

Reactions of Molybdenum Oxo-complexes with Substituted Hydrazines. Part 1. The Preparation of Molybdenum Alkyl- and Aryl-imido-complexes; the Crystal and Molecular Structure of (*N*-Benzoyl-*N'*-*p*-tolyl-diazene-*N'O*)dichloro(dimethylphenylphosphine)(*p*-tolylimido)molybdenum

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The molybdenum(IV) oxo-complexes $[\text{MoOCl}_2(\text{PR}'_3)_3]$ ($\text{PR}'_3 = \text{PMe}_2\text{Ph}$ or PEt_2Ph) react with the substituted hydrazines $\text{RCONHNHR}'$ ($\text{R} = \text{Ph}$, *p*- ClC_6H_4 , *p*- MeC_6H_4 , *p*- MeOC_6H_4 , Et, Prⁿ, Prⁱ, or CH_2Ph ; $\text{R}' = \text{Ph}$, *p*- ClC_6H_4 , *p*- MeOC_6H_4 , 1- C_{10}H_7 , or Me) to give the imido-complexes $[\text{MoCl}_2(\text{NR}')(\text{R}'\text{N}_2\text{COR}')(\text{PR}'_3)]$. The crystal and molecular structure of the title complex has been determined from single-crystal X-ray diffractometer data. The crystals are monoclinic with $a = 8.995$, $b = 19.090$, $c = 17.860$ Å, $\beta = 104.15^\circ$, space group $P2_1/c$, and $Z = 4$. The structure has been solved by Patterson and Fourier methods, and least-squares refinement using 2 279 independent observed reflections has reached $R = 0.066$. The co-ordination geometry is distorted octahedral. The metal-diazene chelate system is quite planar and bond lengths indicate considerable delocalisation within the chelate ring. In particular, the Mo-N length [1.984(8) Å] is shorter than the Mo-O length [2.110(7) Å] and this is taken to indicate partial double-bond character in the Mo-N bond. The remaining metal-ligand distances are Mo-N(imido) 1.726(9), Mo-Cl 2.393(4) (*trans* to P) and 2.406(3) (*trans* to N in chelate ring), and Mo-P 2.528(4) Å.

THE reactions of substituted hydrazines with oxo-complexes of rhenium can give diazenido-,¹ imido-,² or nitrido-complexes³ depending on the hydrazine and reaction conditions. We now report the full details^{4,5} of the preparation and properties of a series of molybdenum aryl- and alkyl-imido-complexes obtained by the reaction of disubstituted hydrazines with molybdenum(IV) oxo-complexes in refluxing methanol.

RESULTS AND DISCUSSION

The alkyl- and aryl-imido-complexes shown in Table 1 were prepared by the reaction of the hydrazines $\text{RCONHNHR}'$ ($\text{R} = \text{R}' = \text{alkyl or aryl}$) with the complexes $[\text{MoOCl}_2(\text{PR}'_3)_3]$ ($\text{PR}'_3 = \text{PMe}_2\text{Ph}$ or PEt_2Ph)⁶ in refluxing methanol. The *N*-alkyl-*N'*-aroylhydrazines were prepared by the catalytic hydrogenation of aroylhydrazones in acidic ethanol. When $\text{R} = \text{Me}$, methanol

TABLE 1
Complexes of the type $[\text{MoCl}_2(\text{NR})(\text{RN}_2\text{COR}')(\text{PR}'_3)]$

	Complex			M.p. ^a (θ _c /°C)	Analysis ^b (%)				<i>M</i> ^b	Far-i.r. spectrum (cm ⁻¹) ^c
	R	R'	PR' ₃		C	H	N	Cl		
(1)	Ph	Ph	PMe ₂ Ph	179—181	53.4 (53.4)	4.6 (4.6)	7.0 (7.0)	12.8 (11.7)	672 (600)	345s, 330 (sh), 308m, 290s
(2)	Ph	<i>p</i> -ClC ₆ H ₄	PMe ₂ Ph	295—297	50.6 (50.6)	4.0 (4.0)	6.6 (6.5)	16.8 (16.5)	638 (641)	345s, 330 (sh), 295s
(3)	Ph	<i>p</i> -MeOC ₆ H ₄	PMe ₂ Ph	190—195	52.4 (52.7)	4.6 (4.4)	6.6 (6.6)		714 (638)	342s, 330 (sh), 285s
(4)	Ph	Ph	PEt ₂ Ph	168—172	53.9 (54.8)	4.8 (4.7)	6.6 (6.6)		666 (634)	345s, 290s
(5)	<i>p</i> -ClC ₆ H ₄	Ph	PMe ₂ Ph	206—209	47.5 (47.7)	3.8 (3.6)	6.1 (6.2)		769 (674)	352s, 325s, 315 (sh), 297s
(6)	<i>p</i> -MeC ₆ H ₄	Ph	PMe ₂ Ph	218—223	54.5 (54.8)	4.8 (4.9)	6.6 (6.6)		739 (634)	350m, 335s, 320s, 290s
(7)	<i>p</i> -MeOC ₆ H ₄	Ph	PMe ₂ Ph	205—208	52.9 (52.9)	4.7 (4.7)	6.3 (6.4)		667 (666)	380m, 365s, 333 (sh), 325s, 308m, 285s
(8)	1-C ₁₀ H ₇	Ph	PMe ₂ Ph	213—216	59.5 (59.4)	4.3 (4.4)	5.9 (5.9)		714 (706)	340 (sh), 330s, 285s
(9)	Ph	1-C ₁₀ H ₇	PMe ₂ Ph	180—183	56.7 (56.7)	4.4 (4.3)	6.5 (6.4)		714 (656)	340s, 325 (sh), 290s
(10)	Et	Ph	PMe ₂ Ph	170—172	45.0 (44.7)	5.0 (5.1)	7.1 (8.2)			229m, 254s, 297m
(11)	Pr ⁿ	Ph	PMe ₂ Ph	178—180	46.8 (46.8)	6.0 (5.6)	7.8 (7.8)		518 (538)	229m, 254s, 293m
(12)	Pr ⁱ	Ph	PMe ₂ Ph	180—182	46.8 (46.8)	6.0 (5.6)	7.8 (7.8)		504 (538)	230m, 254s, 293m, 295m
(13)	CH ₂ Ph	Ph	PMe ₂ Ph	147—149	54.9 (55.6)	4.7 (5.0)	6.6 (6.5)		593 (634)	229m, 254s, 286m, 315m
(14)	<i>p</i> -MeC ₆ H ₄	Me	PMe ₂ Ph		50.7 (50.0)	5.2 (4.9)	7.1 (7.1)			

