DALTON
FULL PAPER

Reactions of oxo- and peroxo-molybdenum complexes with $B(C_6F_5)_3$: crystal structures of *cis*-$[MoO\{OB(C_6F_5)_3\}(\eta^2\text{-}ONEt_2)_2]$ and *cis*-$[MoO\{OB(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$

Linda H. Doerrer,[a] Jane R. Galsworthy,[a] Malcolm L. H. Green,[a] Michael A. Leech[b] and Matthias Müller[b]

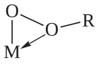
[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford, UK OX1 3PD*

Received 27th April 1998, Accepted 28th July 1998

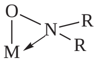
The oxometal complexes $[MoO_2(\eta^2\text{-}O\text{-}NR_2)_2]$, R = Et or CH_2Ph, reacted with the strong Lewis acid $B(C_6F_5)_3$ at their oxo functionality to give *cis*-$[MoO\{OB(C_6F_5)_3\}(\eta^2\text{-}ONR_2)_2]$, (R = Et **1** or CH_2Ph **2**). Reaction of the peroxo complex $[MoO(O_2)\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$ with the same Lewis acid led initially to the formation of $[MoO(O_2)\{B(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$ **3**, which decomposes to form $[MoO\{OB(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$ **4**. Compounds **1** and **4** have been characterised by X-ray crystallography.

Introduction

Alkyl peroxide transition metal complexes, **A**, play a central role as reactive intermediates in selective oxidation reactions which employ alkyl hydrogenperoxide as the oxygen source.[1] Reaction is postulated as proceeding according to Scheme 1 *via* formation of an η^1-co-ordinated O–OR ligand. Co-ordination of the organic substrate to the metal centre followed by oxygen transfer results in oxidation of the organic molecule. Sheldon and Van Doorn[2c] proposed that the main function of the metal catalyst in the co-ordinated peroxide complex was to act as a Lewis acid and remove electron density from the peroxidic oxygen. However, to date, the synthesis of well defined, soluble and reactive molybdenum alkyl peroxide complexes remains an unattainable goal. *N*,*N*-Dialkylhydroxylamino complexes containing an η^2-ONR_2 bound ligand, **B**, are structurally and electronically closely related to metal alkyl peroxide complexes and have been examined as well defined compounds for catalytic activity.[3] Unfortunately these species do not exhibit similar reactivities to those of their alkyl peroxide analogues and are ineffective oxidation catalysts.[4] The lack of reactivity has been attributed to strong complexation of the dialkylhydroxylamino ligand to the metal centre.



A

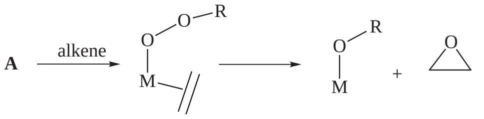


B

In certain catalytic reactions oxometal complexes may be activated by addition of a Lewis acid co-catalyst which is thought to co-ordinate to the M=O functionality thereby increasing the electrophilicity of the metal centre.[5] We have recently reported the synthesis of several oxometal complexes containing a stable, approximately linear, M=O–$B(C_6F_5)_3$ moiety.[6] As part of our continuing studies of the reactivity of $B(C_6F_5)_3$ we describe the reactions of this Lewis acid with oxomolybdenum complexes containing ancillary dialkylhydroxylamino or peroxo ligands.

Results and discussion

Treatment of *cis*-$[MoO_2(\eta^2\text{-}ONEt_2)_2]$ with 1 equivalent of $B(C_6F_5)_3$ in toluene under ambient conditions yields *cis*-$[MoO\{OB(C_6F_5)_3\}(\eta^2\text{-}ONEt_2)_2]$ **1**, which can be isolated as colourless crystals. The ^{11}B NMR spectrum of compound **1** exhibits a signal at δ 2.4, typical of a four-co-ordinate boron species and shifted upfield from that of $B(C_6F_5)_3$ (δ 59). A ^1H NMR spectrum reveals two triplet signals, assignable to the methyl groups, and four multiplet resonances, due to the methylene protons, clearly indicating that co-ordination has occurred at a single Mo=O unit. The methylene protons are also diastereotopic in the parent complex. An IR spectrum of complex **1** exhibits an absorption at 1008 cm^{-1}, tentatively ascribed to the *ν*(N–O) stretching vibration, but assignment of the characteristic Mo=O stretches is hampered by strong absorption of the fluorinated aryl rings in this region. Full characterising data for compound **1** is detailed in Table 1. The solid state structure of compound **1** has been determined by X-ray crystallography; selected bond angles and distances are reported in Table 2.



