Reactions of Molybdenum Oxo-complexes with Substituted Hydrazines. Part 4.† The Preparation and Structure of an Anionic Molybdenum Oxo(diazene) Complex ‡

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The complexes $[MoCl(O)(P-P)_2][MoCl_3O(RCON_2Ph)]$ (R = Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, or Me; P–P = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH{=}CHPPh_2$) have been prepared by reactions of the hydrazines RCONHNHPh with $[\{MoCl_2O(P-P)\}_2]$ or $[MoCl_3O(P-P)]$ in refluxing methanol. The crystal and molecular structure of $[MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2][MoCl_3O(p\text{-}ClC_6H_4CON_2Ph)]$ has been determined by single-crystal *X*-ray diffraction methods. The complex crystallises in the triclinic system, space group $P\bar{1}$ with $a = 14.87(1)$, $b = 11.84(1)$, $c = 18.37(1)$ Å, $\alpha = 96.1(1)$, $\beta = 98.8(1)$, $\gamma = 97.2(1)°$, and $Z = 2$. The geometry of the oxo(diazene) anion is distorted octahedral with the chloride atoms in a *mer* configuration and the oxygen atom of the diazene ligand is *trans* to the oxo-function. The Mo–Cl distances are 2.410(6), 2.412(6), and 2.334(7) Å. The Mo=O terminal distance is 1.620(14) Å and the bond lengths within the diazene ligand indicate considerable delocalisation.

REACTIONS of hydrazines of the type RCONHNHR′ (R = alkyl or aryl, R′ = aryl) with oxo-complexes of molybdenum, rhenium, or osmium can give complexes of the diazene $RCON_2R'$.[1] In certain cases, cleavage of the N–N bond can occur to give alkyl or arylimido-complexes.[2,3] We now report that reaction of these hydrazines with molybdenum oxo-complexes containing ditertiary phosphines gives ionic complexes with an oxo(diazene) anion and a known molybdenum(IV) chloro-oxobis(ditertiary phosphine) cation.

TABLE 1

Complexes of the type $[MoCl(O)(P-P)_2][MoCl_3O(RCON_2R')]$

Complex [a]	Colour	*M* [b]	Analysis (%) [b] C	H	N	Cl	Conductivity [c] S cm² mol⁻¹
(1) $[A][MoCl_3O(PhCONNPh)]$	Red-brown	781	56.4	4.2	2.2	10.3	35.7
		(1 218)	(56.8)	(4.2)	(2.1)	(10.4)	
(2) $[A][MoCl_3O(p\text{-}MeOC_6H_4CONNPh)]$	Red-brown	683	56.7	4.5	2.1		32.3
		(1 402)	(56.5)	(4.3)	(2.0)		
(3) $[A][MoCl_3O(p\text{-}ClC_6H_4CONNPh)]$	Red		55.6	4.2	2.1		38.5
			(55.5)	(4.1)	(2.0)		
(4) $[A][MoCl_3O(PhCONNC_6H_4Cl\text{-}p)]$	Red		55.1	4.2	2.1	12.4	32.8
			(55.5)	(4.1)	(2.0)	(12.6)	
(5) $[A][MoCl_3O(MeCONNPh)]$	Red		54.5	4.4	2.1	11.7	35.6
			(54.9)	(4.3)	(2.1)	(10.8)	
(6) $[B][MoCl_3O(PhCONNPh)]$	Mauve		57.0	4.0	2.1		34.8
			(57.0)	(4.0)	(2.1)		

[a] $[A] = [MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[B] = [MoCl(O)(Ph_2PCH{=}CHPPh_2)_2]^+$. [b] Calculated values are given in parentheses. [c] In dichloromethane solution; values of *ca.* 40 S cm² mol⁻¹ have been reported for 1 : 1 electrolytes in solution.

RESULTS AND DISCUSSION

The complexes $[\{MoCl_2O(P-P)\}_2]$ [4] or $[MoCl_3O(P-P)]$ [4] (P–P = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH{=}CHPPh_2$) react with the hydrazines RCONHNHR′ (R = alkyl or aryl; R′ = aryl) in refluxing methanol to give the complexes $[MoCl(O)(P-P)_2][MoCl_3O(RCON_2R')]$ in 60—70% yield. The complexes prepared in this manner are summarised in Table 1, and are isolated as brown air-stable diamagnetic compounds. These are 1 : 1 electrolytes in solution, and molecular-weight determinations give values approximately half those calculated.