^a With decomposition. ^b Calculated values are given in parentheses. ^c Tentative assignments to $\nu(\text{Mo-Cl})$ are in italics.

TABLE 2
Hydrogen-1 n.m.r. spectra recorded at 100 Hz in CDCl₃ solution

Complex	Resonance (p.p.m.)	Coupling constants (Hz)	Assignments
(1)	1.72 (d, 3), 1.90 (d, 3) <i>ca.</i> 7.3 (m)	[³ J(HCCP)] 8.5	Me of PMe ₂ Ph split by P Ph protons
(3)	1.72 (d, 3), 1.91 (d, 3) 3.91 (s, 3) <i>ca.</i> 7.3 (m)	[³ J(HCCP)] 8.0	Me of PMe ₂ Ph split by P Me of <i>p</i> -MeO Ph protons
(6)	1.72 (d, 3), 1.38 (t, 3) 1.68 (d, 3), 1.94 (d, 3) 3.9 (m), 4.0 (m), 4.6 (m, 4) 7.4 (m), 8.1 (m)	[³ J(HCCP)] 8.2	Me of PMe ₂ Ph split by P Me of <i>p</i> -Me Ph protons
(7)	1.68 (d, 3), 1.80 (d, 3) 3.68 (s, 3), 3.75 (s, 3) <i>ca.</i> 7.3 (m)	[³ J(HCCP)] 7.1	Me of PMe ₂ Ph split by P Me of <i>p</i> -MeO Ph protons
(10)	1.35 (t, 3), 1.38 (t, 3) 1.68 (d, 3), 1.94 (d, 3) 3.9 (m), 4.0 (m), 4.6 (m, 4) 7.4 (m), 8.1 (m)	[³ J(HCCP)] 6.5 [³ J(HCCP)] 10.5	Me of Et Me of PMe ₂ Ph split by P CH ₂ of Et Ph protons
(11)	1.00 (t, 3), 1.13 (t, 3) 1.8 (m), 2.0 (m, 4) 3.8 (m), 4.0 (m), 4.6 (m, 4) 7.5 (m), 8.1 (m)	[³ J(HCCH)] 7.0	Me of Pr ⁿ Me of PMe ₂ Ph split by P and β-CH ₂ of Pr ⁿ α-CH ₂ of Pr ⁿ Ph protons
(12)	0.8–1.9 (m, 12) 1.80 (d, 3), 2.03 (d, 3) 4.5 (m), 5.2 (m, 3) 7.5 (m), 8.1 (m, 10)	[³ J(HCCP)] 9.0	Me of Pr ⁱ Me of PMe ₂ Ph split by P CH of Pr ⁱ Ph protons
(13)	1.49 (d, 3), 1.66 (d, 3) 5.09 (d, 1), 5.20 (d, 1) 4.88 (d), 5.03 (d, 1) 5.56 (d), 5.68 (d, 1) 7.5 (m), 8.1 (m, 15)	[³ J(HCCP)] 9.8 [² J(HCH)] 11.0 [² J(CHNMoP)] 13.5 [⁴ J(HCNMoP)] 3.5	Me of PMe ₂ Ph split by P Inequivalent CH ₂ of diazene CH ₂ Ph split by H Inequivalent CH ₂ of imide CH ₂ Ph split by H and P Ph protons
(14)	1.70 (d, 3), 1.86 (d, 3) 2.34 (s, 3), 2.38 (s, 3) 2.66 (s, 3) 6.2–7.6 (m)	[³ J(HCCP)] 9.5	Me of PMe ₂ Ph split by P Me of <i>p</i> -Me Me of diazene COMe Ph protons

t = Triplet, d = doublet, s = singlet; integrated ratios are given in parentheses.

could not be used as a solvent to prepare the alkylimido-complexes, presumably due to solvolysis of the acetyl group. However, the arylimido-complexes with the *N*-aryl-*N'*-acetyldiazene ligand were prepared in reasonable yield in refluxing toluene.