Scheme 1 Proposed mechanism for alkene oxidation using metal alkyl peroxide complexes.

The structure determination of complex **1** (Fig. 1) reveals that a molecule of $B(C_6F_5)_3$ is bound to one Mo=O unit. The B–O bond length [1.510(2) Å] is typical of those found within this family of compounds and the Mo=O–B unit deviates slightly from linearity [170.09(8)°].[6] The molybdenum centre displays pseudo-tetrahedral geometry with terminal oxo units occupying two of the vertices and the midpoint of the N–O bond of each η^2-$ONEt_2$ ligand occupying the remaining two. The presence of a Mo=$OB(C_6F_5)_3$ moiety and a non-co-ordinated Mo=O unit within compound **1** allows us to assess the electron withdrawing capabilities of the boron Lewis acid. A significant lengthening of the Mo=O bond of approximately 0.1 Å is observed upon co-ordination to the Lewis acid; Mo–O(1) 1.808(1), Mo–O(2) 1.6823(1) Å. For comparison the Mo=O bond distances in the parent complex are 1.714(2) and 1.713(2) Å.[6]

The benzyl compound, $[MoO_2\{\eta^2\text{-}ON(CH_2Ph)_2\}_2]$, was synthesized from $[MoO_2(acac)_2]$ (acac = η^2-$C_5H_7O_2$). The former complex has been previously reported as synthesized from $Na_2MoO_4{\cdot}2H_2O$ and *N*,*N*-dibenzylhydroxylamine.[3e] Colourless

Table 1 Analytical and spectroscopic data for compounds **1**, **2**, **3** and **4**

Complex[a]	Spectroscopic data[b]
1 $[MoO\{OB(C_6F_5)_3\}(\eta^2\text{-}ONEt_2)_2]$ C, 38.4 (38.2); H, 2.6 (2.5); B, 1.3 (1.3); N, 3.2 (3.4)	IR: 3100–2850w, 1646vs, 1517vs, 1469vs, 1386vs, 1373vs, 1284vs, 1108m, 1096vs, 1008s, 978vs, 940m, 911vs, 791m, 772m, 762m, 748m, 729m, 689m, 676m, 668m, 656m, 628m, 588m, 576m ^1H: 2.98 (2 H, m, *J* 7, CH_2), 2.74 (2 H, m, *J* 7, CH_2), 2.66 (2 H, m, *J* 7, CH_2), 2.50 (2 H, m, *J* 7, CH_2), 0.74 (6 H, t, *J* 7, CH_3), 0.48 (6 H, t, *J* 7, CH_3) ^{13}C: 148.3 (d, *J* 240, C_6F_5), 140.1 (d, *J* 240, C_6F_5), 137.5 (d. *J* 250, C_6F_5), 51.7 (s, CH_2), 50.6 (s, CH_2), 10.4 (s, CH_3), 9.4 (s, CH_3) ^{11}B: 2.4 (br)
2 $[MoO\{OB(C_6F_5)_3\}\{\eta^2\text{-}ON(CH_2Ph)_2\}_2]$ C, 51.6 (51.9); H, 2.5 (2.6); B, 1.1 (1.0); N, 2.7 (2.6)	IR: 3100–2820w, 1640m, 1512s, 1488m, 1467vs, 1393m, 1375m, 1354m, 1284m, 1096s, 1015m, 977vs, 949vs, 919s, 904s, 853m, 790m, 773m, 767m, 747m, 699m, 683m, 677m, 668m, 662m, 628m, 613m, 599m ^1H: 7.41–6.92 (5 H, m, C_6H_5), 4.24–3.99 (2 H, m, CH_2) ^{13}C: 148.1 (d, *J* 233, C_6F_5), 140.2 (d, *J* 230, C_6F_5), 137.4 (d, *J* 236, C_6F_5), 131.8 (s, C_6H_5), 131.2 (s, C_6H_5), 130.7 (s, C_6H_5), 130.2 (s, C_6H_5), 130.0 (s, C_6H_5), 128.8 (s, C_6H_5), 61.2 (s, CH_2), 60.1 (s, CH_2) ^{11}B: 2.7 (br)
3 $[MoO(O_2)\{B(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$ C, 48.30 (48.89); H, 2.04 (1.85); B, 0.99 (1.02); N, 2.58 (2.59)	^1H:[c] 7.24–6.65 (m, C_6H_5) ^{11}B:[c] 3.8 (br)
4 $[MoO\{OB(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]\cdot 0.5C_5H_{12}$ C, 50.66 (50.73); H, 2.42 (2.36); B, 1.09 (1.00); N, 2.48 (2.55)	IR: 3120–2840w, 1900–1790w, 1613w, 1596w, 1493vs, 1453vs, 1447vs, 1351s, 1325m, 1237m, 1203m, 1069m, 1026m, 1014m, 920s, 904vs, 845m, 804m, 757s, 746m, 737m, 700s, 620m, 606s, 595m, 515m, 508m ^1H: 7.52–7.17 (m, C_6H_5) ^{13}C: 148.1 (d, *J* 237, C_6F_5), 139.8 (d, *J* 244, C_6F_5), 137.0 (d, *J* 247, C_6F_5), 133.7 (s, C_6H_5), 133.4 (s, C_6H_5), 131.3 (s, C_6H_5), 130.1 (s, C_6H_5), 129.9 (s, C_6H_5), 129.6 (s, C_6H_5), 129.0 (s, C_6H_5), 128.5 (s, C_6H_5), 126.9 (s, C_6H_5), 126.0 (s, C_6H_5), 118 [s(br), BC] ^{11}B: 3.3 (br)

