Bromination of Molybdenum Carbonyls revisited: Oxo Complexes and Routes to New Materials Chemistry†

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The use of *in situ* [$\{MoBr(\mu\text{-}Br)(CO)_4\}_2$] led to considerably improved preparations of [$MoBr_2(CO)_3(PPh_3)_2$] for which the rate of decarbonylation to [$MoBr_2(CO)_2(PPh_3)_2$] is greatly increased by refluxing under reduced pressure (15–20 mmHg). Attempts to prepare [$MoBr_2(CO)_2\{P(C_6H_{11})_3\}_2$] by Br_2 addition to *cis*- or *trans*-[$Mo(CO)_4\{P(C_6H_{11})_3\}_2$] led to [$HP(C_6H_{11})_3$][$Mo(=O)Br_4L$] [L = $OP(C_6H_{11})_3$ or H_2O]. The $OP(C_6H_{11})_3$ complex may be used as a catalyst for the epoxidation of cyclohexene or for the addition of singlet oxygen to α-terpinene (1-isopropyl-4-methylcyclohexa-1,3-diene). The species [$HP(C_6H_{11})_3$][$Mo(=O)Br_4\{OP(C_6H_{11})_3\}$] was adsorbed onto sodium montmorillonite in a new type of reaction for sodium montmorillonite involving multiple abstractions of NaBr from the complex anion. In solution [$HP(C_6H_{11})_3$][$Mo(=O)Br_4\{OP(C_6H_{11})_3\}$] also decomposes to crystalline [$Mo(=O)_2Br_2\{OP(C_6H_{11})_3\}_2$] which is monoclinic, space group *C*2/*c* [*a* = 27.15(5), *b* = 8.486(8), *c* = 18.49(2) Å, β = 110.94(7)°].

The action of elemental halogens on Group 6 carbonyl complexes is an old family of reactions studied by a number of groups over the years.[1] Addition of Cl_2 or Br_2 to $Mo(CO)_6$ results in the formation of thermally labile [$\{MoX(\mu\text{-}X)(CO)_4\}_2$] (X = Cl or Br) dimers which add PPh_3 to yield [$MoX_2(CO)_3(PPh_3)_2$].[2,3] In connection with our interests in molybdenum oxo species and molybdenum Lewis acid studies,[4] we needed large quantities of [$MoBr_2(CO)_n(PPh_3)_2$] (*n* = 3 **1** or 2 **2**) which led us to improve the original preparation of these compounds. We also report here our attempts to prepare [$MoBr_2(CO)_2\{P(C_6H_{11})_3\}_2$] **3** ($C_6H_{11}$ = cyclohexyl) which lead instead to the oxo species [$HP(C_6H_{11})_3$][$Mo(=O)Br_4L$] [L = $OP(C_6H_{11})_3$ or H_2O]. Additionally, oxygenation reactions catalysed by one of these oxides under homogeneous conditions and for montmorillonite-supported materials are reported herein.

Results and Discussion

Bromination Reactions.—In our experience literature preparations[2,3,5] of [$MoBr_2(CO)_2(PPh_3)_2$] **2** encounter two problems. First, synthesis of [$MoBr_2(CO)_3(PPh_3)_2$] **1** normally involves isolation of the reactive thermo-labile compound [$\{MoBr(\mu\text{-}Br)(CO)_4\}_2$].[6] Secondly, decarbonylation of **1** to the dicarbonyl **2** requires long reflux times (five or more hours). The literature methods are poorly described and both steps lead to low chemical yields. We have optimised a small-scale procedure using *in situ* [$\{MoBr(\mu\text{-}Br)(CO)_4\}_2$] which reproducibly yields analytically pure **1** (55–60%) *via* direct crystallisation from the reaction mixture. A linear relationship between the yield of **1** and the temperature to which the reaction is allowed to warm, after initial bromination, but before PPh_3 addition exists; maximum yields are attained with phosphine addition at −40 to −35 °C. The one-pot procedure may be carried out in air. Unfortunately, only non-carbonyl species are formed on scale-up of the procedure, preventing the use of very large preparations. Improved decarbonylation of **1** is effected by carrying out the reflux in xylene under reduced pressure (15–20 mmHg, water aspirator) so that CO gas is removed as fast as it is formed preventing recarbonylation. Using this procedure respectable yields of **2** (65–75%) are obtained quickly (30 min) and the preparation has the advantage that the complex precipitates directly from the reaction mixture.

To test the generality of the improved procedures we repeated the reaction using $P(C_6H_{11})_3$ instead of PPh_3 but in this case no [$MoBr_2(CO)_3\{P(C_6H_{11})_3\}_2$] or [$MoBr_2(CO)_2\{P(C_6H_{11})_3\}_2$] **3** is isolated from the green-yellow reaction mixture, which contains only minor carbonyl species according to IR spectroscopy. Similar reaction mixtures are attained on addition of 2 equivalents of $P(C_6H_{11})_3$ to the dicarbonyl **2**, which contains labile PPh_3 units, but again nothing is isolable.

One alternative route to **3** is the reaction of *cis*/*trans*-[$Mo(CO)_4\{P(C_6H_{11})_3\}_2$] **4** with Br_2. Although *trans*-[$Mo(CO)_4\{P(C_6H_{11})_3\}_2$], *trans*-**4**, is well known[7] the *cis* isomer has only recently been prepared and crystallographically characterised.[8] Room-temperature IR monitoring of the reaction of *cis*- or *trans*-**4** with a standard solution of bromine at −70 °C reveals that extensive decarbonylation occurs, that no IR bands assignable to **3** are formed, and that 2 equivalents of Br_2 are required for total conversion of **4**. It is also apparent from these studies that *cis*-**4** is considerably more reactive than its *trans* isomer. The origin of this reactivity is the enhanced $P(C_6H_{11})_3$ dissociation in *cis*-**4** caused by the severe steric clashes of the two cyclohexyl phosphines (cone angles 170°).[9] Such dissociation effects have been noted before.[10] In preparative reactions, using either 1 or 2 equivalents of Br_2 per mole of **4**, green solutions are formed. While no [$MoBr_2(CO)_2\{P(C_6H_{11})_3\}_2$] **3** is isolated from these reactions exposure of the reaction residues to air in toluene results in the deposition of yellow crystals of [$HP(C_6H_{11})_3$][$Mo(=O)Br_4\{OP(C_6H_{11})_3\}$]·$C_6H_5Me$ **5** and orange crystals of [$HP(C_6H_{11})_3$][$Mo(=O)Br_4(OH_2)$] **6** (Scheme 1) after 6–10 days. The preparation is reproducible but the yield ratio of **5**:**6** is variable suggesting that atmospheric moisture is the source of the water ligand in **6**. Consistent with this idea reaction of **5** with excess moist $4\text{-}MeOC_6H_4OH$ results in low (30%) but significant yields of **6**. The $O{=}P(C_6H_{11})_3$ in **5** is presumably removed by protonation forming the complex salt [$(C_6H_{11})_3POH$][OC_6H_4OMe].