Complexes (1)–(14) of Table 1 are red or orange air-stable crystalline solids which are monomers and non-electrolytes in 1,2-dichloroethane solution. The i.r. spectra of the complexes show no bands assignable to $\nu(\text{N-H})$, $\nu(\text{C=O})$, or $\nu(\text{N=N})$, suggesting that the PhCON₂-Ph ligand is bound *via* the carbonyl group. The far-i.r. spectra are also summarised in Table 1. Two i.r.-active metal-halogen stretching vibrations would be expected for complexes of this symmetry, and two strong bands at *ca.* 340 and 290 cm⁻¹ appear in the spectra of the arylimido-complexes. These are tentatively assigned to $\nu(\text{Mo-Cl})$. The spectra of the alkylimido-complexes show only one strong band in this region, and the two M-Cl stretching vibrations may be accidentally degenerate, or the chlorine atoms arranged mutually *trans*.

Hydrogen-1 N.M.R. Spectra.—The ¹H n.m.r. spectra of some of the complexes are summarised in Table 2. Complex (3) shows two singlets at 3.70 and 3.78 p.p.m. assigned to the *p*-methoxy-groups of the imido-phenyl and the phenyl attached to the diazene ligand nitrogen adjacent to the metal respectively. The methyl groups of the tertiary phosphine ligands appear as a pair of doublets at 1.57 and 1.84 p.p.m., due to splitting by phosphorus and inequivalence imposed by the low overall symmetry of the complex. All the complexes in Table 2 give similar patterns for their phosphine

methyl groups. The protons of the aryl groups of the imido-, diazene, and tertiary phosphine groups appear as a broad complex multiplet in the 7–8 p.p.m. region.

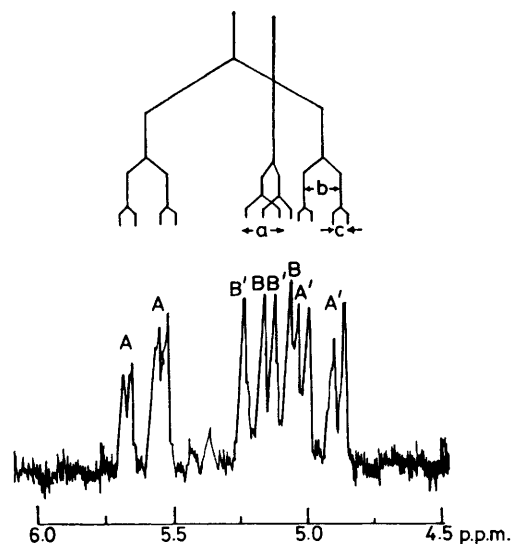


FIGURE 1 Part of the ¹H n.m.r. spectrum of [MoCl₂(NCH₂Ph)(PhCH₂N₂COPh)(PMe₂Ph)] (13): $a = |^2J(\text{HCH})| = 11$, $b = |^2J(\text{HCH})| = 13.2$, and $c = |^4J(\text{HCNMoP})| = 3.5$ Hz

Part of the spectrum of [MoCl₂(NCH₂Ph)(PhCH₂N₂-COPh)(PMe₂Ph)] (13) is shown in Figure 1. The methylene protons of the benzylimido-ligand are both inequivalent and split by phosphorus, appearing as the two pairs of doublets AA and A'A'. An analogous coupling

of the protons of an alkylimido-ligand to phosphorus was observed in the spectrum of $[\text{ReCl}_3(\text{NMe})(\text{PEt}_2\text{Ph})_2]$.² The methylene protons of the diazene benzyl group are inequivalent but not split by phosphorus and appear as the two doublets B and B'. The spectrum of complex (10) shows an analogous pattern, the methylene protons of the ethylimido-group appearing as two multiplets at *ca.* 3.9 and 4.6 p.p.m. and the methylene protons of the diazene ethyl group as a multiplet at *ca.* 4.0 p.p.m. There is no phosphorus splitting for the methyl protons of the ethylimido-ligand and the methyl protons of both ethyl groups appear as triplets at 1.35 and 1.38 p.p.m. None of the complexes studied shows the anomalous ¹H n.m.r. spectra observed for the diazene protons of the complexes $[\text{OsCl}_2(\text{R}'\text{N}_2\text{COR})(\text{PPh}_3)_2]$.⁷

The rhenium alkylimido-complexes $[\text{ReCl}_3(\text{NMe})(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PEt_2Ph , or PPh_3) react with pyridine (py) to give the methyleneamido-complexes $[\text{ReCl}_2(\text{N}=\text{CH}_2)(\text{py})(\text{PR}_3)_2]$.⁸ Although the molybdenum alkylimido-complexes reacted with base, the products could not be characterised.

As part of our systematic structural investigations of complexes with molybdenum-nitrogen multiple bonds we have determined the structure of the complex $[\text{MoCl}_2(\text{NC}_6\text{H}_4\text{Me-}p)(p\text{-MeC}_6\text{H}_4\text{N}_2\text{COPh})(\text{PMe}_2\text{Ph})]$.