[a] Analytical data given as found (calculated) in %, IR data (cm^{-1}) determined for KBr discs. [b] The NMR data ($CDCl_3$, 298 K), unless otherwise stated, given as: chemical shift (*δ*) [relative intensity, multiplicity (*J* in Hz), assignment]. [c] In C_6D_6.

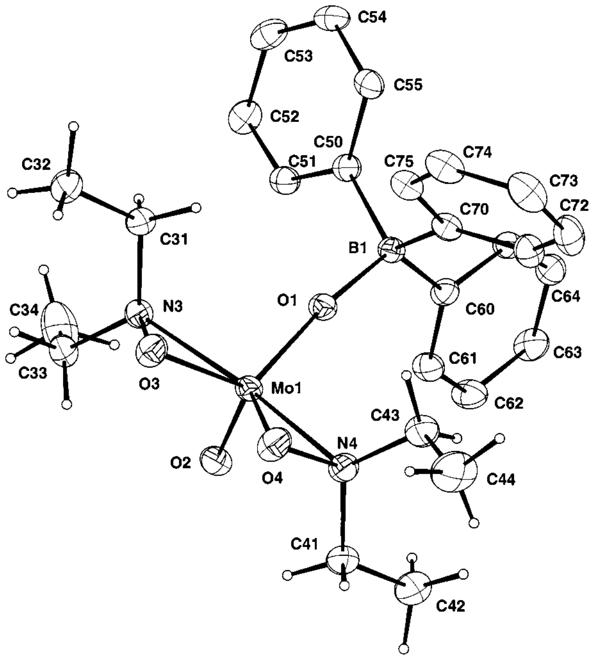


Fig. 1 View of the structure of $[MoO\{OB(C_6F_5)_3\}(\eta^2\text{-}ONEt_2)_2]$ **1**. Fluorine atoms omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Mo(1)–O(1)	1.808(1)	O(1)–Mo(1)–O(2)	122.94(5)
Mo(1)–O(2)	1.683(1)	O(1)–Mo(1)–O(3)	114.32(4)
Mo(1)–O(3)	1.936(1)	O(1)–Mo(1)–O(4)	113.89(5)
Mo(1)–O(4)	1.938(1)	O(2)–Mo(1)–O(3)	107.84(5)
Mo(1)–N(3)	2.140(1)	O(2)–Mo(1)–O(4)	108.02(5)
Mo(1)–N(4)	2.140(1)	O(3)–Mo(1)–N(3)	40.47(4)
O(1)–B(1)	1.510(2)	O(4)–Mo(1)–N(4)	40.54(4)
O(3)–N(3)	1.423(2)	B(1)–O(1)–Mo(1)	170.09(8)
O(4)–N(4)	1.425(2)		