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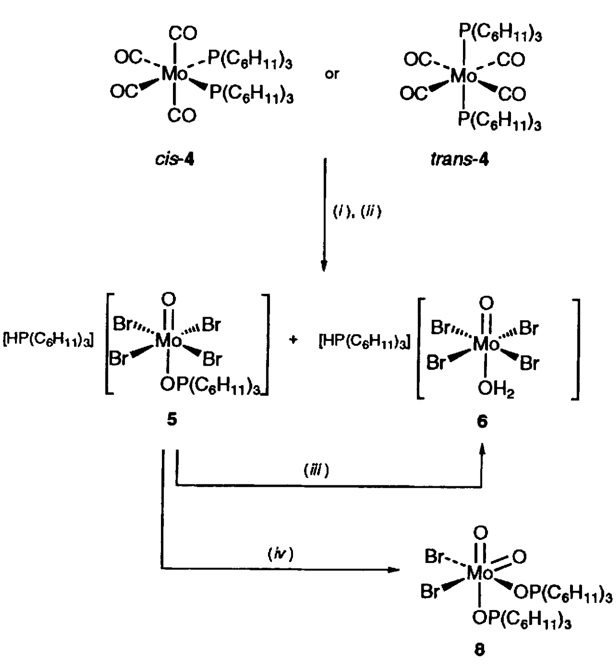
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI units employed: mmHg ≈ 133 Pa, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, eV ≈ 1.602×10^{-19} J G = 10^{-4} T.



Scheme 1 (*i*) 1–2 equivalents Br_2; (*ii*) air, 6–10 days; (*iii*) $4MeOC_6H_4OH$, water (trace); (*iv*) EtOH, 10 days

The IR spectrum of **5** shows two clear co-ordinated P=O stretches [ν_{max}/cm^{-1} (KBr disc) 1118m, 1103m] shifted with respect to free $(C_6H_{11})_3P{=}O$ [ν_{max}/cm^{-1} (KBr disc) 1152m]; such shifts are expected.[11] The higher frequency band often shows a batch dependent shoulder feature of variable intensity which may be due to an impurity. A very weak P–H stretch is apparent [ν_{max}/cm^{-1} (KBr disc) 2360vw], while the Mo=O stretch appears at 965 cm^{-1}. Low-intensity tricyclohexyl phosphonium P–H stretches are known.[12] Consistent with its formulation as a molybdenum(v) species, the complex is paramagnetic as judged by its solution ESR spectrum in CH_2Cl_2 (g_{iso} = 1.994, A_{iso} = 46.3 G, 20 °C) and diamagnetic corrected room-temperature magnetic moment [μ_{eff} (292 K) = 1.68 μ_B]. These values are in the expected range.[13] The ESR spectrum also shows the presence of an impurity, g_{iso} *ca.* 1.97. We believe the origin of this signal to be due to loss of $OP(C_6H_{11})_3$ in solution. As a consequence of its paramagnetism, NMR spectra of $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ toluene **5** show rather broad signals. This is most apparent in the ^{31}P NMR spectrum where only one broad signal at δ −6.2 is observed despite the presence of two phosphorus environments in the molecule. In one run it proved possible to obtain a sample of **5** suitable for crystallographic study. Although the quality of the data is not good enough to allow accurate discussion of the structure, the nature of **5** could be confirmed including its toluene solvate.

Water-ligated $[HP(C_6H_{11})_3][Mo({=}O)Br_4(OH_2)]$ **6** shows similar spectroscopic properties to the phosphine oxide complex **5**. In particular, the solution ESR spectrum (g_{iso} = 1.992, A_{iso} = 45.48 G; acetone, 20 °C) and diamagnetic-corrected magnetic moment [μ_{eff} (292 K) = 1.71 μ_B] confirm the presence of a molybdenum(v) complex. The presence of co-ordinated water in **6** is evident from the IR spectrum [ν_{max}/cm^{-1} (KBr disc) 3420m br (OH)], while the Mo=O stretch in **6** is shifted slightly compared to that of **5** appearing at 987 cm^{-1}. These values compare well with the Mo=O stretch observed in crystallographically characterised $[AsPh_4][Mo({=}O)Br_4(OH_2)]$ (981 cm^{-1}, Nujol).[14] Although ^1H NMR spectra of **6** in $[^2H_6]$acetone show typical paramagnetic line broadening equivalent samples run in $CDCl_3$ containing traces of $[^2H_6]$dimethyl sulfoxide demonstrate considerably sharper $HP(C_6H_{11})_3$ resonances. This may be due to solvent exchange with **6** forming $[HP(C_6H_{11})_3]OH$ and '$H[MoBr_4(Me_2SO)]$'. Exchange of the ligand *trans* to an oxo function is a commonly recognised process in molybdenum(v) chemistry.[15]

Materials Chemistry.—One of our interests is in the preparation of hybrid materials by the adsorption of metal oxide complexes onto expandable layer silicates such as smectite clay minerals, specifically Na^+–montmorillonite *via* sodium cation exchange. These new layered materials are interesting as potential oxidation catalysts. Normally one attempts only simple cation metathesis reactions with Na^+–montmorillonite [Fig. 1(*a*)], where *x* is the cation exchange capacity of the Na^+–montmorillonite. However, we became interested in the possibility of adsorption of both halves of a salt $M_A[M_BBr_n]$ *via* abstraction of NaBr from the complex anion [Fig. 1(*b*)]. This possibility was investigated using **5** as a model compound.