The Structure of $[\text{MoCl}_2(\text{NC}_6\text{H}_4\text{Me-}p)(p\text{-MeC}_6\text{H}_4\text{N}_2\text{COPh})(\text{PMe}_2\text{Ph})]$.—The structure analysis has confirmed the presence in the molecule of both imido and chelating diazene ligands. A diagram of the molecule, in which the metal has a distorted octahedral co-ordination, is given

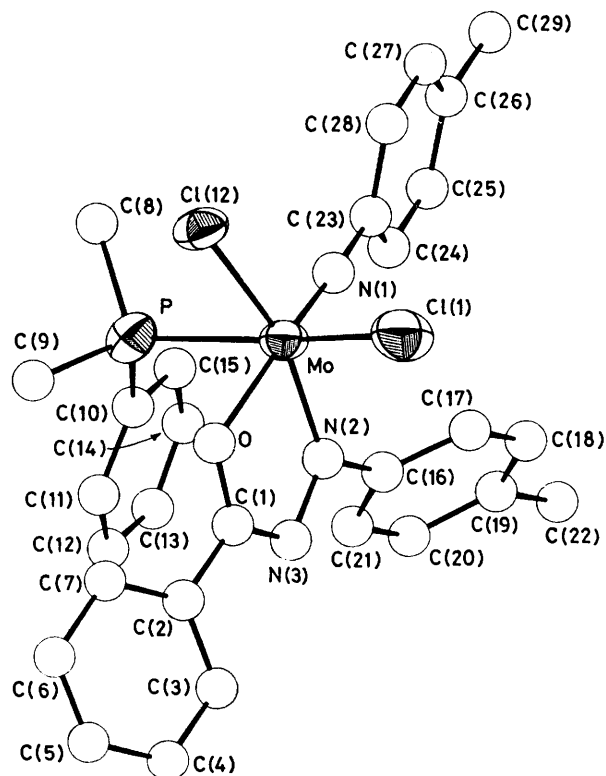


FIGURE 2 A single molecule of $[\text{MoCl}_2(\text{NC}_6\text{H}_4\text{Me-}p)(p\text{-MeC}_6\text{H}_4\text{N}_2\text{COPh})(\text{PMe}_2\text{Ph})]$

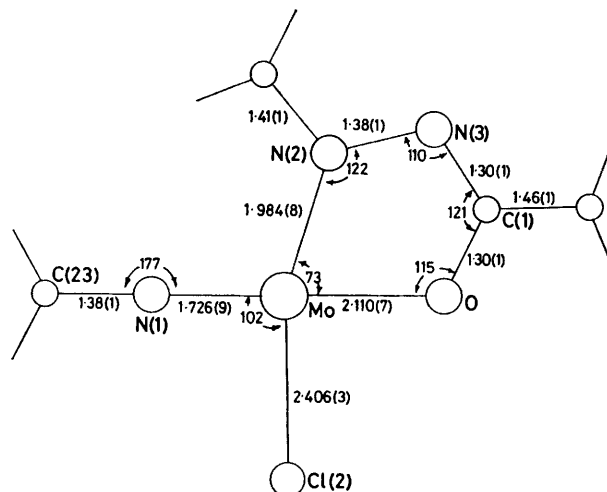


FIGURE 3 Bond lengths and angles in the chelate ring and imido-ligand

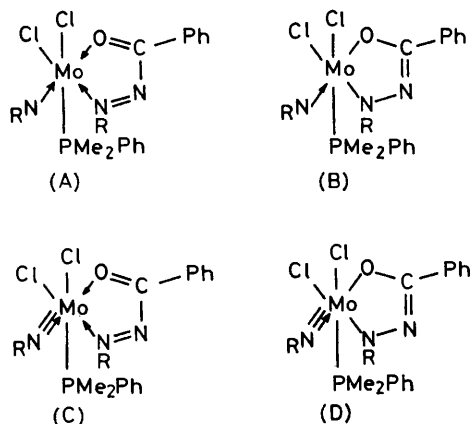
in Figure 2.⁹ Bond lengths and angles in the chelate ring and imido-ligand are given in Figure 3; further values relating to the central part of the molecule are listed in Table 2, whilst parameters for the phenyl rings have been deposited as a Supplementary publication.

Chatt and Dilworth have suggested⁵ that this and related complexes may be formulated as arylnitrene derivatives of Mo^{II} (A) or Mo^{IV} (B) or arylimido-derivatives of Mo^{IV} (C) or Mo^{VI} (D), all of which may be regarded as canonical forms of the true structure. The nitrene and imido-representations are merely formalisms, since they lead to the same result in terms of both the Mo-N bond order and spin pairing. In the nitrene representation the initial $\text{N} \rightarrow \text{Mo}$ σ bond can be considered to be reinforced by π interactions between the two unpaired *p* electrons on the nitrogen atom and the two unpaired *t*_{2g} electrons present in both the Mo^{II} (*d*⁴) and Mo^{IV} (*d*²) cases. In the imido-representation, the formal σ - π double bond is reinforced by π donation from the nitrogen lone pair. Thus, in each case the Mo-N link is considered to be a triple bond, and in terms of electron counting the ligand is a four-electron donor.