The complexes generally show two strong bands in their i.r. spectra (see Table 2) in the region 940—980 cm⁻¹ assigned to ν(Mo=O). Since the complex $[MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2]Cl$ has an i.r. band at 942 cm⁻¹ assigned to ν(Mo=O),[4] the bands at *ca.* 945 cm⁻¹ of the complexes in Table 1 are assigned to the cation. The observed bands at *ca.* 965 cm⁻¹ are then attributed to the oxo(diazene) anion. Complex (2) shows a strong i.r. band at 960 cm⁻¹ which may be due to the diazene ligand, obscuring the bands due to ν(Mo=O).

The ^1H n.m.r. spectrum of complex (2) in dichlorodeuteriomethane (Table 2) shows a singlet at 3.87 p.p.m. assigned to the methoxy-group. For this and the other complexes, broad multiplets between 7 and 8 p.p.m. and at *ca.* 2.90 p.p.m. are attributed to aryl groups and diphosphine methylene protons respectively.

Addition of sodium tetraphenylborate to an acetone solution of (1) gives a 45% yield of the known $[MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2][BPh_4]$ complex. Attempts to isolate anionic $[MoCl_3O(RCON_2R')]$ complexes by the addition of large cations were not successful.

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† Part 3, preceding paper.

‡ Bis[1,2-bis(diphenylphosphino)ethane]chloro(oxo)molybdenum(IV) trichloro(*N*′-*p*-chlorobenzoyl-*N*-phenyldiazene-*NO*)-oxomolybdate(IV).

TABLE 2

Spectroscopic data for the complexes $[MoCl(O)(P{-}P)_2][MoCl_3O(RCON_2R')]$

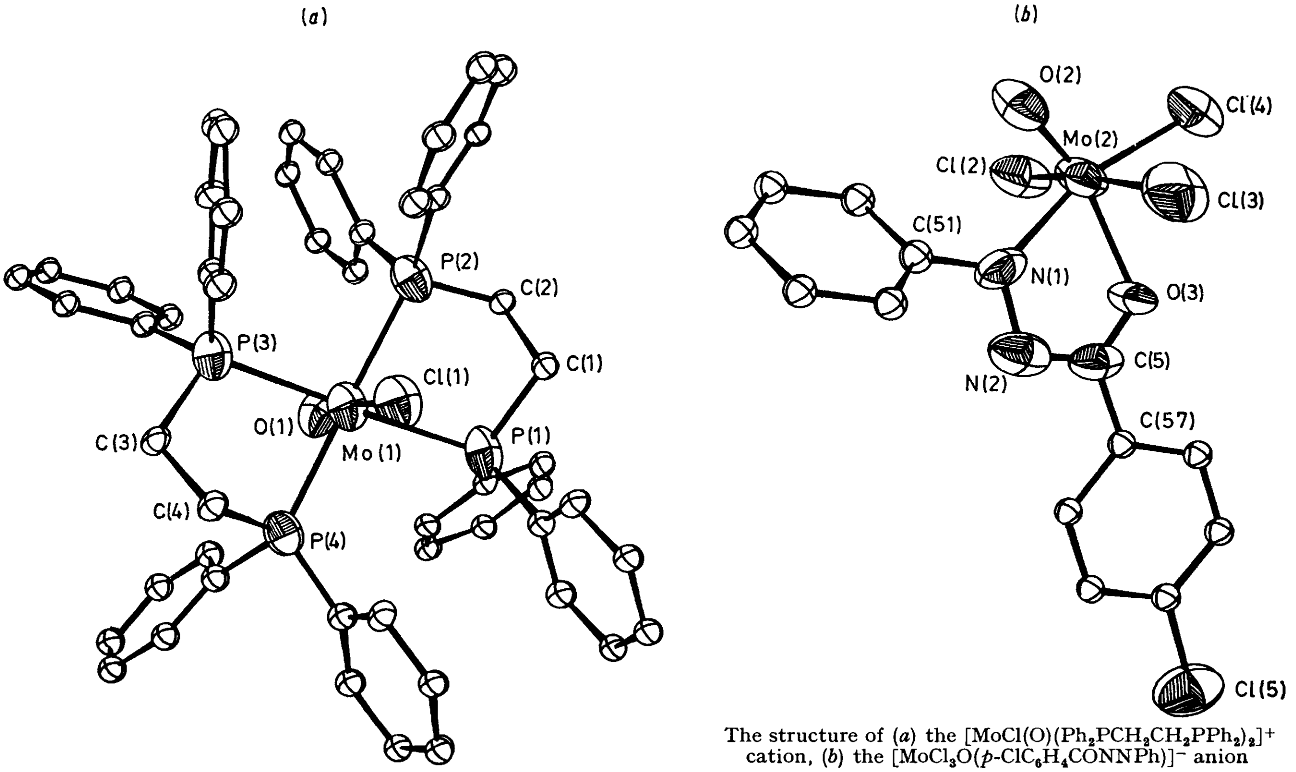
Complex	Infrared data (cm^{-1}) [a]		^{1}H N.m.r. data	
	ν(Mo=O)	Far-i.r.	δ/p.p.m.[b]	Assignment of protons
(1)	945, 971	284m, 322s, 343, 386m	2.90 (br, 8)	Methylene
			7.0—8.0 (m, 50)	Aryl
(2)		263m, 317s, 340s, 375m	2.90 (br, 8)	Methylene
			3.87 (s, 3)	Methoxy
			7.0—8.1 (m, s, 49)	Aryl
(3)	945, 970	302s, 347s, 383m		
(4)	945, 971	318s, 350s, 375m		
(5)	952, 965	317s, 342m, 375m	2.67 (s 3)	Acetyl
			2.90 (br, 8)	Methylene
			7.0—7.8 (m, 45)	Aryl
(6)	946, 966	318s, 348s, 372m		
$[MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2]Cl$	942	300s		