Contact of Na^+–montmorillonite with a 0–50% by weight loading of **5** as an EtOH solution over 10 days leads to a new material **7**, which shows a reproducible expansion of the montmorillonite interlayer from 12.4 to 14.2 Å by powder X-ray diffraction examination of the clay basal spacings. No expansion of the interlayers in EtOH or toluene is observed. The expansion is similar to that of $[HP(C_6H_{11})_3]^+$–montmorillonite obtained by contact of Na^+–montmorillonite with $[HP(C_6H_{11})_3]Cl$ as an EtOH solution.[16] However, energy dispersive spectroscopy (EDS) of the new material **7** shows the presence of *both* molybdenum and phosphorus, which is not expected if only phosphonium exchange has taken place. Neither of these elements is detected in the Na^+–montmorillonite starting material by EDS. On the other hand, the sodium interlayer cations in the starting montmorillonite disappear once **5** has been added. The amount of Na^+ released from the montmorillonite interlayers to the solution can be determined by flame photometry after separation and evaporation of the supernatant EtOH. At 20 wt% loadings of **5** per montmorillonite, the Na^+ released approaches 100% of the cation exchange capacity of Na^+–montmorillonite [approximately 74 millimolar equivalents (mequiv.) Na^+/100 g clay]. The Na^+ released before 100% exchange is reached would require near to 4 equivalents of $[HP(C_6H_{11})_3]^+$ per molecule of **5** even though the Na^+ ions in Na^+–montmorillonite are cleanly displaced by approximately the same amounts of $[HP(C_6H_{11})_3]^+$ cations from $[HP(C_6H_{11})_3]Cl$ (Fig. 2). These results indicate that Na^+ in the montmorillonite is displaced by $[HP(C_6H_{11})_3]^+$ and other positively charged species derived from the anion in **5**.

The solid, obtained from the supernatant reaction solution, has two different brighter back scattered electron (BSE) reflections. The EDS spectrum of the bright phase shows that Na and Br are detected as the predominant elements of NaBr. The powder X-ray diffraction pattern of this species confirmed it to be NaBr. The dark phase, which consists of the elements Mo, P and Br, as detected by EDS, corresponds to the unadsorbed **5** and/or other molybdenum oxide species as reaction products, but their exact nature could not be determined with the EDS equipment used in this study. It is possible to isolate one molybdenum oxo species from the supernatant EtOH solution of those preparations of **7** where the molybdenum to clay molar ratio is relatively high. An identical product is formed if ethanol solutions of **5** are left to stand in the absence of Na^+–montmorillonite. The solid-state IR spectrum of the isolated yellow crystals [$\nu_{Mo=O}/cm^{-1}$ (KBr disc) 933s, 897s] strongly suggests that this recovered compound is the dioxo species $[Mo({=}O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ **8** rather than **5**. Due to its low solubility **8** could only be fully characterised by a crystallographic study. An ORTEP view of the $[Mo({=}O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ molecule is shown in Fig. 3. Final positional parameters for the structure are given in Table 1. The bond distances and angles are given in Table 2. The nature of **8** is also confirmed by its independent synthesis from ammonium molybdate(vi) tetrahydrate, HBr and $O{=}P(C_6H_{11})_3$ using a literature method,[17] although in this case the purity of the

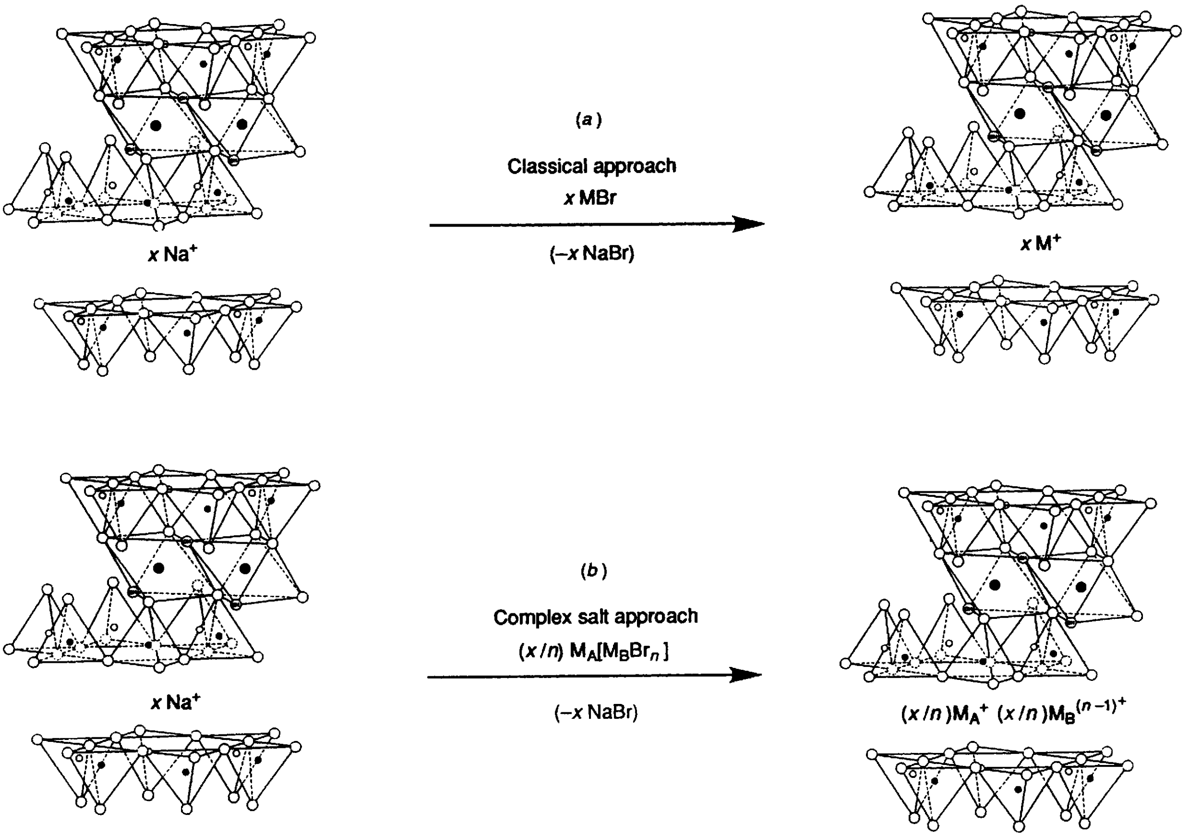


Fig. 1 Comparison of a classical approach (*a*) and complex salt approach (*b*) to sodium cation metathesis with sodium montmorillonite