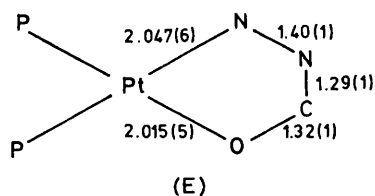
It is relevant to note here that this $\text{Mo} \equiv \text{N}$ bond is longer than the formal $\text{Mo} \equiv \text{N}$ bond found for some nitrido-complexes.⁴ Whilst this might be expected, it contrasts with results obtained for some similar rhenium species where Re-N bonds of the type $\text{Re} \equiv \text{N-R}^{10}$ have been found to be shorter than or equal to bonds of the type $\text{Re} \equiv \text{N}$.¹¹ This has been further discussed¹² and to some extent discounted, but the whole subject is rather clouded by the fact that in some cases different metal co-ordination numbers are involved.

In view of the practical equivalence of the nitrene and imido-representations, the mode of bonding of the diazene ligand can be discussed using only one of them, and since it is more conventional to consider imido-ligands we shall discuss structures (C) and (D). Examination of the bond lengths in the chelate ring (Figure 3) reveals that

the ligand has a resonance structure, in keeping with results from studies of similar ligands.^{13,14} Of these studies, the structure analysis of the complex $[\text{Pt}(\text{PhCON}_2\text{COPh})(\text{PPh}_3)_2]\cdot\text{EtOH}$ ¹⁴ is most significant



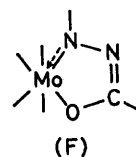
since the ligand is comparable to that in the present study. Bond lengths in the chelate ring of the platinum complex are shown in (E). Comparison of the N-N,



N-C, and C-O distances here with those in Figure 3 shows that, although the differences are only just significant, there seems to be a systematic indication that in our molybdenum complex the neutral form of the ligand makes a larger contribution to the overall structure than it does in the platinum complex. A possible explanation for this could be that adoption of structure (C) would give the molybdenum atom an 18-electron configuration, whereas structure (D) produces only a 16-electron configuration. A similar situation occurs with the platinum complex where the choice lies between a Pt^0 or a Pt^{II} representation. Sixteen-electron platinum(II) configurations are quite common and since this complex has a square-planar co-ordination geometry this must be the case here. The adoption of this geometry indicates a clear-cut choice of the platinum(II) configuration since a platinum(0) system would have tetrahedral co-ordination. The ligand is therefore essentially frozen out in a 2- form and so the bond lengths in the ligand provide a useful reference set for comparison with other systems where the metal oxidation state and ligand electronic structure are less well defined, as in the present molybdenum complex.

In the present molybdenum complex the situation is more complicated by the fact that an 18-electron configuration could also be obtained if structure (D) is modified to include a $p_\pi-d_\pi$ interaction involving the lone pair formally sited on the molybdenum-bonded

nitrogen atom, as in (F). The Mo-N and Mo-O bond lengths actually lend some support to this interpretation also. Whilst it is difficult to comment on the absolute values of the lengths (see later) it is significant that in this complex the Mo-N bond is shorter than the Mo-O bond. This is the opposite effect to that found in the platinum complex [see (E)] and the complex $[\text{Re}(\text{Me}_2\text{CNNCO-Ph})\text{Cl}_2\text{O}(\text{PPh}_3)]$.¹⁴ Another possibility is that the Mo-O bond is lengthened due to the *trans* influence of the multiply bonded imide function. However, since the more strongly bound oxide function in the rhenium complex¹⁴ does not seem to influence the Re-O bond *trans* to it we tend to favour the first idea, that in the present complex the M-N bond is indeed shortened by a contribution to the overall structure from the form (F).



It is seen therefore that the bonding picture for this complex is quite complicated, with contributions from a number of formal electronic structures, involving not only different canonical forms of the ligands but also different oxidation states for the metal.

In principle, it might be possible to examine the actual oxidation state of the metal by studying the bond lengths to the other ligands, but this is fraught with uncertainty. Numerous attempts have been made to determine acceptable values for the octahedral 'covalent radii' for the various oxidation states of molybdenum but, not surprisingly, the results are inconclusive.¹⁵ Now, it is clear that the nature of the ligand is the dominant factor in the determination of the relevant bond lengths. Nevertheless, in the present case, we might look at the values of the Mo-Cl and Mo-P bond lengths since these occur in many different kinds of complex. The first result to notice is the fact that the two Mo-Cl bond lengths are experimentally equal, and are therefore unaffected or equally affected by the two ligands, a phosphine and the nitrogen of the chelate, *trans* to them. Of the two possibilities, the former is more likely since the two *trans* ligands have almost opposite character, one a π acceptor and the other a π donor. Thus it is possible that the common value for the two Mo-Cl bond lengths may be used as an indicator of the metal oxidation state when compared with Mo-Cl values in other complexes. If this is so then the indications are that the oxidation state is fairly high, but perhaps not as high as six, where $\text{Mo}^{\text{VI}}\text{-Cl}$ distances seem to be generally $<2.4 \text{ \AA}$.¹⁶ The Mo-P distance also seems to indicate an effective oxidation state of *ca.* IV.