[a] As Nujol mulls. [b] In CD_2Cl_2 solutions relative to tetramethylsilane. Integrated values are given in parentheses; br = broad, m = multiplet, s = singlet.

The spectroscopic properties outlined above were not sufficient to distinguish between several possible structures, and accordingly an *X*-ray analysis of complex (3) was undertaken.

Crystal Structure.—This showed that the complex can be formulated as the ionic $[MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2]$-$[MoCl_3O(p\text{-}ClC_6H_4CONNPh)]$. The Figure [(*a*) and (*b*)] shows the structures of the two ions and important bond lengths and angles are given in Table 4. In both ions the metal atoms have octahedral co-ordination, with the three chloride ligands in the anion adopting a *mer* configuration and the oxygen atom of the chelating diazene ligand being *trans* to the oxo-function. The cation, in which the chlorine atom and oxo-group are *trans* to each other, has been identified previously in the compound $[MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2][ZnCl_3(OCMe_2)]$.[5] Bond lengths and angles found in our structure agree quite well with those found earlier.

Discussion of the anion structure is obviously limited by the lack of precision in parameters but a number of features are worthy of comment. The nature of the bonding in the molybdenum diazenido-heterocycle has been discussed in detail in a previous paper in this series.[3] Points of interest in these discussions have been the distribution of bond lengths in the chelate ring and its degree of planarity. In the present complex both of these aspects point towards a mode of bonding similar to that proposed for the complexes $[MoCl_2(NC_6H_4Me\text{-}p)$-$(p\text{-}MeC_6H_4N_2COPh)(PMe_2Ph)]$ [3] and $[MoCl(PhCON_2)$-$(PhCON_2H)(PMe_2Ph)_2]$ [6] since the ring is quite planar (maximum deviation of any atom is 0.03 Å) and the Mo–N bond is shorter than the Mo–O bond. In addition,



The structure of (*a*) the $[MoCl(O)(Ph_2PCH_2CH_2PPh_2)_2]^+$ cation, (*b*) the $[MoCl_3O(p\text{-}ClC_6H_4CONNPh)]^-$ anion

