Crystal and Molecular Structure of [1,2-Bis(diethylphosphino)ethane mono-oxide-*P,O*]trichloro-oxomolybdenum(V) †

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The novel diphosphine mono-oxide complex $[MoCl_3O\{Et_2PCH_2CH_2P(O)Et_2\}]$ forms from the oxidation by adventitious oxygen of the mixture produced in the reaction of HCl with $[Mo(N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$). The structure of this new complex was determined.

It has recently been shown by Berners-Price *et al.*[1] that the diphosphine $Et_2PCH_2CH_2PEt_2$ (depe) undergoes oxidation in $CDCl_3$ to produce the diphosphine mono-oxide and then the dioxide. This autoxidation was studied by ^{31}P n.m.r. spectroscopy. We have recently shown[2] that the reaction of $[Mo(N_2)_2(depe)_2]$ with anhydrous HCl in benzene does not lead to the isolation of any nitrogen-containing complex. In fact, the analysis of the molybdenum-containing material from this reaction showed that the product contained less than two molecules of depe per molybdenum atom. It was never properly characterized, and its ^1H n.m.r. spectrum suggested that it might be paramagnetic. Over a period of weeks, the solution of the brown material in $CDCl_3$ contained in the n.m.r. tube deposited green crystals, and *X*-ray structural analysis has shown that these crystals are of a diphosphine mono-oxide complex, *viz.* $[MoCl_3O\{Et_2PCH_2CH_2P(O)Et_2\}]$.

Experimental

A yellow-brown solid was obtained from the reaction of $[Mo(N_2)_2(depe)_2]$ with 10 molar equivalents of HCl in anhydrous benzene.[2] It could not be characterized by analysis, and its ^1H n.m.r. spectrum indicates that it is paramagnetic. The crystals of $[MoCl_3O\{Et_2PCH_2CH_2P(O)Et_2\}]$ which deposited from the solution in $CDCl_3$ presumably arise by reaction with adventitious oxygen, though the usual procedures to exclude dioxygen were observed.

Crystal Structure Analysis of $[MoCl_3O\{Et_2PCH_2CH_2P(O)Et_2\}]$.—*Crystal data.* $C_{10}H_{24}Cl_3MoO_2P_2$, $M = 440.5$, monoclinic, space group $P2_1/c$ (no. 14), $a = 8.768(5)$, $b = 15.054(3)$, $c = 13.975(4)$ Å, $\beta = 104.86(3)°$, $U = 1\,783.0$ Å^3, $Z = 4$, $D_c = 1.641$ g cm^{-3}, $F(000) = 892$, μ(Mo-K_α) = 13.4 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

The crystals were emerald-green, translucent cuboids. One, *ca.* 0.66 × 0.61 × 0.47 mm, was mounted in a glass capillary under dinitrogen. After preliminary photographic examination, the crystal was transferred to our Enraf-Nonius CAD4 diffractometer (with monochromated Mo-K_α radiation) for determination of accurate cell parameters (by refinement from the settings of 25 reflections with θ *ca.* 13.5°) and measurement of diffraction intensities (to $\theta_{max.} = 25°$). During processing, corrections were made for Lorentz polarization effects, absorption and, by Bayesian methods, to ensure no negative intensities.

3 140 Unique intensities [2883 reflections with $I > 2\sigma(I)$] were read into the SHELX system.[3] The structure was determined using the automated Patterson routines in SHELXS,[4] and refined by full-matrix least-squares methods in SHELX. Hydrogen atoms, located in difference maps, were refined independently with isotropic thermal parameters; all other atoms were refined anisotropically. After refinement to convergence ($R = 0.052$, $R' = 0.057$ for all data), a difference map showed a large peak (*ca.* 4 e Å^{-3}) at 1.0 Å from the Mo atom. This appears to be a molybdenum atom of a second, disordered molecule occupying almost the same region in the cell. Three Cl atoms and two O atoms of this disordered molecule were also identified: the $Et_2PCH_2CH_2PEt_2$ group appears common to the molecules in both orientations. The site occupancy ratio for the two molecules was refined to 0.91:0.09, and on further refinement (with the six extra atoms of the minor molecule allowed isotropic thermal parameters) convergence was reached with $R = 0.036$, $R' = 0.038$ for all data, weighted $w = \sigma_F^{-2}$.

A final difference map now showed one peak of 0.73 e Å^{-3} at 0.9 Å from the major Mo atom (almost opposite the minor Mo atom), and other peaks less than 0.4 e Å^{-3}. Atom co-ordinates for the molecule in both orientations are in Table 1, and principal molecular dimensions of the major component are in Table 2.

Scattering factor curves for neutral atoms were taken from ref. 5. Computer programs used in this analysis have been noted above and in Table 4 of ref. 6; they were run on the VAX 11/750 machine at the AFRC-IHR Littlehampton Laboratory (G.C.R.I.).

