

Reactions of oxo- and peroxy-molybdenum complexes with $B(C_6F_5)_3$: crystal structures of *cis*-[MoO{OB(C₆F₅)₃}(η²-ONeEt₂)₂] and *cis*-[MoO{OB(C₆F₅)₃}{η²-PhN(O)C(O)Ph}₂]

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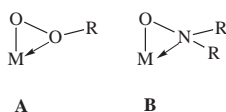
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The oxometal complexes [MoO₂(η²-O-NR₂)₂], R = Et or CH₂Ph, reacted with the strong Lewis acid B(C₆F₅)₃ at their oxo functionality to give *cis*-[MoO{OB(C₆F₅)₃}(η²-ONR₂)₂], (R = Et **1** or CH₂Ph **2**). Reaction of the peroxy complex [MoO(O₂){η²-PhN(O)C(O)Ph}₂] with the same Lewis acid led initially to the formation of [MoO(O₂){B(C₆F₅)₃}{η²-PhN(O)C(O)Ph}₂] **3**, which decomposes to form [MoO{OB(C₆F₅)₃}{η²-PhN(O)C(O)Ph}₂] **4**. Compounds **1** and **4** have been characterised by X-ray crystallography.

Introduction

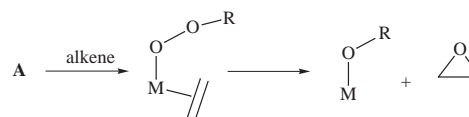
Alkyl peroxide transition metal complexes, **A**, play a central role as reactive intermediates in selective oxidation reactions which employ alkyl hydrogenperoxide as the oxygen source.¹ Reaction is postulated as proceeding according to Scheme 1 *via* formation of an η¹-co-ordinated O-OR ligand. Co-ordination 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 η²-ONR₂ 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.



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(C₆F₅)₃ moiety.⁶ As part of our continuing studies of the reactivity of B(C₆F₅)₃, we describe the reactions of this Lewis acid with oxo-molybdenum complexes containing ancillary dialkylhydroxylamino or peroxy ligands.

Results and discussion

Treatment of *cis*-[MoO₂(η²-ONeEt₂)₂] with 1 equivalent of B(C₆F₅)₃ in toluene under ambient conditions yields *cis*-



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

[MoO{OB(C₆F₅)₃}(η²-ONeEt₂)₂] **1**, which can be isolated as colourless crystals. The ¹¹B 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(C₆F₅)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.

