oxygen[11] and is further evidence for the delocalisation of the P=O π-bond electron density over the Mo–O bond. We have synthesized several other complexes containing potentially bidentate hydroxyphosphoryl ligands attached to $MoO(O_2)_2$. All retain H_2O in their co-ordination spheres and all reveal similar, large shifts in δ(P) upon co-ordination, including $[MoO(O_2)_2L^1(H_2O)]$ (see Table 1). These values compare with shifts of only 1–14 ppm for complexes of Mo^{VI}, Zr^{IV} and Ti^{IV} in which the ligands are bidentate.[5,6] The clear implication is that strong Mo–O–P π-bond delocalisation is a general phenomenon in these $[MoO(O_2)_2L(H_2O)]$ compounds, producing near linear Mo–O–P bond angles which prevent chelate formation in a way that reduces their efficacy as chiral oxidation catalysts.

Acknowledgements

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