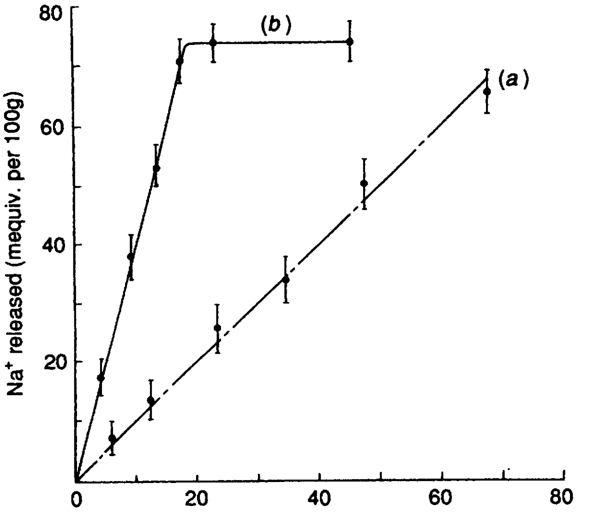


Fig. 2 A plot, with error bars, of Na^+ released/millimolar equivalents (mequiv.) per 100 g clay *vs.* $[HP(C_6H_{11})_3]^+$ used in preparation/mmol per 100 g clay for (*a*) preparations using $[HP(C_6H_{11})_3]Cl$ and (*b*) preparations using $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]{\cdot}C_6H_5Me$ **5**

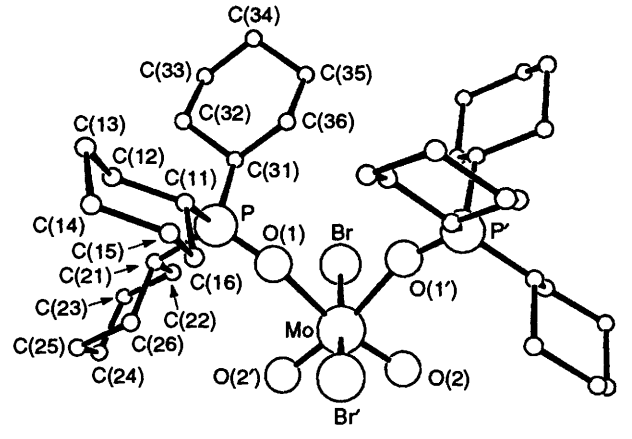


Fig. 3 An ORTEP representation of $[Mo({=}O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ **8** including the atomic numbering scheme but neglecting hydrogen atoms

material isolated was not as high as that obtained by the decomposition of **5**. The slow decomposition of **5** in EtOH solution to **8** raises the question of whether compound **8** forms first in solution and it is this rather than **5** that is adsorbed onto the montmorillonite. This appears to not to be the case, exposure of sodium montmorillonite to ethanol solutions of **8** leads to little or no expansion of the clay interlayer basal spacing (12.4 Å) as determined by powder X-ray diffraction.

IR spectra of material **7** do not provide much information on the adsorbed species. Two weak C–H stretches at 2938 and 2860 cm^{-1} (KBr disc) show the presence of $HP(C_6H_{11})_3$ on the clay; these vibrations which are relatively strong in **5**, are also observed in $[HP(C_6H_{11})_3]^+$–montmorillonite.[16] A Mo=O stretch is not observed for **7** but this is probably masked by the strong Si–O stretch of montmorillonite (1045vs br cm^{-1}). Neutron excitation and inductively coupled plasma mass spectrometry (ICPMS) analysis of **7** shows the presence of a 0.5 (± 0.05) wt% loading of molybdenum. This value is lower than that predicted by the chemistry in Fig. 1; a *ca.* wt% loading is calculated. These results indicate that although the chemistry of Fig. 1 is applicable $\{M_A = HP(C_6H_{11})_3, M_B = [Mo({=}O)(L)]$ $[L = H_2O$ or $OP(C_6H_{11})_3]$ with $n = 4\}$ complications result in lower molybdenum adsorption than expected. We suggest that the two most likely explanations are competitive Na^+ exchange with HBr (formed *in situ* from the decomposition of **5** to **8** or other oxides), and leaching of the molybdenum from the clay during isolation of the material.

The ESR spectrum of solid **7** exhibits two broad signals

Table 1 Positional parameters for non-hydrogen atoms in $[MO(=O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ **8**

Atom	*x*	*y*	*z*
Mo	1.000 0	0.283 0(1)	0.750 0
Br	0.994 57(3)	0.241 72(9)	0.883 27(4)
P(1)	0.896 76(6)	−0.010 0(2)	0.707 8(1)
O(1)	0.945 2(1)	0.083 3(4)	0.716 0(2)
O(2)	1.052 9(2)	0.410 3(4)	0.784 2(2)
C(11)	0.883 8(2)	−0.146 0(7)	0.627 0(3)
C(12)	0.828 2(3)	−0.215 6(9)	0.597 4(4)
C(13)	0.823 0(3)	−0.342 2(9)	0.534 7(4)
C(14)	0.837 4(3)	−0.273 2(9)	0.468 8(4)
C(15)	0.890 7(3)	−0.202 (1)	0.497 6(4)
C(16)	0.897 7(2)	−0.078 8(8)	0.560 8(4)
C(21)	0.838 6(2)	0.108 6(7)	0.691 6(3)
C(22)	0.842 4(2)	0.214 1(8)	0.760 1(3)
C(23)	0.791 8(3)	0.305 5(8)	0.747 7(4)
C(24)	0.775 6(3)	0.401 1(8)	0.673 9(4)
C(25)	0.771 9(2)	0.299 2(8)	0.605 5(4)
C(26)	0.823 8(2)	0.209 5(8)	0.619 1(4)
C(31)	0.907 7(2)	−0.117 5(6)	0.796 7(3)
C(32)	0.860 4(2)	−0.203 9(7)	0.803 5(3)
C(33)	0.873 5(3)	−0.276 8(8)	0.882 9(4)
C(34)	0.921 1(3)	−0.382 1(8)	0.903 8(4)
C(35)	0.968 9(2)	−0.301 0(8)	0.896 3(4)
C(36)	0.955 7(2)	−0.226 3(7)	0.816 8(3)