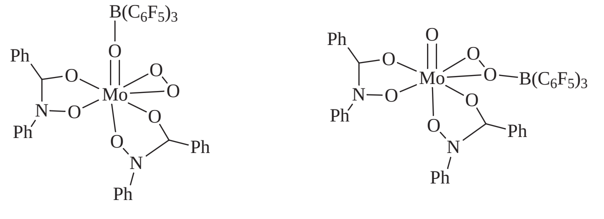


Fig. 2 Possible structures of $[MoO(O_2)\{B(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$ **3**.

crystals of $[MoO_2\{\eta^2\text{-}ON(CH_2Ph)_2\}_2]$ were obtained, the single crystal structure of which confirmed the *cis*-oxo geometry of the starting material but the data were not of sufficient quality to be published.

Upon reaction of $[MoO_2\{\eta^2\text{-}ON(CH_2Ph)_2\}_2]$ with 1 equivalent of $B(C_6F_5)_3$ *cis*-$[MoO\{OB(C_6F_5)_3\}\{\eta^2\text{-}ON(CH_2Ph)_2\}_2]$ **2** was obtained as colourless, diamond shaped crystals. Compound **2** was fully characterised by spectroscopic techniques and elemental analysis (Table 1) and displays similar features to those of its ethyl analogue, **1**.

A general structural feature of *cis*-$[MoO_2(\eta^2\text{-}ONR_2)_2]$ complexes is a relatively large O=Mo=O bond angle,[3a,4] compared to related *cis*-$[MoO_2L_2]$ complexes. This suggests that such dialkylhydroxylamino- complexes might be sterically capable of binding two molecules of $B(C_6F_5)_3$. However, reaction of $[MoO_2\{\eta^2\text{-}ON(CH_2Ph)_2\}_2]$ with 2 equivalents of the Lewis acid yielded only compound **2**, even using prolonged reaction times.

We then investigated the reaction of $B(C_6F_5)_3$ with the peroxomolybdenum complex $[MoO(O_2)\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$. This compound has been shown effectively to oxidise primary and secondary alcohols to the corresponding carbonyl compounds and to be capable of stereospecifically epoxidising allylic alcohols.[7] Treatment of $[MoO(O_2)\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$ with 1 equivalent of $B(C_6F_5)_3$, in hexanes, gave a red-orange precipitate, **3**. Elemental analysis data for **3** is consistent with the empirical formula $[MoO(O_2)\{B(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2]$. The compound exhibits a signal at *δ* 3.8 in its ^{11}B NMR spectrum indicative of a four-co-ordinate boron atom whilst the ^1H NMR spectrum shows several resonances in the phenyl region, shifted from those of the starting complex. These data suggest that the Lewis acid is bound to either the oxo or peroxo functionality (Fig. 2) and that the organic ligands have

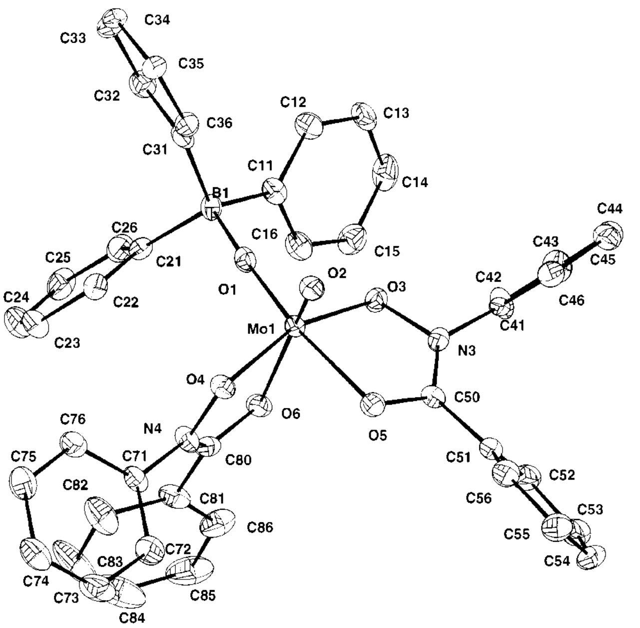


Fig. 3 View of the structure of [MoO{OB(C_6F_5)$_3$}{η^2-PhN(O)C(O)-Ph}$_2$] **4**. Fluorine and hydrogen atoms omitted for clarity.