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

Results and Discussion

Description of Structure.—The molecule is disordered in the crystal in two orientations. Except for very minor shifts, the $Et_2PCH_2CH_2PEt_2$ group is common to both orientations; there is a pseudo-two-fold symmetry axis passing through the C(1)–C(2) bond (Figure), and the second orientation of the molecule is derived approximately from the first by rotation of the whole molecule about this axis. In the minor component the phosphine oxide oxygen atom O(2′) is thus attached to the phosphorus atom at (or very close to) the position of P(1).

In the minor component, present in only 9% of the sites in the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Final atomic co-ordinates (fractional × 10^4) with estimated standard deviations (e.s.d.s) in parentheses for $[MoCl_3O\{Et_2PCH_2CH_2P(O)Et_2\}]$

Atom	*x*	*y*	*z*	S.o.f.*
Mo	3 505.6(3)	5 591.1(2)	2 653.3(2)	0.9123
C(11)	6 182(5)	3 993(3)	4 193(3)	
C(12)	7 677(7)	3 431(4)	4 519(5)	
C(13)	7 680(4)	4 945(3)	2 863(3)	
C(14)	8 309(6)	5 669(3)	3 620(5)	
P(1)	5 810(1)	4 472.9(6)	2 958.0(7)	
C(1)	5 489(4)	3 546(3)	2 092(3)	
C(2)	3 891(4)	3 101(2)	1 956(3)	
P(2)	2 313.7(9)	3 743.5(5)	1 180.8(6)	
C(21)	2 382(5)	3 617(3)	−85(3)	
C(22)	2 316(7)	2 670(3)	−460(4)	
C(23)	492(4)	3 287(3)	1 312(3)	
C(24)	−943(5)	3 802(4)	752(4)	
O(2)	2 489(3)	4 713(2)	1 454(2)	0.9123
Cl(3)	2 235(2)	4 619(1)	3 567(1)	0.9123
Cl(4)	1 211(1)	6 502.7(7)	2 172.1(8)	0.9123
Cl(5)	4 626(1)	6 279.9(7)	1 465.0(8)	0.9123
O(6)	4 551(3)	6 143(2)	3 639(2)	0.9123
Mo(1′)	2 569(9)	5 404(4)	2 254(5)	0.0877
O(2′)	4 802(31)	4 954(19)	2 933(20)	0.0877
Cl(3′)	3 990(30)	5 994(19)	1 179(19)	0.0877
Cl(4′)	3 083(31)	6 594(19)	3 278(20)	0.0877
Cl(5′)	2 202(57)	4 719(32)	3 572(37)	0.0877
O(6′)	1 015(123)	5 661(65)	2 201(75)	0.0877

* Site occupancy factor, if different from 1.0.

Table 2. Bond dimensions (lengths in Å, angles in °) in the major component molecule of $[MoCl_3O\{Et_2PCH_2CH_2P(O)Et_2\}]$ with e.s.d.s in parentheses

(*a*) About the Mo atoms

Mo–P(1)	2.580(1)	Mo–Cl(4)	2.385(1)
Mo–O(2)	2.142(2)	Mo–Cl(5)	2.374(1)
Mo–Cl(3)	2.397(1)	Mo–O(6)	1.667(2)
P(1)–Mo–O(2)	83.0(1)	Cl(3)–Mo–Cl(5)	166.4(1)
P(1)–Mo–Cl(3)	88.0(1)	Cl(4)–Mo–Cl(5)	91.3(1)
O(2)–Mo–Cl(3)	83.3(1)	P(1)–Mo–O(6)	87.0(1)
P(1)–Mo–Cl(4)	172.0(1)	O(2)–Mo–O(6)	169.9(1)
O(2)–Mo–Cl(4)	89.0(1)	Cl(3)–Mo–O(6)	95.5(1)
Cl(3)–Mo–Cl(4)	91.6(1)	Cl(4)–Mo–O(6)	101.0(1)
P(1)–Mo–Cl(5)	87.3(1)	Cl(5)–Mo–O(6)	97.0(1)
O(2)–Mo–Cl(5)	83.5(1)		

(*b*) In the diphosphine oxide ligand

C(11)–C(12)	1.528(6)	C(2)–P(2)	1.804(3)
C(11)–P(1)	1.821(4)	P(2)–O(2)	1.506(2)
C(13)–C(14)	1.521(6)	P(2)–C(21)	1.795(4)
C(13)–P(1)	1.823(4)	P(2)–C(23)	1.791(3)
P(1)–C(1)	1.822(4)	C(21)–C(22)	1.514(6)
C(1)–C(2)	1.521(5)	C(23)–C(24)	1.513(6)
C(12)–C(11)–P(1)	115.7(4)	C(2)–P(2)–C(21)	108.7(2)
C(14)–C(13)–P(1)	113.7(3)	C(2)–P(2)–C(23)	107.4(2)
Mo–P(1)–C(11)	110.9(1)	C(21)–P(2)–C(23)	108.4(2)
Mo–P(1)–C(13)	114.5(2)	C(2)–P(2)–O(2)	110.8(1)
C(11)–P(1)–C(13)	106.2(2)	C(21)–P(2)–O(2)	109.0(2)
Mo–P(1)–C(1)	114.2(1)	C(23)–P(2)–O(2)	112.4(2)
C(11)–P(1)–C(1)	106.6(2)	P(2)–C(21)–C(22)	115.7(3)
C(13)–P(1)–C(1)	103.8(2)	P(2)–C(23)–C(24)	113.3(3)
P(1)–C(1)–C(2)	113.6(3)	Mo–O(2)–P(2)	142.3(1)
C(1)–C(2)–P(2)	112.2(3)		