Table 2 Selected bond distances (Å) and angles (°) for $[Mo(=O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ **8***

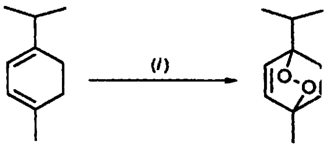
Mo–Br	2.544(4)	Mo–O(1)	2.194(5)
Mo–O(2)	1.726(5)	P(1)–O(1)	1.495(5)
P(1)–C(11)	1.820(6)	P(1)–C(21)	1.806(7)
Br–Mo–Br′	164.18(6)	Br–Mo–O(1)	84.4(1)
Br–Mo–O(1′)	83.3(1)	Br–Mo–O(2)	93.4(2)
Br–Mo–O(2′)	96.5(2)	O(1)–Mo–O(1′)	78.9(3)
O(1)–Mo–O(2)	168.2(2)	O(1)–Mo–O(2′)	89.3(3)
O(2)–Mo–O(2′)	102.5(3)	Mo–O(1)–P(1)	156.9(2)

* Primed atoms are related to unprimed ones by symmetry operation $2 - x, y, \frac{3}{2} - z$.

around $g = 4.2$ and 1.9. The signal at $g = 4.2$, attributed to Fe^{III} in octahedral sites, is observed for other clay minerals.[18–22] The signal at $g = 1.9$, which is not present in Na^+–montmorillonite, shows the presence of another paramagnetic species in the montmorillonite. It is undoubtedly due to molybdenum(V) complex(es) adsorbed onto the clay. However, because of the weak and broad nature of the signal little further information can be extracted.

Various techniques (powder XRD, IR, EDS, neutron excitation, ICPMS and ESR) including determination of the cation exchange mechanism confirm the adsorption of the molybdenum compound **5** onto Na^+–montmorillonite in EtOH. The results obtained so far also suggest the $[HP(C_6H_{11})_3]^+$ ions in **5** are incorporated between the silicate layers of the montmorillonite by the displacement of Na^+ and this incorporation prevents or minimises the decomposition of **5** in solution to $[Mo(=O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ **8**. The sodium cations released, the molybdenum content in the material **7**, and the formation of NaBr seem to suggest that **5** is mainly incorporated between the silicate layers as $[Mo(=O)Br_nL]^{(3-n)+}$ [$L = H_2O$ or $OP(C_6H_{11})_3$], or some aggregate thereof with $n \approx 0$, generated by loss of multiple bromide ligands from the $[Mo(=O)Br_4\{OP(C_6H_{11})_3\}]^-$ ions but that competition reactions prevent full attainment of the regime of Fig. 1.

Catalysis.—Both $[HP(C_6H_{11})_3][Mo(=O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** and montmorillonite based **7** are rather poor oxygen transfer catalysts with the simple oxygen or O_2 in the presence of a zinc co-reductant (Gif conditions[23]). Negligible yields of oxidation products from styrene are obtained. Both species are also rather poor epoxidising agents when H_2O_2 is used as an O-atom source for styrene epoxidation. However, decomposition of H_2O_2 results in quantitative oxidation of α-terpinene (1-isopropyl-4-methylcyclohexa-1,3-diene) **9** to ascaridole (1-isopropyl-4-methyl-2,3-dioxabicyclo[2.2.2]oct-5-ene) **10** by H_2O_2 due to formation of singlet O_2 catalysed by 1.5 mol% **5** in the presence of excess NaOH (Scheme 2). This reaction is probably mediated by $Na_2[MoO_n]$ ($n = 4, 6, 8$), formed *in situ* from **5**, as the reaction soon develops the characteristic red-brown colour of these anions.[24,25] Complex **5** (1.5 mol%) also shows some activity for cyclohexene epoxidation in the presence of *tert*-butyl hydroperoxide. No allylic oxidation products are observed in these reactions, but **5** leads to a relatively short-lived catalyst. The yield of cyclohexene oxide exceeds 30% within 1 h at room temperature, after this time the reactions become much less active, and all catalytic activity ceases within 48 h. By heating the reaction mixture to 70 °C slightly higher yields of epoxide (30–45%) are obtained but after this time the catalyst again becomes deactivated. Montmorillonite-absorbed **5** was also screened for epoxidation activity using Bu^tOOH but only very low yields (< 1%) of cyclohex-2-en-1-one, and cyclohex-2-en-1-ol were realised at 70 °C. Such products are indicative of free radical alkene autooxidation rather than metal-centred events. This behaviour is not altogether unexpected and is probably due to the small surface area associated with the material **7** restricting access of the substrates to the molybdenum centres. Currently, we are attempting to use our new complex-salt exchange processes to prepare a new generation of materials with far greater surface areas allowing effective epoxidation catalysis. These results will be reported in due course.