TABLE 3

Final positional parameters (× 10^4) with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Mo(1)	8 071(1)	0 930(1)	7 641(1)
Cl(1)	9 076(3)	−0 134(4)	8 447(3)
O(1)	7 310(7)	1 640(10)	7 139(7)
P(1)	6 808(3)	−0 050(4)	8 247(3)
P(2)	7 531(4)	−0 897(4)	6 715(3)
P(3)	9 507(3)	1 710(4)	7 150(3)
P(4)	8 792(4)	2 565(4)	8 665(3)
C(1)	6 546(13)	−1 544(16)	7 790(10)
C(2)	6 494(13)	−1 566(17)	6 946(10)
C(3)	10 229(13)	2 825(16)	7 881(10)
C(4)	10 051(13)	2 683(17)	8 653(11)
C(11)	5 730(10)	0 540(9)	8 024(8)
C(12)	4 885(10)	−0 166(9)	7 816(8)
C(13)	4 082(10)	0 317(9)	7 640(8)
C(14)	4 971(10)	2 211(9)	7 882(8)
C(15)	4 125(10)	1 505(9)	7 673(8)
C(16)	5 773(10)	1 728(9)	8 058(8)
C(17)	6 907(10)	−0 208(13)	9 229(8)
C(18)	7 497(10)	−0 945(13)	9 510(8)
C(19)	7 562(10)	−1 139(13)	10 250(8)
C(110)	7 038(10)	−0 596(13)	10 710(8)
C(111)	6 449(10)	0 141(13)	10 429(8)
C(112)	6 383(10)	0 335(13)	9 688(8)
C(21)	7 185(9)	−0 553(11)	5 769(7)
C(22)	6 477(9)	0 109(11)	5 645(7)
C(23)	6 219(9)	0 423(11)	4 940(7)
C(24)	6 668(9)	0 075(11)	4 360(7)
C(25)	7 376(9)	−0 587(11)	4 484(7)
C(26)	7 635(9)	−0 901(11)	5 189(7)
C(27)	8 185(7)	−2 082(11)	6 569(7)
C(28)	7 780(7)	−3 062(11)	6 082(7)
C(29)	8 257(7)	−3 997(11)	5 998(7)
C(210)	9 319(7)	−3 952(11)	6 401(7)
C(211)	9 544(7)	−2 973(11)	6 887(7)
C(212)	9 067(7)	−2 038(11)	6 971(7)
C(31)	10 255(8)	0 693(11)	6 935(6)
C(32)	10 116(8)	0 126(11)	6 212(6)
C(33)	10 649(8)	−0 720(11)	6 033(6)
C(34)	11 320(8)	−0 998(11)	6 576(6)
C(35)	11 458(8)	−0 431(11)	7 298(6)
C(36)	10 925(8)	0 414(11)	7 477(6)
C(37)	9 345(7)	2 440(11)	6 317(7)
C(38)	8 475(7)	2 403(11)	5 895(7)
C(39)	8 381(7)	2 908(11)	5 240(7)
C(310)	9 155(7)	3 449(11)	5 007(7)
C(311)	10 025(7)	3 485(11)	5 428(7)
C(312)	10 120(7)	2 981(11)	6 083(7)
C(41)	8 569(9)	3 994(10)	8 486(7)
C(42)	7 894(9)	4 205(10)	7 921(7)
C(43)	7 782(9)	5 332(10)	7 814(7)
C(44)	8 345(9)	6 247(10)	8 272(7)
C(45)	9 021(9)	6 036(10)	8 836(7)
C(46)	9 133(9)	4 910(10)	8 943(7)
C(47)	8 665(9)	2 515(11)	9 618(8)
C(48)	8 110(9)	3 219(11)	9 941(8)
C(49)	8 010(9)	3 185(11)	10 682(8)
C(410)	8 467(9)	2 447(11)	11 099(8)
C(411)	9 022(9)	1 743(11)	10 777(8)
C(412)	9 121(9)	1 777(11)	10 036(8)
Mo(2)	6 967(1)	4 664(1)	3 237(1)
Cl(2)	7 515(4)	6 495(5)	2 883(3)
Cl(3)	6 455(4)	2 681(5)	3 338(4)
Cl(4)	8 314(4)	4 071(6)	2 925(4)
Cl(5)	3 241(5)	3 576(6)	−1 072(3)
O(2)	7 139(9)	5 059(12)	4 125(8)
O(3)	6 256(9)	4 195(11)	2 109(7)
N(1)	5 674(11)	5 071(12)	3 178(9)
N(2)	5 046(11)	4 793(14)	2 527(12)
C(5)	5 441(17)	4 342(17)	1 973(13)
C(51)	5 311(9)	5 619(10)	3 756(8)
C(52)	4 462(9)	5 144(10)	3 906(8)
C(53)	4 086(9)	5 678(10)	4 479(8)
C(54)	4 559(9)	6 686(10)	4 902(8)
C(55)	5 408(9)	7 160(10)	4 751(8)
C(56)	5 783(9)	6 627(10)	4 178(8)

TABLE 3 (*Continued*)