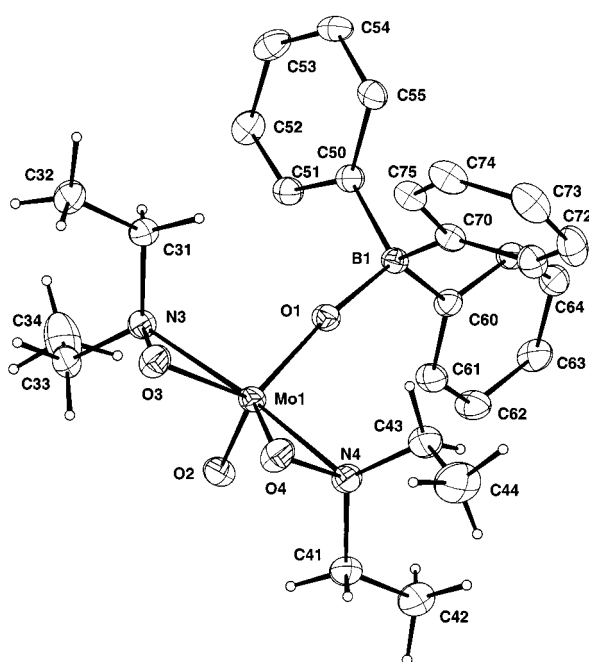
The structure determination of complex **1** (Fig. 1) reveals that a molecule of B(C₆F₅)₃ is bound to one Mo=O unit. The B-O bond length [1.510(2) Å] is typical of those found within this family of compounds and the Mo=O-B unit deviates slightly from linearity [170.09(8)°].⁶ The molybdenum centre displays pseudo-tetrahedral geometry with terminal oxo units occupying two of the vertices and the midpoint of the N-O bond of each η²-ONeEt₂ ligand occupying the remaining two. The presence of a Mo=OB(C₆F₅)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, [MoO₂{η²-ON(CH₂Ph)₂}]₂, was synthesized from [MoO₂(acac)₂] (acac = η²-C₅H₇O₂). The former complex has been previously reported as synthesized from Na₂MoO₄·2H₂O 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 ₆ F ₅) ₃ } ₃](η ² -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 ¹ H: 2.98 (2 H, m, <i>J</i> 7, CH ₂), 2.74 (2 H, m, <i>J</i> 7, CH ₂), 2.66 (2 H, m, <i>J</i> 7, CH ₂), 2.50 (2 H, m, <i>J</i> 7, CH ₂), 0.74 (6 H, t, <i>J</i> 7, CH ₃), 0.48 (6 H, t, <i>J</i> 7, CH ₃) ¹³ C: 148.3 (d, <i>J</i> 240, C ₆ F ₅), 140.1 (d, <i>J</i> 240, C ₆ F ₅), 137.5 (d, <i>J</i> 250, C ₆ F 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 ₆ F ₅) ₃ } ₃](η ² -ON(CH ₂ -Ph) 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 ¹ H: 7.41–6.92 (5 H, m, C ₆ H ₅), 4.24–3.99 (2 H, m, CH ₂) ¹³ C: 148.1 (d, <i>J</i> 233, C ₆ F ₅), 140.2 (d, <i>J</i> 230, C ₆ F ₅), 137.4 (d, <i>J</i> 236, C ₆ F ₅), 131.8 (s, C ₆ H ₅), 131.2 (s, C ₆ H ₅), 130.7 (s, C ₆ H ₅), 130.2 (s, C ₆ H ₅), 130.0 (s, C ₆ H ₅), 128.8 (s, C ₆ H ₅), 61.2 (s, CH ₂), 60.1 (s, CH ₂) ¹¹ B: 2.7 (br)
3 [MoO(O ₂){B(C ₆ F ₅) ₃ } ₃](η ² -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)	¹ H: ^c 7.24–6.65 (m, C ₆ H ₅) ¹¹ B: ^c 3.8 (br)
4 [MoO{OB(C ₆ F ₅) ₃ } ₃](η ² -PhN(O)C(O)Ph) ₂ ·0.5C ₅ H 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 ¹ H: 7.52–7.17 (m, C ₆ H ₅) ¹³ C: 148.1 (d, <i>J</i> 237, C ₆ F ₅), 139.8 (d, <i>J</i> 244, C ₆ F ₅), 137.0 (d, <i>J</i> 247, C ₆ F ₅), 133.7 (s, C ₆ H ₅), 133.4 (s, C ₆ H ₅), 131.3 (s, C ₆ H ₅), 130.1 (s, C ₆ H ₅), 129.9 (s, C ₆ H ₅), 129.6 (s, C ₆ H ₅), 129.0 (s, C ₆ H ₅), 128.5 (s, C ₆ H ₅), 126.9 (s, C ₆ H ₅), 126.0 (s, C ₆ H 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 (CDCl₃, 298 K), unless otherwise stated, given as: chemical shift (δ) [relative intensity, multiplicity (*J* in Hz), assignment]. ^c In C₆D₆.

**Fig. 1** View of the structure of [MoO{OB(C₆F₅)₃}₃](η²-ONEt₂)₂ **1**. Fluorine atoms omitted for clarity.

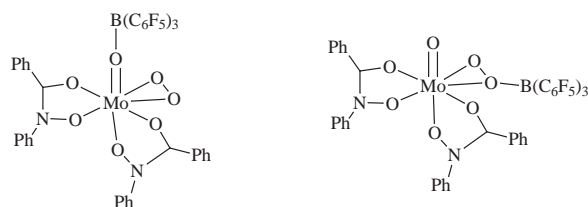
crystals of [MoO₂{η²-ON(CH₂Ph)₂}₂] were obtained, the single crystal structure of which confirmed the *cis*-oxo geometry of the starting material but the data were not of sufficient quality to be published.

Upon reaction of [MoO₂{η²-ON(CH₂Ph)₂}₂] with 1 equivalent of B(C₆F₅)₃ *cis*-[MoO{OB(C₆F₅)₃}₃](η²-ON(CH₂Ph)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*-[MoO₂(η²-ONR₂)₂] complexes is a relatively large O=Mo=O bond angle,^{3a,4} compared to related *cis*-[MoO₂L₂] complexes. This suggests that such dialkylhydroxylamino-complexes might be sterically capable of

