Reactions of Molybdenum Oxo-complexes with Substituted Hydrazines. Part 2.† The Reactions of Molybdenum(IV) Oxo-complexes with Aroylhydrazines and the Crystal and Molecular Structure of (*N*-Benzoyldiazene-*N'O*)[*N*-benzoyldiazenido(1−)-*N'*]chlorobis(dimethylphenylphosphine)molybdenum

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The aroylhydrazines RCONHNH$_2$ (R = Ph, *p*-ClC$_6$H$_4$, *p*-NO$_2$C$_6$H$_4$, *m*-NO$_2$C$_6$H$_4$, or 1-C$_{10}$H$_7$) react with [MoOCl$_2$(PR'$_3$)$_3$] (PR'$_3$ = PMe$_2$Ph, PEt$_2$Ph, PPr$^n{}_2$Ph, PMePh$_2$, or PEt$_3$) to give red complexes [MoCl(N$_2$COR)(NHNCOR)(PR'$_3$)$_2$]. Crystals of the title complex with R = Ph and PR'$_3$ = PMe$_2$Ph are triclinic with a = 8.710, b = 23.000, c = 16.370 Å, α = 97.43, β = 89.21, γ = 101.33°, space group $P\bar{1}$, and Z = 4. The structure has been solved by Patterson and Fourier methods, and refined, using 3 939 independent reflections, to R 0·098. It is composed of two crystallographically independent monomeric molecules, both having distorted octahedral co-ordination. They are considered to be chemically equivalent, each containing a unidentate diazenido-ligand [Mo–N 1.770, 1.793(9) Å] and a chelating benzoyldiazene ligand [Mo–N 1.945, 1.945(8); Mo–O 2.130, 2.131(7) Å]. The chelate ring is planar in both molecules, indicating incorporation of the metal atom in the delocalised system.

WE have shown that [ReOCl$_3$(PPh$_3$)$_2$] reacts with benzoylhydrazinium chloride in refluxing ethanol to form a chelated benzoyldiazenido(1−)-derivative (A) which can be degraded to yield dinitrogen complexes.[1] We attempted to extend this reaction to molybdenum chemistry, and here we describe the full details [2] of an investigation of the reaction of various benzoylhydrazines with [MoOCl$_2$(PMe$_2$Ph)$_3$] and its analogues.

If aroylhydrazines RCONHNH$_2$ are added to boiling solutions of [MoOCl$_2$(PR'$_3$)$_3$] (PR'$_3$ = tertiary phosphine) in methanol the green solutions immediately turn red, and, on cooling, red crystals separate. These complexes analysed as [MoCl(N$_2$COR)$_2$(PR'$_3$)$_2$] (R = aryl) and are monomeric. Analytical and spectroscopic data are summarised in Table 1. The complexes have no bands in the i.r. spectrum clearly assignable to ν(Mo=O) or ν(N–H), and are diamagnetic in the solid state and in solution. The ^{1}H n.m.r. spectrum of derivatives (9)—(12) show a 1 : 2 : 1 triplet at 2.0 p.p.m. (see Table 1), characteristic of *trans*, virtually coupled, methyl groups of phosphines. The dimethylphenylphosphine complexes give quartets in this region, suggesting that the *trans* stereochemistry of the phosphines is retained, but with overall lower symmetry in the complex.

The i.r. spectra show a band at 1 580—1 600 cm^{-1}, which, by comparison with the spectrum of [ReCl$_2$(N$_2$COPh)(PEtPh$_2$)$_3$],[1] is assignable to ν(C=O). There is another band at *ca.* 1 240 cm^{-1} which is also found for the rhenium complex (1 233 cm^{-1}). These data suggest that at least one of the benzoyldiazene groups in the molybdenum complexes is linear and non-chelating. There is no i.r. evidence for a chelating benzoyldiazenido(1−) ring as found in (A), and the molybdenum

TABLE 1

The complexes [MoCl(N$_2$COR)(NHNCOR)L$_2$] (R = aryl, L = tertiary phosphine)