9 **10**

Scheme 2 (*i*) H_2O_2–NaOH, **5** (1.5 mol%)

Experimental

General.—All manipulations involving molybdenum(0) complexes were carried out under nitrogen atmospheres using standard Schlenk techniques, all other reactions were performed in air. Dichloromethane was distilled from CaH_2 immediately prior to use, hexane, light petroleum (b.p. 40–60 °C) and Et_2O were dried over sodium wire. All other reagents were used as supplied. Infrared spectra were recorded using a Perkin-Elmer 983G instrument. Proton NMR spectra were recorded on a JEOL-270 (270 MHz) or Bruker WH-400 (400 MHz) spectrometers. Carbon-13 (67.8 MHz) and ^{31}P NMR (109.3 MHz) spectra were recorded on the JEOL-270. ESR spectra were measured using solutions, frozen solvent glasses, or solid powdered samples on a Bruker ESP-300E instrument. Unless noted otherwise all spectroscopic investigations were carried out at ambient temperature. Mass spectra were obtained on Finnigan 1020 (electron impact ionisation, EI) or VG-ZAB (fast atom bombardment ionisation, FAB) machines. Magnetic moments were measured on a Johnson Matthey digital balance as the average of three samples. Diamagnetic corrections were applied using tables of standard values. Powder X-ray diffraction (XRD) was carried out on a Philips PW1130 diffractometer with nickel-filtered Cu-Kα radiation. Back scattered electron (BSE) micrographs and energy dispersive spectra (EDS) were obtained using a Lieca-

Cambridge Stereoscan 360 scanning electron microscope equipped with a Link System QX200 energy dispersive spectrometer. The sodium contents of solutions were determined with a Corning 400 flame spectrometer. The molybdenum content in **7** was measured by neutron excitation by the Centre for Analytical Research in the Environment, or by (ICPMS) on a VG PlasmaQuad. The compounds *cis*- and *trans*-$[Mo(CO)_4\{P(C_6H_{11})_3\}_2]$ *cis*/*trans*-**4** were prepared by literature procedures.^{7,8}

Improved Preparations of $[MoBr_2(CO)_n(PPh_3)_2]$ (n = 3 **1** *or* 2 **2**).—A stirred solution of $Mo(CO)_6$ (0.50 g, 1.89 mmol) in CH_2Cl_2 (20 cm^3) was cooled (−70 °C) in an *unlagged* bath and to the resultant suspension Br_2 (1.1 cm^3, 1.8 mol dm^{-3} solution in 1,2-dichloroethane, 1.98 mmol) was added at −70 °C. The orange suspension was allowed to warm to −40 °C (*ca.* 10 min, longer on a large scale) and PPh_3 (1.00 g, 3.81 mmol) added. Carbon monoxide was evolved (**CAUTION**) and occasionally a green colouration observed. The reaction was allowed to warm to 0 °C (*ca.* 40 min, longer on a large scale) and promptly filtered through a bed of Celite {prolonged filtrations resulted in partial decarbonylation to $[MoBr_2(CO)_2(PPh_3)_2]$ **2** which could be reversed by admission of CO (**CAUTION**) to the filtrate}. Light petroleum (20 cm^3) was added to the orange solution slowly. Cooling afforded orange crystals of $[MoBr_2(CO)_3(PPh_3)_2]$ **1** 0.93–0.98 g (57–60%) with literature properties.^{3} $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3071w (CH), 3058w (CH), 2018s (CO), 1955s (CO), 1893s (CO), 1486m (CC) and 1441m (CC); δ_H(270 MHz, $CDCl_3$) 7.04–7.88 (m, 30 H, Ph); δ_P(109.3 MHz, $CDCl_3$) 39.1 (PPh_3).

The crude $[MoBr_2(CO)_3(PPh_3)_2]$ **1** (0.80 g, 0.93 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and xylene (25 cm^3) added. Using a water aspirator the reaction was refluxed under reduced pressure (70–75 °C, 15–20 mmHg) causing rapid formation of blue $[MoBr_2(CO)_2(PPh_3)_2]$ **2** (30 min). Occasionally traces of the tricarbonyl remained which were removed by repeating the reflux. Filtration, washing with acetone (2 × 10 cm^3), Et_2O (2 × 10 cm^3) and drying yielded $[MoBr_2(CO)_2(PPh_3)_2]$ **2** as a blue powder 0.50–0.56 g (67–76%) with literature properties:^{3} $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3057w (CH), 1973m (CO), 1887s (CO), 1481m (CC) and 1431m (CC); δ_H(270 MHz, $CDCl_3$) 7.34–7.65 (m, 30 H, Ph); δ_P(109.3 MHz, $CDCl_3$) 71.1 (PPh_3).

Both preparations were conveniently carried out in air (for which the initial reaction was protected from moisture by a 4 Å-molecular sieve guard tube).

Preparation of $[HP(C_6H_{11})_3][Mo({=}O)Br_4L]$ [L = $OP(C_6H_{11})_3$ **5** *or* H_2O **6**].—A bromine solution (3.2 cm^3, 1.86 mol dm^{-3} 1,2-dichloroethane solution, 5.95 mmol) was added to a cold (−78 °C) stirred solution of *cis*-$[Mo(CO)_4\{P(C_6H_{11})_3\}_2]$ (2.31 g, 3.01 mmol) dissolved in CH_2Cl_2 (125 cm^3). The solution was allowed to warm to room temperature (2 h) during which time it turned deep green and an IR spectrum indicated the presence of only minor carbonyl-containing products. The solvent was evaporated to leave a dark oil which was extracted with toluene and filtered through Celite. On standing in air (6–10 days) the solution deposited canary-yellow microneedles of $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** in somewhat variable yield 0.96–1.65 g (29–50%). Lower yields (0–30%) were attained in equivalent preparations using *trans*-$[Mo(CO)_4\{P(C_6H_{11})_3\}_2]$ **4**: m.p. (toluene solvate) 149–150 °C (Found: C, 46.9; H, 6.8. $C_{43}H_{75}Br_4MoO_2P_2$ requires C, 46.9; H, 6.9%); m/z (FAB) 297 [$(C_6H_{11})_3P{=}O$] and 281 [$HP(C_6H_{11})_3$]; $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2933s (CH), 2855m (CH), 2360vw (PH), 1118m, 1103m (P=O) and 965m (Mo=O); δ_H(400 MHz, $CDCl_3$) 0.81–2.05 (m, C_6H_{11}), 2.35 (s, toluene) and 3.98–4.26 (m, toluene) paramagnetic effects caused unreliable signal integration, the PH was not apparent; δ_P(109.3 MHz, $CDCl_3$, 0 °C) −6.2 (vbr); ESR (CH_2Cl_2, 20 °C) g_{iso} = 1.994, A_{iso} = 46.3 G; $\chi_{M(corr)} = 1.52 \times 10^{-8}$ m^3 mol^{-1}; μ_{eff}(292 K) = 1.68 μ_B. Crystalline $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** is monoclinic, $P2_1/c$, a = 12.053(9), b = 10.731(2), c = 38.269(9) Å, β = 91.42(5)°.