(*c*) Torsion angle in diphosphine group

P(1)–C(1)–C(2)–P(2)	76.4(3)

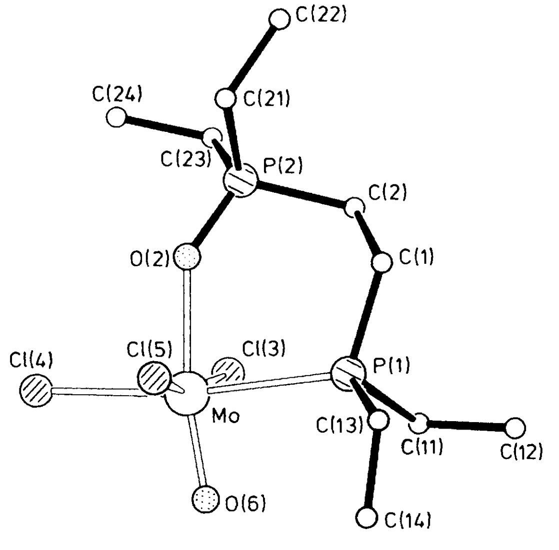

Figure. View of the major component molecule (with atomic numbering scheme) in crystals of $[MoCl_3O\{Et_2PCH_2CH_2P(O)Et_2\}]$

crystal, some of the atoms are not well defined and the bond dimensions are rather imprecise. The major molecule, however, is very well defined; in the diphosphine portions the hydrogen atoms were located and refined independently and satisfactorily. We shall therefore confine all further remarks to the major component.

The molecule forms a much distorted octahedral complex about the Mo atom. The oxo-ligand is *trans* to the phosphine oxide, and the bond dimensions clearly distinguish the multiply bonded terminal O atom, Mo–O(6) 1.667(2) Å, from the neutral oxygen donor atom, Mo–O(2) 2.142(2) Å. This *trans* alignment, with the weaker π-donor *trans* (and the halide and phosphorus ligands *cis*) to the terminal oxo-group, and these bond dimensions, are typical of monophosphine oxide oxomolybdenum complexes such as $[MoCl_3O(OPPh_3)_2]$,[7] *cis*-$[MoX_2O_2(OPPh_3)_2]$ (X = Cl or Br),[8] and $[MoCl_2(NH)O(OPEtPh_2)_2]$.[9]

The three Cl atoms are in a *meridional* arrangement, with Mo–Cl(5), *trans* to P(1), slightly shorter than the other, mutually *trans* Mo–Cl bonds. With P(1), the three Cl atoms form a virtually square equatorial plane. Typically, the Mo atom is displaced 0.21 Å out of this plane towards the oxo-ligand, O(6).

The dimensions of the diphosphine mono-oxide ligand are also as expected: the P–C bonds about P(1) [mean 1.822(1) Å] are slightly longer than those about P(2) [mean 1.797(4) Å], and the P(2)–O(2) bond length of 1.506(2) Å is close to values found in several monophosphine oxide complexes. The Mo–O–P angle in in these monophosphine oxides has been noted to have a wide range of values, from 137.1 to *ca.* 170(1)°;[7] our value of 142.3(1)° presumably reflects the requirement for chelate ring formation. In the only other reported example of a chelating diphosphine mono-oxide, $[RuCl_2(MePhPC_6H_4PPhMe)\{MePhPC_6H_4P(O)MePh\}]$, the Ru–O–P angle is 134.9(3)°;[10] here, the metal–O and O–P lengths are similar to ours, but the diphosphine group has a rigid *o*-phenylene P–C–C–P link and the Ru–P distance is shorter, at 2.346(2) Å.

One side of our molecule has a hydrophobic, hydrocarbon exterior, whilst the other side is bounded by chloride and oxide groups. All the principal intermolecular contacts, at slightly less than van der Waals distances, are between the C (and H) atoms of one molecule and the Cl or O atoms of the neighbour.

The oxidation of depe to yield the mono-, di-oxide, and other so far uncharacterized species in an n.m.r. tube in solution in $CDCl_3$ has been described.[1] It was suggested that phosphinites may be involved. Presumably the processes occurring in our n.m.r. tubes were similar, with the difference that we also had a complexing agent present. We have sought no evidence for other materials, but presumably under conditions of limited dioxygen access the mono-oxide is the first oxidation product. There is only one other structurally characterized complex of a diphosphine mono-oxide,[10] and the isolation of our product would appear to be a consequence of rather specific and unusual circumstances.

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