One other factor that could be operative here is the steric effect. Whilst none of the ligands here would normally be classed as bulky, the high electron density in the Mo-N(imido) bond does influence the geometry. Atoms *cis* to the Mo=N bond are all bent away from it. The Cl(1) \cdots Cl(2) and Cl(2) \cdots P contacts, 3.33 and

3.16 Å respectively, whilst still reflecting the difference between Cl and P van der Waals radii, are short, as also is the contact of 2.83 Å between C(10) of the phosphorus phenyl ring and N(3). It is worth noting here that, in spite of this contact, the whole chelate ring is very planar, with a maximum deviation of 0.004 Å, in contrast to those found in the rhenium and platinum complexes mentioned above where the metal atom deviates by 0.13 and 0.33 Å respectively. This may again be a reflection of the greater involvement of the

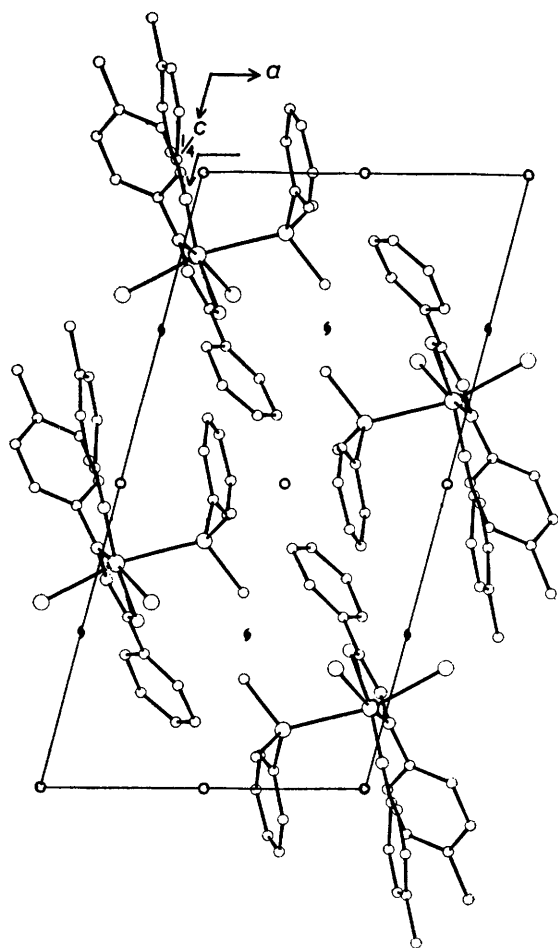


FIGURE 4 The unit-cell contents, viewed down b

molybdenum atom in delocalisation. Thus atoms in the immediate co-ordination sphere seem to be under strain, and this may have resulted already in some bond-length expansion for the softer Cl and phosphine ligands.

The geometry of the remaining portions of the molecule is normal.

Figure 4 shows the contents of the unit cell as seen down the b axis. There are no unacceptably short intermolecular contacts, the smallest being 3.48 Å between atom C(6) of one phenyl ring and atom C(8) of a phosphine methyl group on a neighbouring molecule. It is unlikely therefore that packing forces have any effect on the molecular geometry.

TABLE 3

Fractional co-ordinates x, y, z ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Mo	10 497(1)	2 227(1)	11 328(1)
P	13 017(4)	2 396(2)	10 963(2)
Cl(1)	8 548(4)	1 953(2)	11 984(2)
Cl(2)	11 904(4)	1 234(2)	11 966(2)
N(1)	9 690(10)	1 893(5)	10 422(5)
N(2)	9 819(9)	3 208(2)	11 082(5)
N(3)	10 338(10)	3 750(5)	11 586(5)
O	11 630(8)	2 849(4)	12 272(4)
C(1)	11 297(12)	3 515(6)	12 202(6)
Ring (1)	R(1)		
C(2)	12 101(12)	3 993(6)	12 807(6)
C(3)	11 525(16)	4 680(7)	12 825(8)
C(4)	12 315(18)	5 132(8)	13 437(9)
C(5)	13 633(18)	4 917(8)	13 927(9)
C(6)	14 220(17)	4 235(8)	13 918(9)
C(7)	13 396(15)	3 759(7)	13 329(7)
C(8)	13 618(20)	1 616(9)	10 517(10)
C(9)	14 629(17)	2 585(8)	11 799(8)
Ring (2)	R(2)		
C(10)	12 958(14)	3 111(7)	10 291(7)
C(11)	13 515(17)	3 774(8)	10 544(9)
C(12)	13 341(20)	4 333(9)	9 984(11)
C(13)	12 635(22)	4 172(10)	9 243(11)
C(14)	12 132(20)	3 545(10)	8 974(10)
C(15)	12 299(17)	2 969(8)	9 505(9)
Ring (3)	R(3)		
C(16)	8 827(12)	3 453(6)	10 392(6)
C(17)	7 408(14)	3 135(7)	10 105(7)
C(18)	6 481(15)	3 368(7)	9 407(7)
C(19)	6 954(15)	3 894(7)	8 985(8)
C(20)	8 375(16)	4 223(7)	9 278(8)
C(21)	9 324(14)	4 002(6)	9 998(7)
C(22)	5 934(18)	4 128(8)	8 204(9)
Ring (4)	R(4)		
C(23)	9 100(12)	1 601(6)	9 702(6)
C(24)	8 792(14)	2 009(6)	9 020(7)
C(25)	8 175(14)	1 695(6)	8 319(7)
C(26)	7 900(14)	969(6)	8 277(7)
C(27)	8 246(15)	557(7)	8 948(8)
C(28)	8 856(14)	873(6)	9 668(7)
C(29)	7 190(16)	632(7)	7 492(8)