Occasionally, the formation of **5** was accompanied by the presence of large dark orange needles of $[HP(C_6H_{11})_3][Mo({=}O)Br_4(OH_2)]$ **6** in variable yield 0.00–0.73 g (0–33%). Mixtures of the two compounds were separated by dissolution in hot toluene in which **5** is soluble but **6** is not. Data for $[HP(C_6H_{11})_3][Mo({=}O)Br_4(OH_2)]$ **6**: m.p. 202–203 °C (Found: C, 30.0; H, 5.0. $C_{18}H_{36}Br_4MoO_2P_2$ requires C, 29.6; H, 5.0%); m/z (FAB) 432 [$Mo({=}O)Br_4$]; $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3420m br (OH), 2938s (CH), 2860m (CH), 2393vw (PH), 1608m, 1445m and 987m (Mo=O); δ_H(270 MHz, [$^2H_6$]acetone) 1.21–2.25 (m, C_6H_{11}), 2.87 (br, H_2O or PH) and 3.45 (br, H_2O or PH), paramagnetic effects caused unreliable signal integration; δ_H[270 MHz, $CDCl_3$–$(CD_3)_2SO$] 1.19–1.58 (m, 15 H, C_6H_{11}), 1.74–2.05 (m, 15 H, C_6H_{11}), 2.07–2.28 (m, 3 H, C_6H_{11}) and 8.00 (br, 1 H, PH); δ_P(109.3 MHz, $CDCl_3$) 44.5 (vbr); ESR (acetone, 20 °C) g_{iso} = 1.992, A_{iso} = 45.48 G; $\chi_{M(corr.)} = 1.58 \times 10^{-8}$ m^3 mol^{-1}; μ_{eff}(292 K) = 1.71 μ_B. Crystals of **6** are monoclinic $P2_1/n$, a = 14.19(1), b = 11.52(2), c = 15.81(2) Å, β = 97.6(1)°. Extraction of the data beyond the unit-cell parameters was not possible.

Reaction of $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** *with* 4-$MeOC_6H_4OH$.—An excess of 4-$MeOC_6H_4OH$ (1.00 g, 8.06 mmol) was added to a solution of $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** (0.20 g, 0.18 mmol) in hot (90 °C) toluene (25 cm^3) over 5 min. The resulting green-brown solution was filtered through Celite and allowed to cool overnight, yielding dark orange crystals of $[HP(C_6H_{11})_3][Mo({=}O)Br_4(OH_2)]$ **6** 0.04 g (30%) with identical properties to that prepared above.

Adsorption of $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** *onto* Na^+*–montmorillonite*.—The montmorillonite used was the < 2 μm fraction of Wyoming bentonite (South Dakota area, Wyoming), obtained from Steetly Minerals Limited. The < 2 μm fraction obtained by conventional sedimentation techniques was practically free from impurities as determined by powder XRD. The < 2 μm fraction was exchanged with aqueous 1 mol dm^{-3} NaCl solutions to form high purity Na^+–montmorillonite. The Na^+–montmorillonite was separated by centrifuge and then repeatedly washed with doubly distilled deionized water until chloride ions were absent by $AgNO_3$ test.

Typically, Na^+–montmorillonite [d(001) = 12.4 Å] (80 mg) was mixed with $[HP(C_6H_{11})_3][Mo({=}O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** (0–40 mg), in nitrogen purged EtOH (20 cm^3). The mixture was sonicated in a conventional cleaning bath (360 W, 10 min) and shaken (2 min). The clay suspension was aged at room temperature over ten days. The new material **7**, montmorillonite adsorbed **5**, was separated by centrifuge and then washed with EtOH (8 × 20 cm^3). The material **7** was dried in air and examined as thin, oriented clay layer on glass slides at about 55% relative humidity and room temperature by powder XRD. Otherwise, the montmorillonite absorbed **5** was dried in air stored in a desiccator filled with nitrogen for all examinations.

Data for the new material **7**. Powder XRD d(001) values due to weight percent loading of **5** per Na^+–montmorillonite: d(001) = 12.4 Å (sample A, 0 wt%, Na^+–montmorillonite treated with EtOH in the absence of **5**); 12.4 Å (sample B, 5 wt%); 13.3 Å (sample C, 10 wt%); 13.8 Å (sample D, 15 wt%); 14.2 Å (sample E, 20 wt%); 14.2 Å (sample F, 25 wt%) and 14.2 Å (sample G, 50 wt%). Energy dispersive spectra (0–20 keV, samples E–G) 2.293 (Mo-Lα$_1$), 2.395 (Mo-Lβ$_1$), 2.518 (Mo-Lβ$_2$), three weak overlapped signals; 17.478 (Mo-Kα$_1$), 17.373 (Mo-Kα$_2$) two very weak overlapped signals; 19.607 (Mo-Kβ$_1$), 19.964 (Mo-Kβ$_2$) two very weak overlapped signals; and 2.015 (P-Kα) weak. Equivalent molybdenum and phosphorus signals were present in samples B–D but at much lower intensity.

Sodium-EDS data (Na-Kα 1.041 keV) indicated that some Na^+ remains in the interlayers of samples A–E; weak (sample A) to trace (sample E) signals were observed. None was present in samples F–G. IR (samples B–G): IR $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3625s (structural OH in mineral sheets), 3430s br (H_2O), 2938w [CH of $(C_6H_{11})_3$], 2860w [CH of $(C_6H_{11})_3$], 1640m (H_2O bend), 1045vs br (SiO), 525s (Si–O–Al bend) and 465s (Si–O bend). ESR (sample F as the typical sample of **7**, powder, 20 °C) g = 4.2 [Fe^{III}] and g = 1.9br [Mo^V]. Neutron excitation studies and ICPMS indicated typical molybdenum contents of 0.5 (±0.05) wt% (sample F, 25 wt% **5** used in preparation) for the clay material **7**.