Complex					Analysis [a] (%)				I.r. spectrum (cm^{-1})		^{1}H N.m.r. spectrum (p.p.m.)
R	L	Colour	M.p. (θ_c/°C)	*M* [a]	C	H	N	Cl	ν(CO)	ν (Mo–Cl)	(P–Me) [b]
(1) Ph	PMe$_2$Ph	Red	141—145		52.5 (53.2)	5.0 (4.8)	8.5 (8.3)		1 589	298	1.6 (q)
(2) *p*-ClC$_6$H$_4$	PMe$_2$Ph	Red	187—190	735 (743)	48.4 (48.5)	4.3 (4.0)	8.5 (7.5)		1 587	302	1.6 (q)
(3) *p*-MeOC$_6$H$_4$	PMe$_2$Ph	Red	163—165		52.6 (52.3)	5.2 (5.0)	7.5 (7.5)		1 602	295	1.65 (q)
(4) 1-C$_{10}$H$_7$	PMe$_2$Ph	Red	123—127		59.3 (59.0)	5.1 (4.7)	7.5 (7.3)		1 600	325	
(5) Ph	PEt$_2$Ph	Red	138—142		55.9 (55.9)	5.8 (5.5)	7.8 (7.7)		1 595	298	
(6) *p*-ClC$_6$H$_4$	PEt$_2$Ph	Red	184—188	810 (799)	51.1 (51.1)	5.2 (5.0)	7.0 (6.8)	13.2 (13.3)	1 590	301	
(7) Ph	PPr$^n{}_2$Ph	Red	158—159	791 (786)	57.6 (58.0)	6.7 (6.1)	7.1 (7.1)	3.9 (4.0)	1 589	299	
(8) Ph	PMePh$_2$	Red	100—103		59.4 (60.1)	5.0 (4.5)	6.8 (7.0)		1 599	307	1.97 (t)
(9) *p*-ClC$_6$H$_4$	PMePh$_2$	Red	188—190		55.4 (55.4)	4.1 (4.2)	6.6 (6.5)		1 602, 1 580	303	1.98 (t)
(10) *p*-MeC$_6$H$_4$	PMePh$_2$	Red	165—168		61.0 (61.0)	5.2 (5.1)	7.0 (6.8)		1 588	295	1.96 (t), 2.4 (s)
(11) *p*-O$_2$NC$_6$H$_4$	PMePh$_2$	Red	175—176	870 (868)	54.2 (54.1)	4.0 (3.8)	9.5 (9.5)	4.2 (4.0)	1 614, 1 586	296	2.00 (t)
(12) *m*-O$_2$NC$_6$H$_4$	PMePh$_2$	Red-brown	155—157	878 (868)	54.0 (54.1)	4.3 (3.8)	9.3 (9.4)	4.0 (4.0)	1 595	298	2.02(t)
(13) Ph	PEt$_3$	Red	214—218	630 (632)	49.3 (49.3)	6.5 (6.3)	8.8 (8.8)	5.5 (5.6)	1 587	300	

[a] Calculated values are given in parentheses. [b] q = 1 : 3 : 3 : 1 quartet, t = 1 : 2 : 1 triplet, s = singlet.

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† Part 1, preceding paper.

complexes are all recovered unchanged from the boiling solvents acetonitrile, pyridine, ethanol, and benzene containing a large excess of the appropriate phosphine.

The diamagnetism of the complexes requires that, if one of the aroyldiazene moieties is a linear aroyldiazenido(1—) ligand and therefore functioning as a one- or three-electron donor, the other must contribute zero or two electrons to the metal. This suggests that a proton is present (*i.e.* $RCON_2H$) and in order to maintain a reasonable co-ordination number for the molybdenum the benzoylhydrazide must be chelated. However, there were no bands in the i.r. assignable to ν(N–H) and a variable-temperature study of the ^1H n.m.r. spectrum of (3) failed to show any inequivalence of the *p*-MeO protons, which might be expected were there one linear $RCON_2$ ligand and one chelated $RCON_2H$ ligand. Since it was difficult to reconcile the chemical and physical data for these complexes, an *X*-ray crystallographic study of complex (1) was undertaken.