TABLE 4

Important bond lengths (Å) and angles ($^\circ$) *

(a) Bond lengths			
Mo-P	2.528(4)	P-C(8)	1.83(2)
Mo-Cl(1)	2.393(4)	P-C(9)	1.85(1)
		P-C(10)	1.81(1)
(b) Bond angles			
N(1)-Mo-O	165.4(4)	N(2)-Mo-N(1)	96.1(4)
Cl(1)-Mo-N(2)	95.3(3)	Cl(1)-Mo-O	90.0(2)
Cl(1)-Mo-Cl(2)	87.7(1)	Cl(2)-Mo-O	88.3(2)
Cl(2)-Mo-P	79.7(1)	P-Mo-O	81.1(2)
P-Mo-N(2)	94.0(3)	P-Mo-N(1)	90.2(3)
Cl(1)-Mo-N(1)	100.8(4)	N(2)-Mo-O	73.0(3)
Mo-P-C(8)	113(1)	C(8)-P-C(9)	105(1)
Mo-P-C(9)	113(1)	C(8)-P-C(10)	107(1)
Mo-P-C(10)	113(1)	C(9)-P-C(10)	106(1)

* Parameters relating to the phenyl rings have been deposited as SUP 22438.

EXPERIMENTAL

Crystal Data.— $C_{29}H_{30}Cl_2MoN_3OP$, $M = 634.4$, Monoclinic, $a = 8.995(1)$, $b = 19.090(1)$, $c = 17.860(1)$ Å, $\beta = 104.15(5)^\circ$, $U = 2 973.8$ Å³, D_c (by flotation) = 1.40, $Z = 4$, $D_c = 1.417$ g cm⁻³, $F(000) = 1 296$, space group $P2_1/c$, Cu- $K\alpha$ radiation, $\lambda = 1.541 8$ Å, $\mu(\text{Cu-}K\alpha) = 60.3$ cm⁻¹.

TABLE 5
Displacements (Å) of atoms from the planes

A		B		C	
Mo	0.003	N(3)	-0.007	Mo	-0.004
N(2)	-0.004	O	-0.007	N(2)	0.013
N(3)	0.003	C(1)	0.020	N(3)	-0.004
O	-0.003	C(2)	-0.006	C(16)	-0.005
C(1)	0.001				

Equations of planes

A	-8.005x - 2.759y + 11.376z = 3.866
B	-7.896x - 2.294y + 11.862z = 4.727
C	-8.123x - 2.708y + 10.964z = 3.294

The crystals are bright red plates, stable in dry air. Intensity data were collected for a fragment, cut from a larger crystal, of dimensions *ca.* 0.12 × 0.12 × 0.22 mm mounted about the *b* axis on a General Electric XRD 6 manual diffractometer. The cell dimensions were determined by accurate measurement of the 2θ , ϕ , and χ values of axial reflections. The intensities of 3 168 independent reflections ($2\theta < 90^\circ$) were recorded using Cu- K_α radiation with a Ni β -filter, by the stationary-crystal-stationary-counter method. Throughout the collection of the data the intensities of four reference reflections were measured every 100 reflections as a check on electronic and crystal stability. No significant change in any of the standard reflections was detected. Of the reflections measured, 2 279 had intensities significantly ($> 3\sigma$)¹⁷ above background.

The structure was solved by standard Patterson and electron-density syntheses and refined by least-squares methods. With all atoms assigned isotropic thermal parameters, the *R* factors before and after correction of intensities for absorption were 0.13 and 0.11. Assignment of anisotropic thermal parameters for Mo, P, and Cl atoms and adoption of the weighting scheme $w^2 = 1$ if $F_o < F^*$ and F^*/F_o if $F_o > F^*$, with an optimum value for F^* of 55 on an absolute scale, led to a final, stationary, *R* value of 0.066. Programs, computers, and procedures used during the refinement were the same as those referred to in the previous paper in this series.¹⁴

The final atomic fractional co-ordinates are given in Table 1. Observed and calculated structure amplitudes, thermal parameters, bond lengths and angles, and inter- and intra-molecular contacts < 3.6 Å are available as Supplementary Publication No. SUP 22438 (17 pp).*

Preparation of Complexes.—All the reactions were carried out under dinitrogen in dry distilled solvents, but recrystallisations were performed in air with reagent-grade solvents. The hydrazines used were prepared by literature methods previously cited¹ with the exception of the *N*-alkyl-*N'*-arylhydrazines prepared as below.