retained their integrity. The interaction of a related oxoperoxomolybdenum complex, [MoO(O_2)$_2$$L_2$], L = 2-(1-octylpyrazol-3-yl)pyridine, with Brønsted and Lewis acids has been described.[8] The NMR spectroscopic studies (^{17}O and ^{1}H) indicate that trifluoroacetic anhydride selectively attacks the peroxo ligand in the pyrazolylpyridine complex to form a mixture of isomers of the type [MoO(OR)$_{4-x}$(OR′)$_x$$L_2$] [R = C(O)$CF_3$, R′ = OC(O)$CF_3$, x = 0–4]. In contrast, electrophilic attack of chlorotrimethylsilane occurs preferentially, but not selectively, at the peroxo ligands.[8] These studies suggest that the peroxo ligands may provide the most likely site within [MoO(O_2){η^2-PhN(O)C(O)Ph}$_2$] for electrophilic attack by B(C_6F_5)$_3$. However, any stretches due to the Mo=O and Mo(O_2) units in the IR spectrum of **3** are masked by those of the Lewis acid and so, without structural determination or ^{17}O labelling studies, the exact location of the B(C_6F_5)$_3$ moiety cannot be confidently predicted.

In order to determine the bonding mode of the Lewis acid moiety attempts were made to crystallise compound **3** from toluene solutions. However it decomposes under these conditions to give small orange crystals of [MoO{OB(C_6F_5)$_3$}{η^2-PhN(O)C(O)Ph}$_2$] **4**. Compound **4** can be independently synthesized in good yield by reaction of [MoO_2{η^2-PhN(O)-C(O)Ph}$_2$] with B(C_6F_5)$_3$ and has been fully characterised by IR and NMR spectroscopies, elemental analyses (Table 1) and a crystal structure determination. The NMR spectroscopic data for compound **4** are significantly different from those of **3**.

The structure of compound **4** is shown in Fig. 3 and significant bond angles and distances are detailed in Table 3. The structure determination reveals the presence of a *cis*-MoO{OB(C_6F_5)$_3$} unit with similar features to those described for compound **1**; B(1)–O(1) 1.508(3), Mo(1)–O(1) 1.775(3), Mo(1)–O(2) 1.674(3) Å, and Mo(1)–O(1)–B(1) 169.07(18)°.

It has been observed that the oxoperoxo-complex [MoO(O_2){η^2-PhN(O)C(O)Ph}$_2$] will undergo gradual conversion into [MoO_2{η^2-PhN(O)C(O)Ph}$_2$] and so the formation of **4** from **3** is unsurprising.

In conclusion, we have demonstrated that oxo- and perhaps peroxo-functionalities in molybdenum complexes are sufficiently nucleophilic to form a dative interaction with B(C_6F_5)$_3$. In the case of dioxomolybdenum complexes containing ancillary η^2-ONR_2 ligands, attack of the Lewis acid occurs preferentially at the oxometal unit and no evidence for reaction at the η^2-ONR_2 ligand is observed. Whilst the analogous reaction of B(C_6F_5)$_3$ with a peroxooxomolybdenum complex may initially occur at the peroxo ligand it is followed by decomposition on standing to yield a B(C_6F_5)$_3$ substituted dioxomolybdenum species. The Mo=OB(C_6F_5)$_3$ unit is reasonably stable to air and two complexes containing this motif have been crystallographically characterised.

Table 3 Selected bond distances (Å) and angles (°) for compound **4**

Mo(1)–O(1)	1.775(3)	O(1)–Mo(1)–O(2)	103.68(13)
Mo(1)–O(2)	1.674(3)	O(1)–Mo(1)–O(3)	86.22(11)
Mo(1)–O(3)	1.982(2)	O(1)–Mo(1)–O(4)	105.95(11)
Mo(1)–O(4)	1.979(2)	O(2)–Mo(1)–O(3)	106.33(12)
Mo(1)–O(5)	2.088(3)	O(2)–Mo(1)–O(4)	87.47(12)
Mo(1)–O(6)	2.164(3)	O(2)–Mo(1)–O(5)	91.06(13)
O(1)–B(1)	1.508(3)	B(1)–O(1)–Mo(1)	169.07(18)

Experimental

Fourier-transform ^{1}H and ^{11}B NMR spectra were recorded on a Bruker WM 300 spectrometer at 300 and 96 MHz respectively, ^{13}C NMR spectra on a Bruker WM 300 spectrometer at 75.5 MHz or Varian Unity 500 spectrometer at 125.7 MHz: ^{1}H and ^{13}C shifts are reported with respect to δ 0 for SiMe_4, ^{11}B with respect to δ 0 for BF_3·OEt_2; all downfield shifts are positive. Infrared spectra were recorded on either a Mattson 'Polaris' Fourier-transform, Perkin-Elmer FT 1710 spectrophotometer, or Perkin-Elmer 457 grating spectrometers. Microanalyses were obtained from the microanalytical department of this department.