EXPERIMENTAL

All the reactions were carried out under an atmosphere of pure dry dinitrogen using dry solvents, whereas recrystallisations were performed in air using reagent-grade solvents. The aroylhydrazines were prepared as previously described [1] and the complexes $[MoOCl_2(PR_3)_3]$ prepared by the literature procedures.[3]

The i.r. spectra were recorded on a Unicam SP 1200 spectrophotometer (Nujol mulls, 400—4 000 cm^{-1}) and an R.I.I.C. F.S. 620 interferometer (Polythene discs, 40—400 cm^{-1}). Varian A60 and HA 100 instruments were used to obtain ^1H n.m.r. spectra in $CDCl_3$ solutions with $SiMe_4$ as internal standard. Melting points were recorded on a Kofler hot-stage and are uncorrected.

(Benzoyldiazene)[benzoyldiazenido(1—)]chlorobis(dimethylphenylphosphine)molybdenum, (1).—Dichlorotris(dimethylphenylphosphine)oxomolybdenum (0.5 g) and benzoylhydrazine (0.5 g) were heated in methanol under reflux (30 cm^3) for 0.5 h. On cooling, the red solution deposited the *complex* as red crystals which were recrystallised from dichloromethane–methanol in 62% yield.

Complexes (2)—(13) were prepared analogously in similar yields using the appropriate oxo-complexes and aroylhydrazines: *chloro*(p-*chlorobenzoyldiazene*)[p-*chlorobenzoyldiazenido*(1—)]*bis(dimethylphenylphosphine)molybdenum*, (2); *chlorobis(dimethylphenylphosphine)*(p-*methoxybenzoyldiazene*)[p-*methoxybenzoyldiazenido*(1—)]-*molybdenum*, (3); *chlorobis(dimethylphenylphosphine)*(1-*naphthoyldiazene*)[1-*naphthoyldiazenido*(1—)]*molybdenum*, (4); *(benzoyldiazene)[benzoyldiazenido(1—)]chlorobis(diethylphenylphosphine)molybdenum*, (5); *chloro*(p-*chlorobenzoyldiazene*)[p-*chlorobenzoyldiazenido*(1—)]bis(*dimethylphenylphosphine*)*molybdenum*, (6); *(benzoyldiazene)[benzoyldiazenido(1—)]chlorobis(di-n-propylphenylphosphine)-molybdenum*, (7); *(benzoyldiazene)[benzoyldiazenido(1—)]-chlorobis(methyldiphenylphosphine)molybdenum*, (8); *chloro*(p-*chlorobenzoyldiazene*)[p-*chlorobenzoyldiazenido*(1—)]-bis(*methyldiphenylphosphine*)*molybdenum*, (9); *chlorobis-(methyldiphenylphosphine)*(p-*toluoyldiazene*)[p-*toluoyldiazenido*(1—)]*molybdenum*, (10); *chlorobis(methyldiphenylphosphine)*(p-*nitrobenzoyldiazene*)[p-*nitrobenzoyldiazenido-*(1—)]*molybdenum*, (11); *chlorobis(methyldiphenylphosphine)-*(m-*nitrobenzoyldiazene*)(m-*nitrobenzoyldiazenido*(1—)]*molybdenum*, (12); *(benzoyldiazene)[benzoyldiazenido(1—)]-chlorobis(triethylphosphine)molybdenum*, (13).

X-*Ray Crystallography*.—*Crystal data*. Crystals of (1) were obtained by recrystallisation from dichloromethane–methanol as orange-red needles, stable in dry air. $C_{30}H_{33}ClMoN_4O_2P_2$, $M = 675.0$, Triclinic, $a = 8.710(1)$, $b = 23.000(1)$, $c = 16.370(1)$ Å, $\alpha = 97.43(3)$, $\beta = 89.21(5)$, $\gamma = 101.33(3)°$, $U = 3\,188.4$ Å^3, D_m (by flotation) $= 1.38$, $Z = 4$, $D_c = 1.406$ g cm^{-3}, $F(000) = 1\,384$, space group $P\bar{1}$, Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) $= 54.5$ cm^{-1}.