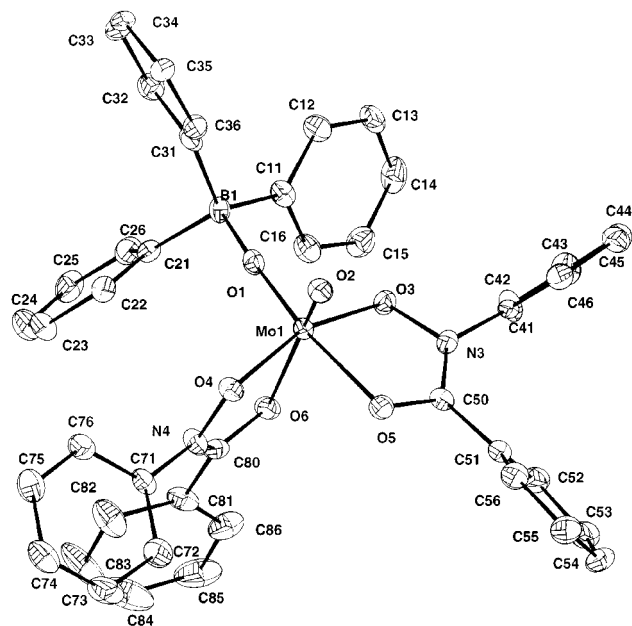
Table 2 Selected bond distances (Å) and angles (°) for compound **1**

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(O₂){B(C₆F₅)₃}₃](η²-PhN(O)C(O)Ph)₂ **3**.

binding two molecules of B(C₆F₅)₃. However, reaction of [MoO₂{η²-ON(CH₂Ph)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(C₆F₅)₃ with the peroxomolybdenum complex [MoO(O₂){η²-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(O₂){η²-PhN(O)C(O)Ph]₂ with 1 equivalent of B(C₆F₅)₃, in hexanes, gave a red-orange precipitate, **3**. Elemental analysis data for **3** is consistent with the empirical formula [MoO(O₂){B(C₆F₅)₃}₃](η²-PhN(O)C(O)Ph)₂. The compound exhibits a signal at δ 3.8 in its ¹¹B 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



[MoO(O₂){B(C₆F₅)₃}{η²-PhN(O)C(O)Ph}]₂ **3**. Yellow [MoO(O₂){η²-PhN(O)C(O)Ph}]₂ (0.568 g, 1 mmol) was suspended in hexane (20 cm³) and a hexane solution (20 cm³) of B(C₆F₅)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 cm³) and then dried *in vacuo*.

cis-[MoO{OB(C₆F₅)₃}{η²-PhN(O)C(O)Ph}]₂ **4**. Off-white [MoO₂{η²-PhN(O)C(O)Ph}]₂ (0.552 g, 1 mmol) was suspended in toluene (20 cm³) and a toluene solution (20 cm³) of B(C₆F₅)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**, C₂₆H₂₀BF₁₅MoN₂O₄·0.5C₇H₈, *M* = 816.21 + 46.04, triclinic, space group *P* $\bar{1}$, *a* = 10.764(1), *b* = 12.107(1), *c* = 12.563(1) Å, *a* = 86.673(2), *β* = 85.919(2), *γ* = 86.480(2)°, *V* = 1627.6 Å³, *Z* = 2, *D*_c = 1.76 g cm⁻³, *μ* = 5.138 cm⁻¹, colourless, crystal dimensions 0.23 × 0.31 × 0.18 mm.

Compound **4**, C₄₄H₂₀BF₁₅MoN₂O₆·0.5C₆H₁₂, *M* = 1094.45, triclinic, space group *P* $\bar{1}$, *a* = 10.2840(8), *b* = 12.4090(8), *c* = 18.598(2) Å, *a* = 102.500(5), *β* = 98.190(4), *γ* = 106.397(4)°, *V* = 2169.74 Å³, *Z* = 2, *D*_c = 1.68 g cm⁻³, *μ* = 4.14 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 (*λ* = 0.71069 Å). For compound **1** 19362 reflections were measured (1 < *θ* < 26°, -13 ≤ *h* ≤ 13, -15 ≤ *k* ≤ 15, -15 ≤ *l* ≤ 15). 6304 Unique reflections were obtained giving 5950 reflections with *I* > 3σ(*I*). For compound **4** 4580 reflections were measured (2 < *θ* < 25°, 0 ≤ *h* ≤ 12, -13 ≤ *k* ≤ 13, -21 ≤ *l* ≤ 20). 4580 Unique reflections were obtained giving 4201 reflections with *I* > 3σ(*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 scheme¹¹ 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 scheme¹¹ 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.

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