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under N_2 before use. The compounds HONEt_2, HON(CH_2Ph)$_2$, [MoO_2(acac)$_2$] were used as received (Aldrich); [MoO_2(η^2-ONEt_2)$_2$],[4] [MoO_2{η^2-PhN(O)C(O)Ph}$_2$],[7] [MoO(O_2){η^2-PhN(O)C(O)Ph}$_2$][7] and B(C_6F_5)$_3$[9] were prepared as previously described.

Preparations

***cis*-[MoO{OB(C_6F_5)$_3$}(η^2-ONEt_2)$_2$] 1.** White [MoO_2(η^2-ONEt_2)$_2$] (0.304 g, 1 mmol) was partially dissolved in toluene (20 cm^3) and a toluene solution (20 cm^3) of B(C_6F_5)$_3$ (0.512 g, 1 mmol) added. The mixture was stirred for 4 h during which time a yellow solution formed. After removal of solvent *in vacuo* the residue was washed with pentane and the desired product then extracted with toluene. This solution was concentrated and cooled to −20 °C resulting in the formation of colourless crystals of compound **1**. Yield: 0.63 g, 77%.

Alternative preparation of *cis*-[MoO_2{η^2-ON(CH_2Ph)$_2$}$_2$]. Orange [MoO_2(acac)$_2$] (1.22 g, 3.74 mmol) was suspended in CH_2Cl_2 and HON(CH_2Ph)$_2$ (1.22 g, 3.74 mmol) dissolved in CH_2Cl_2 (50 cm^3) added. Ethanol (50 cm^3) was added and the reaction mixture stirred for 1 h until an off-white precipitate had formed. The solvent was removed under vacuum and the residue washed with Et_2O to remove any unchanged hydroxylamine. The residue was extracted with CH_2Cl_2. Concentration and cooling to −20 °C resulted in the formation of colourless crystals. Yield: 0.57 g, 74%.

***cis*-[MoO{OB(C_6F_5)$_3$}{η^2-ON(CH_2Ph)$_2$}$_2$] 2.** White [MoO_2-{η^2-ON(CH_2Ph)$_2$}$_2$] (0.552 g, 1 mmol) was suspended in CH_2Cl_2 (20 cm^3) and a CH_2Cl_2 solution (20 cm^3) of B(C_6F_5)$_3$ (512 mg, 1 mmol) added. Over about 15 min the solid dissolved and a very pale yellow solution formed. After stirring for 1.5 h in total the solvent was removed *in vacuo* and the residue washed with hexane. The residue was extracted with toluene and the solution filtered off. Both the hexane and toluene filtrates were separately concentrated and cooled to −20 °C leading to the formation of colourless crystals. Combined yield: 0.92 g, 86%.

[$\mathrm{MoO(O_2)\{B(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2}$] 3. Yellow [$\mathrm{MoO(O_2)\{\eta^2\text{-}PhN(O)C(O)Ph\}_2}$] (0.568 g, 1 mmol) was suspended in hexane (20 $\mathrm{cm^3}$) and a hexane solution (20 $\mathrm{cm^3}$) of $\mathrm{B(C_6F_5)_3}$ (512 mg, 1 mmol) added. There was an immediate change to red-orange and the reaction stirred for 30 min. The pale yellow filtrate was removed and the red-orange precipitate washed with hexane (3 × 10 $\mathrm{cm^3}$) and then dried *in vacuo*.