Evaporation of the mother-liquors afforded variable yields of a yellow solid which could be recrystallised from toluene containing small amounts of EtOH to yield $[Mo(=O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ **8**: m.p. 230–231 °C (Found: C, 49.05; H, 7.7. $C_{36}H_{66}Br_2MoO_4P_2$ requires C, 49.1; H, 7.55%); m/z (FAB) 866 [M^+ – O]; $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2922s (CH), 2845s (CH), 1138s, 1118s, 1103s, 1094s (O=P), 933 and 897s (Mo=O). The complex proved too insoluble to allow the acquisition of solution spectra once isolated.

Oxidation of α-Terpinene by H_2O_2 *in the Presence of* $[HP(C_6H_{11})_3][Mo(=O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5**.—A solution of NaOH (0.08 g, 3.47 mmol) in water (5 cm^3) was added to a mixture of α-terpinene **9** (55 mg, 0.40 mmol), H_2O_2 (1.0 cm^3, 100 vol., *ca.* 8 mmol) and $[HP(C_6H_{11})_3][Mo(=O)Br_4\{OP(C_6H_{11})_3\}]\cdot C_6H_5Me$ **5** (0.13 g, 0.12 mmol, 30 mol% based on α-terpinene **9**, *ca.* 1.5 mol% based on H_2O_2). The yellow solution decolourised and then became a dark red-orange that lightened to pale yellow over 4 h. Dichloromethane was added, the organic layer separated, dried (Na_2SO_4) and evaporated. Extraction with cold pentane and filtration through Celite afforded, on removal of the pentane, an oil (62 mg) for which ^1H NMR spectroscopy showed a quantitative conversion to ascaridol **10** [δ_H(270 MHz, $CDCl_3$) 1.00 (d, 6 H, J_{HH} = 7, $CHMe_2$), 1.38 (s, 3 H, CMe), 1.52 (apparent d, J_{HH} = 9, CH_2), 1.92 (heptet, J_{HH} = 7 Hz, $CHMe_2$), 2.03 (m, 2 H, CH_2) and 6.45 (AB, J_{AB} = 8.5 Hz, 2 =CH)] and some $O=P(C_6H_{11})_3$.

Epoxidation of Cyclohexene.—The following procedures are representative. To a solution of cyclohexene (31 μl, 0.31 mmol) and chlorobenzene (100 μl, internal standard) in 1,2-$C_6H_4Cl_2$ (1.5 cm^3) was added either **5** (5.0 mg, 4.5 μmol, 1.5 mol%) or the montmorillonite complex of **5** (30 mg, *ca.* 2% Mo, *ca.* 6.1 μmol, *ca.* 2 mol%) followed by Bu^tOOH (110 μl, 2.78 mol dm^{-3} toluene solution, 0.31 mmol). The mixture was stirred at room temperature. Periodically aliquots (0.1 cm^3) were withdrawn, quenched with PPh_3 (5.0 mg) and analysed by GC on a BP-20 column isothermally at 100 °C. Cyclohexene oxide yields of 30–35% were attained within 48 h at ambient temperatures after which the catalytic activity ceased. The yield increased slightly with heating (70 °C); 35–40% yields were attained within 4 h. No reaction occurred in the absence of added catalysts.

Crystallography.—A yellow prismatic crystal of $[Mo(=O)_2Br_2\{OP(C_6H_{11})_3\}_2]$ **8** mounted on a glass fibre was used for the analysis and this gave the following data for **8**: $C_{36}H_{66}Br_2MoO_4P_2$, M_r = 881, space group $C2/c$, Z = 4, a = 27.15(5), b = 8.486(8), c = 18.49(2) Å, β = 110.94(7)°, U = 3978(18) Å^3, D = 1.47 g cm^{-3}, μ(Mo-Kα) = 24.2 cm^{-1}, F(000) = 1824, crystal dimensions 0.45 × 0.40 × 0.33 mm, maximum, minimum transmission coefficients 1.24, 0.68.

Data collection. Cell dimensions and space-group data were obtained on a four-circle Rigaku AFC6S single crystal diffractometer with graphite-monochromated Mo-Kα radiation. The ω–2θ scan technique was used at 298 K to record the intensities for all non-equivalent reflections for which $1 \leqslant 2\theta \leqslant 55.1°$, scan widths were calculated as $(1.47 + 0.3 \tan \theta)$.

The intensities of three standard reflections showed no greater fluctuations during data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarisation effects and for absorption (DIFABS program).[26] A total of 5012 intensities were collected of which 4907 were unique. These included 2088 with $F_o^2 \geqslant 3\sigma(F_o^2)$ where $\sigma(F_o^2)$ was estimated from counting statistics.[27] These data were used in the final refinement of the structural parameters.

Structure determination. A three-dimensional Patterson function was used to determine the metal position, which phased the intensity data sufficiently well to permit location of the other non-hydrogen atoms from Fourier syntheses based on the FORDAP program.[28] Full-matrix least-squares refinement, based on F, was carried out using highly modified versions of ORFLS (W. R. Busing, K. O. Martin and H. A. Levy). The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2\{(C + R^2B) + 0.03F_o^2\}^2]/L_p^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count and L_p = Lorentz polarisation factor. Atomic scattering factors for both non-hydrogen[29] and hydrogen[30] atoms were taken from literature values. The effects of anomalous dispersion were included using literature values for $\delta f'$ and $\delta f''$.[31]

Anisotropic thermal parameters were introduced for all non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles of least squares and then held fixed. The model converged with R = 0.0396, R_w = 0.034. GOF = 1.92, n_{var} = 204, max. shift/error = 0.01. The principal programs used are contained in the TEXRAY set.[32] The successful refinement confirmed the choice of the centric space group.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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