Atom	*X*	*Y*	*Z*
C(57)	4 872(9)	4 059(12)	1 258(7)
C(58)	4 003(9)	4 402(12)	1 133(7)
C(59)	3 490(9)	4 227(12)	0 419(7)
C(510)	3 845(9)	3 710(12)	−0 172(7)
C(511)	4 713(9)	3 367(12)	−0 048(7)
C(512)	5 227(9)	3 542(12)	0 667(7)

TABLE 4

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) The cation			
Mo(1)–Cl(1)	2.492(5)	Mo(1)–P(2)	2.565(5)
Mo(1)–O(1)	1.708(12)	Mo(1)–P(3)	2.549(6)
Mo(1)–P(1)	2.546(6)	Mo(1)–P(4)	2.554(5)
O(1)–Mo(1)–Cl(1)	174.9(5)	P(2)–Mo(1)–P(3)	99.7(2)
O(1)–Mo(1)–P(1)	91.7(4)	P(4)–Mo(1)–P(3)	78.7(2)
Cl(1)–Mo(1)–P(1)	83.4(2)	P(4)–Mo(1)–P(1)	100.6(2)
P(2)–Mo(1)–P(1)	79.5(2)		
P(1)–C(1)	1.843(18)	P(4)–C(4)	1.862(21)
P(2)–C(2)	1.774(20)	C(1)–C(2)	1.538(27)
P(3)–C(3)	1.878(17)	C(3)–C(4)	1.506(29)
P(1)–C(1)–C(2)	109.9(1.3)	P(3)–C(3)–C(4)	113.2(1.3)
P(2)–C(2)–C(1)	111.9(1.2)	P(4)–C(4)–C(13)	109.5(1.3)
(*b*) The anion			
Mo(2)–Cl(2)	2.410(6)	Mo(2)–O(2)	1.620(14)
Mo(2)–Cl(3)	2.412(6)	Mo(2)–O(3)	2.159(12)
Mo(2)–Cl(4)	2.335(7)	Mo(2)–N(1)	2.030(17)
Cl(2)–Mo(2)–Cl(3)	168.2(2)	Cl(3)–Mo(2)–O(2)	94.2(5)
Cl(2)–Mo(2)–Cl(4)	86.3(2)	Cl(4)–Mo(2)–O(2)	108.0(5)
Cl(3)–Mo(2)–Cl(4)	87.1(2)	O(2)–Mo(2)–O(3)	160.0(6)
Cl(2)–Mo(2)–O(2)	97.0(5)		
O(3)–C(5)	1.237(29)	N(2)–N(1)	1.380(24)
C(5)–N(2)	1.346(33)		
Mo(2)–N(1)–N(2)	120.8(1.3)	N(2)–C(5)–O(3)	124.4(2.1)
N(1)–N(2)–C(5)	111.0(1.7)	C(5)–O(3)–Mo(2)	117.6(1.4)
N(1)–C(51)	1.399(22)	Cl(5)–C(510)	1.737(13)
C(5)–C(57)	1.432(25)		

the O–C, C–N, and N–N bond lengths also indicate extensive delocalisation.

Other aspects of the anion structure follow expected patterns. The three chlorine atoms *cis* to the oxo-function are all bent away from the high electron density in the Mo=O bond. The Mo–Cl(2) and Mo–Cl(3) bond lengths compare very well with similar bonds in the compounds mentioned above, but the short Mo–Cl(4) bond length of 2.335 Å is somewhat perplexing, since no significant shortening occurs in the tolylimido-complex [3] where a similar ligand arrangement occurs.

EXPERIMENTAL

Preparation of Complexes.—All reactions were carried out using dry distilled solvents, but recrystallisations were performed using reagent grade solvents. The hydrazines used were prepared as described previously.[3] The i.r. spectra were recorded on Pye–Unicam SP 1200 and 2000 spectrophotometers, and a JEOL PS 100 instrument used to obtain ^{1}H n.m.r. spectra in $CDCl_3$ or CD_2Cl_2 with tetramethylsilane as internal standard. Elemental analyses were performed by Mr. A. G. Olney at the University of Sussex.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*oxo*)*molybdenum*(IV) (N′-*benzoyl*-N-*phenyldiazene*-NO)*trichloro*(*oxo*)-*molybdate*(IV), (1). [1,2-Bis(diphenylphosphino)ethane]trichloro(oxo)molybdenum(V) (0.50 g, 9.1×10^{-4} mol) and 1-benzoyl-2-phenylhydrazine (0.50 g, 2.4×10^{-3} mol) were heated under reflux in methanol (40 cm^3) for 0.5 h to give a clear red solution which deposited the *complex* as brown crystals on cooling. These were recrystallised as red-brown needles from dichloromethane–hexane (0.23 g, 46.5%). Complex (1) was also prepared similarly in 57% yield starting from $[\{MoCl_2O(Ph_2PCH_2CH_2PPh_2)_2\}_2]$.