***cis*-[$\mathrm{MoO\{OB(C_6F_5)_3\}\{\eta^2\text{-}PhN(O)C(O)Ph\}_2}$] 4**. Off-white [$\mathrm{MoO_2\{\eta^2\text{-}PhN(O)C(O)Ph\}_2}$] (0.552 g, 1 mmol) was suspended in toluene (20 $\mathrm{cm^3}$) and a toluene solution (20 $\mathrm{cm^3}$) of $\mathrm{B(C_6F_5)_3}$ (512 mg, 1 mmol) added. There was an immediate change to orange and after 1 h all the solid had dissolved. The solvent was removed *in vacuo* and the residue washed with hexane. The residue was extracted with toluene and the filtrate concentrated and layered with pentane leading to the formation of orange microcrystals. Yield: 0.87 g, 82%.

Crystal structure determination of compounds 1 and 4

Crystals of compound **1** were grown from toluene solution at 253 K and of **4** from toluene layered with pentane at 298 K. In each case a crystal from the mother-liquid was immersed in highly viscous perfluoropolyether to exclude oxygen and prevent solvent loss. It was mounted on a glass fibre and plunged into a cold (150 K) nitrogen stream.

Crystal data. Compound **1**, $\mathrm{C_{26}H_{20}BF_{15}MoN_2O_4\cdot 0.5C_7H_8}$, $M = 816.21 + 46.04$, triclinic, space group $P\bar{1}$, $a = 10.764(1)$, $b = 12.107(1)$, $c = 12.563(1)$ Å, $\alpha = 86.673(2)$, $\beta = 85.919(2)$, $\gamma = 86.480(2)°$, $V = 1627.6$ Å^3, $Z = 2$, $D_c = 1.76\ \mathrm{g\ cm^{-3}}$, $\mu = 5.138\ \mathrm{cm^{-1}}$, colourless, crystal dimensions 0.23 × 0.31 × 0.18 mm.

Compound **4**, $\mathrm{C_{44}H_{20}BF_{15}MoN_2O_6\cdot 0.5C_6H_{12}}$, $M = 1094.45$, triclinic, space group $P\bar{1}$, $a = 10.2840(8)$, $b = 12.4090(8)$, $c = 18.598(2)$ Å, $\alpha = 102.500(5)$, $\beta = 98.190(4)$, $\gamma = 106.397(4)°$, $V = 2169.74$ Å^3, $Z = 2$, $D_c = 1.68\ \mathrm{g\ cm^{-3}}$, $\mu = 4.14\ \mathrm{cm^{-1}}$, yellow block, crystal dimensions 0.25 × 0.25 × 0.10 mm.

Data collection and processing. The data for compounds **1** and **4** were collected at 150 and 100 K respectively on an Enraf-Nonius DIP2000 image plate diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). For compound **1** 19362 reflections were measured ($1 < \theta < 26°$, $-13 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 15$). 6304 Unique reflections were obtained giving 5950 reflections with $I > 3\sigma(I)$. For compound **4** 4580 reflections were measured ($2 < \theta < 25°$, $0 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-21 \leqslant l \leqslant 20$). 4580 Unique reflections were obtained giving 4201 reflections with $I > 3\sigma(I)$. The images were processed with the DENZO and SCALEPACK programs.[10] Corrections for Lorentz-polarisation effects were performed but not for absorption.

Structure solution and refinement. The crystal structures were solved by direct methods and refined by the full-matrix least-squares method. Compound **1** crystallised with toluene in a 1 : 0.5 ratio. The toluene molecules are disordered at the crystallographic inversion centre with a translation of about 1.4 Å along their molecular twofold axis. All non-hydrogen atoms of **1** were refined with anisotropic displacement parameters. All hydrogen atoms of the molybdenum compound could be located in Fourier-difference maps and were refined isotropically. The hydrogen atoms of the disordered toluene were added geometrically and included in the final refinement with fixed positional and thermal parameters. For compound **1**, 548 refined parameters and 5960 observations resulted in an observation/refined parameter ratio of 10.9 : 1. Corrections for secondary extinction were applied and refinement completed using a Chebyshev weighting scheme[11] with parameters 1.67, 0.875, 1.28. Refinement on F converged at $R = 0.025$, $R' = 0.031$ and goodness of fit = 1.07. A final Fourier-difference synthesis showed minimum and maximum residual electron densities of −0.46 and 0.37 e Å^{-3}. Compound **4** was crystallised from toluene solution layered with pentane. One molecule of pentane is incorporated in the unit cell with the central carbon atom, C(101), lying on the centre of inversion such that one half of a pentane molecule is in the asymmetric unit. Hydrogen atoms were generated geometrically and allowed to ride on the corresponding carbon atoms. For **4**, 646 refined parameters and 4201 observations resulted in an observation/refined parameter ratio of 6.50 : 1. Corrections for secondary extinction were applied and refinement completed using a Chebyshev weighting scheme[11] with parameters 1.30, 0.078, 0.968. Refinement on F converged at $R = 0.0465$, $R' = 0.0455$ and goodness of fit = 1.1318. A final Fourier-difference synthesis showed minimum and maximum residual electron densities of −0.62 and 0.75 e Å^{-3}. All crystallographic calculations were carried out using the CRYSTALS program package.[12] Neutral atom scattering factors were taken from ref. 13.