The i.r. spectra were recorded on a Unicam SP 1200 (Nujol mulls 400–4 000 cm^{-1}) or Grubbs-Parsons DM4 spectrophotometer (Nujol mulls 200–500 cm^{-1}). Varian HA 100 and JEOL PS 100 instruments were used to obtain ¹H n.m.r. spectra in CHCl_3 or CD_2Cl_2 with SiMe_4 as internal standard. Microanalyses were performed by A. G. Olney at the University of Sussex.

***N*-Benzoyl-*N*-ethylhydrazine.**—Acetaldehyde benzoylhydrazone, $\text{PhCONHN}=\text{CHMe}$ (8.9 g, 0.54 mol), dissolved in ethanol saturated with hydrogen chloride gas (150 cm^3), was treated with Adam's catalyst (0.1 g) and shaken under

dihydrogen at 1 atm † until the theoretical quantities of dihydrogen had been absorbed. The resulting suspension was filtered and evaporated at 10^{-2} mmHg to 20 cm^3 . Addition of diethyl ether (200 cm^3) gave a cream precipitate of the hydrazinium(2+) chloride. This was dissolved in water (20 cm^3), the pH adjusted to 9 by the addition of dilute sodium hydroxide, and the aqueous solution was extracted with chloroform ($3 \times 50 \text{ cm}^3$). The dried chloroform extracts were evaporated at 10^{-3} mmHg to give the hydrazine as a yellowish solid, which was recrystallised from chloroform-hexane as white needles (7.2 g, 80%).

The hydrazines $\text{Pr}^n\text{NHNHCOPh}$, $\text{Pr}^1\text{NHNHCOPh}$, and $\text{PhCH}_2\text{NHNHCOPh}$ were prepared similarly using the appropriate hydrazones.

(*N*-Benzoyl-*N'*-phenyldiazene-*N'*O)dichloro(dimethylphenylphosphine)(phenylimido)molybdenum,⁹ (1).—Dichlorotris(dimethylphenylphosphine)oxomolybdenum(IV) (1.0 g, 0.001 7 mol) and *N*-benzoyl-*N'*-phenylhydrazine (1.0 g, 0.004 6 mol) were heated under reflux in methanol (4 cm^3) for 0.5 h. The resulting clear red solution was evaporated to 5 cm^3 at 10^{-2} mmHg. Addition of diethyl ether (40 cm^3) precipitated the complex as a red solid which was recrystallised from dichloromethane-diethyl ether, yield 0.73 g (72%). Complexes (2)–(13) were prepared in a similar manner using the appropriate molybdenum(IV) oxo-complexes and hydrazines: dichloro(*N*-*p*-chlorobenzoyl-*N'*-phenyldiazene-*N'*O)(dimethylphenylphosphine)(phenylimido)molybdenum, (2); dichloro(*N*-*p*-methoxybenzoyl-*N'*-phenyldiazene-*N'*O)(dimethylphenylphosphine)(phenylimido)molybdenum, (3); (*N*-benzoyl-*N'*-phenyldiazene-*N'*O)dichloro(diethylphenylphosphine)(phenylimido)molybdenum, (4); (*N*-benzoyl-*N'*-*p*-chlorophenyldiazene-*N'*O)dichloro(*p*-chlorophenylimido)(dimethylphenylphosphine)molybdenum, (5); (*N*-benzoyl-*N'*-*p*-tolylidiazene-*N'*O)dichloro(dimethylphenylphosphine)(*p*-tolylimido)molybdenum, (6); (*N*-benzoyl-*N'*-*p*-methoxyphenyldiazene-*N'*O)dichloro(dimethylphenylphosphine)(*p*-methoxyphenylimido)molybdenum, (7); (*N*-benzoyl-*N'*-1-naphthylidiazene)dichloro(dimethylphenylphosphine)(1-naphthylimido)molybdenum, (8); dichloro(dimethylphenylphosphine)(*N*-1-naphthyl-*N'*-phenyldiazene-*N'*O)(phenylimido)molybdenum, (9); (*N*-benzoyl-*N'*-ethylidiazene-*N'*O)dichloro(dimethylphenylphosphine)(ethylimido)molybdenum, (10); (*N*-benzoyl-*N'*-*n*-propylidiazene-*N'*O)dichloro(dimethylphenylphosphine)(*n*-propylimido)molybdenum, (11); (*N*-benzoyl-*N'*-isopropylidiazene-*N'*O)dichloro(dimethylphenylphosphine)(isopropylimido)molybdenum, (12); (*N*-benzoyl-*N'*-benzylidiazene-*N'*O)(benzylimido)dichloro(dimethylphenylphosphine)molybdenum, (13).

(*N*-Acetyl-*N'*-tolylidiazene-*N'*O)dichloro(dimethylphenylphosphine)(tolylimido)molybdenum(14).—The complex $[\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3]$ (0.5 g, 0.000 87 mol) and *NN*-acetyl-*N'*-tolylhydrazine (0.5 g, 0.003 7 mol) were heated under reflux in toluene (40 cm^3) for 0.5 h, and the resulting orange solution evaporated to 10 cm^3 at 10^{-2} mmHg. Addition of diethyl ether precipitated the complex as an orange solid which was recrystallised as orange plates from dichloromethane-diethyl ether yield 0.28 g (62%).

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

† Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg \approx 13.6 × 9.8 Pa.

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