The following complexes were prepared analogously in similar yields: *bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*oxo*)*molybdenum*(IV) *trichloro*(N′-p-*methoxybenzoyl*-N-*phenyl diazene*-NO)*oxomolybdate*(IV), (2); *bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*oxo*)*molybdenum*(IV) *trichloro*(N′-p-*chlorobenzoyl*-N-*phenyldiazene*-NO)*oxomolybdate*(IV), (3); *bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*oxo*)*molybdenum*(IV) (N′-*benzoyl*-N-p-*chlorophenyldiazene*-NO)*trichloro*(*oxo*)*molybdate*(IV), (4); *bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*oxo*)*molybdenum*(IV) (N′-*acetyl*-N-*phenyldiazene*-NO)*trichloro*(*oxo*)*molybdate*(IV), (5); *bis*[1,2-*bis*(*diphenylphosphino*)*ethylene*]*chloro*(*oxo*)*molybdenum*(IV) (N′-*benzoyl*-N-*phenyldiazene*-NO)*trichloro*(*oxo*)*molybdate*(IV), (6).

Crystallography.—*Crystal data*. $C_{65}H_{57}Cl_5Mo_2N_2O_3P_4$, $M = 1\,407.1$, Triclinic, $a = 14.87(1)$, $b = 11.84(1)$, $c = 18.37(1)$ Å, $\alpha = 96.1(1)$, $\beta = 98.8(1)$, $\gamma = 97.2(1)°$, $U = 3\,144.9$ Å^3, $D_m = 1.35$ g cm^{-3}, $Z = 2$, $D_c = 1.40$ g cm^{-3}, $\mu(Cu\text{-}K_\alpha) = 63.1$ cm^{-1}, space group $P\bar{1}$.

A tabular crystal of dimensions *ca.* $0.65 \times 0.35 \times 0.07$ mm was set with a^* parallel to the ϕ axis of a GEXRD6 manual diffractometer. Cell dimensions were determined by careful measurement of axial 2θ values and interaxial angles (in ϕ and ψ). Intensity data were collected by the stationary-crystal–stationary counter technique in a manner described previously.[3,6] Of the 5 024 reflections measured within the range $1.5 < \theta < 45°$, 3 918 were considered significant $[I > 2.6\sigma(I)]$. These data were corrected for Lorentz polarisation effects and for absorption. The structure was solved by standard heavy-atom methods and refined by least squares [7] to a final R value of 0.092 with the Mo, Cl, P, and O(oxo) atoms assigned anisotropic thermal parameters and all other atoms treated isotropically. Phenyl rings were refined as rigid groups with identical geometry. The atomic scattering factor for Mo was taken from ref. 8, corrected for anomalous dispersion using f' and f'' values from ref. 9, whilst scattering factors for C, N, O, P, and Cl were taken from ref. 10. Final atomic co-ordinates are given in Table 3. Full lists of bond lengths and angles, observed and calculated structure factors, and thermal parameters have been deposited in Supplementary Publication No. SUP 22548 (25 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

REFERENCES

[1] J. Chatt, J. R. Dilworth, and T. Ito, *J.C.S. Dalton*, 1975, 2348.

[2] J. Chatt, J. R.Dilworth, and G. J. Leigh, *J. Chem. Soc.* (*A*), 1970, 2239.

[3] M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, S. A. A. Jayaweera, and A. Quick, *J.C.S. Dalton*, 1979, 914.

[4] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1971, 2356.

[5] V. C. Adam, U. A. Gregory, and B. T. Kilbourn, *Chem. Comm.*, 1970, 1400.

[6] A. V. Butcher, J. Chatt, J. R. Dilworth, G. J. Leigh, M. B. Hursthouse, S. A. A. Jayaweera, and A. Quick, *J.C.S. Dalton*, 1979, 921.

[7] SHELX-76 Crystallographic Calculations Program, G. M. Sheldrick, University of Cambridge.

[8] P. A. Doyle and P. S. Turners, *Acta Cryst.*, 1968, **A24**, 390.

[9] D. T. Cromer and P. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.