CCDC reference number 186/1105.

See http://www.rsc.org/suppdata/dt/1998/3191/ for crystallographic files in .cif format.

Acknowledgements

We thank the University of Oxford for a Violette and Samuel Glasstone Fellowship (J. R. G.), the Deutsche Gemeinschaft Forschung (M. M.), St. John's College, Oxford (L. H. D.) and the EPSRC for support of this work.

References

1 For reviews concerning transition-metal catalysis of epoxidation reactions see: J. E. Lyons, in *Aspects of Homogeneous Catalysis*, ed. R. Ugo, Reidel, Dordrecht, Boston, 1977, vol. 3, ch. 1 and refs. therein; R. A. Sheldon and J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.

2 (*a*) S. Chan-Cheng, J. W. Reed and E. S. Gould, *Inorg. Chem.*, 1973, **12**, 337; (*b*) R. A. Sheldon, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 253, 367; (*c*) R. A. Sheldon and J. A. Van Doorn, *J. Catal.*, 1973, **31**, 427; (*d*) M. N. Sheng and J. G. Zajacek, *Adv. Chem. Ser.*, 1968, **76**, 418; (*e*) M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, 1970, **35**, 1839; (*f*) T. N. Baker, G. J. Mains, M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, 1973, **38**, 1145; (*g*) G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, 1971, **36**, 2493; (*h*) J. Sobczak and J. Ziolkowski, *Inorg. Chim. Acta*, 1976, **19**, 15.

3 (*a*) K. Wieghardt, W. Holzbach, J. Weiss, B. Nuber and B. Prikner, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 548; (*b*) P. Jaitner, W. Huber, A. Gieren and H. Betz, *Z. Anorg. Allg. Chem.*, 1986, **538**, 53; (*c*) K. Wieghardt, W. Holzbach, E. Hofer and J. Weiss, *Inorg. Chem.*, 1981, **20**, 343; (*d*) C. Redshaw, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1992, 555; (*e*) K. Wieghardt, E. Hofer, W. Holzbach, B. Nuber and J. Weiss, *Inorg. Chem.*, 1980, **19**, 2927.

4 L. Saussine, H. Mimoun, A. Mitschler and J. Fisher, *New J. Chem.*, 1980, **4**, 235.

5 J. Fischer, J. Kress, J. A. Osborn, L. Ricard and M. Wesolek, *Polyhedron*, 1987, **6**, 1839; J. Kress, M. Wesolek, J.-P. Le Ny and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1982, 514.

6 J. R. Galsworthy, M. L. H. Green, M. Müller and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1997, 1308; J. R. Galsworthy, J. C. Green, M. L. H. Green and M. Müller, *J. Chem. Soc., Dalton Trans.*, 1998, 15.

7 H. Tomioka, K. Takai, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1980, **21**, 4843.

8 W. R. Thiel, *Chem. Ber.*, 1996, **129**, 575.

9 A. N. Chernega, A. J. Graham, M. L. H. Green, J. Haggitt, J. Lloyd, C. P. Mehnert, N, Metzler and J. Souter, *J. Chem. Soc., Dalton Trans.*, 1997, 2293.

10 D. Gewirth, *The HKL Manual*, written with the co-operation of the program authors, Z. Otwinowski and W. Minor, Yale University, 1995.

11 E. Prince, *Mathematical Techniques in Crystallography and Material Sciences*, Springer, New York, 1982.

12 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, CRYSTALS, Issue 10, Chemical Crystallography Laboratory, University of Oxford, 1996.

13 *International Tables for Crystallography*, Kluwer, Dordrecht, 1992, vol. C.

Paper 8/03126F