Intensity data were collected for a fragment of a crystal of dimensions *ca.* $0.45 \times 0.15 \times 0.45$ mm mounted about the *a* axis on a General Electric XRD6 manual diffractometer. The intensities of 3 939 reflections ($2\theta < 80°$) 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 the electronic and crystal stability. No change in any of the standard reflections was noticed during the course of data collection. Of the reflections measured, 3 489 had intensities significantly ($>3\sigma$) above background.[4] The data were corrected for Lorentz and polarisation effects.

The structure was determined using Patterson and electron-density syntheses and the atomic co-ordinates refined by least-squares methods. With anisotropic thermal parameters for the metal atoms and isotropic for the rest, the *R* factor was reduced to 0.098. At this stage an absorption correction was applied according to the method of Busing and Levy [5] with the crystal path lengths determined by the vector-analysis procedure of Coppens *et al.*[6] With anisotropic thermal parameters for the metal, phosphorus, and chlorine atoms, further refinement reduced *R* to 0.078. The positions of the phosphine phenyl-group hydrogen atoms were calculated, assigned isotropic thermal parameters equal to those of the carbon atom to which they were attached, and included in the next structure-factor calculation and difference electron-density synthesis. From the latter, the positions of the phenyl hydrogen atoms in the benzoyl groups were found, and also the position of one attached to the nitrogen atom of the chelating 'N_2-COPh' group in molecule 1. This ligand was therefore identified as benzoyldiazene. Confirmation of the presence of this hydrogen atom was subsequently given by its successful refinement. No reliable crystallographic evidence could be found for a hydrogen on the corresponding nitrogen atom of molecule 2.

With the phenyl hydrogen atoms included as a fixed contribution, further refinement gave a stationary *R* value of 0.068. Adoption of a weighting scheme of the type $w^{\frac{1}{2}} = 1$ for $F_o < F^*$ and F_o/F^* for $F_o > F^*$, with an optimum value for F^* of 40 on an absolute scale, improved the agreement analysis but left *R* unchanged. Omission of three low-angle reflections thought to be suffering from extinction and two further cycles of least squares gave a final *R* value of 0.066. The final difference map showed no peak $>$ *ca.* 0.6—0.8 e Å^{-3}.

Calculations were performed on the University of London CDC6600 and Imperial College IBM 7094 computers using the ' X-RAY '63 ' and '70 ' systems.[7,8]

The scattering factors used for P, Cl, N, C, O, and H were from ref. 9, those for Mo from ref. 10, and the real and imaginary parts of the anomalous-dispersion correction were those given by Cromer.[11] Table 2 gives the final fraction co-ordinates of the refined atoms [including the

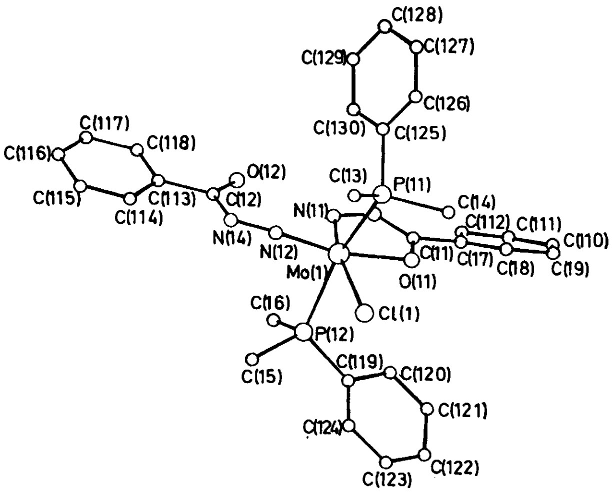

FIGURE 1 A single molecule of $[MoCl(N_2COPh)(NHNCOPh)(PMe_2Ph)_2]$

hydrogens attached to N(11)], together with their estimated standard deviations. The observed and calculated structure amplitudes, thermal parameters, and bond lengths and angles in the phenyl rings are listed in Supplementary Publication No. SUP 22439 (18 pp.).*

TABLE 2

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

Atom	x	y	z
(*a*) Molecule 1			
Mo(1)	3 715(1)	9 294(1)	1 795(1)
Cl(1)	6 263(3)	9 977(1)	1 798(2)
P(11)	5 521(3)	8 576(1)	1 982(2)
P(12)	2 787(4)	10 239(1)	1 592(2)
N(11)	1 656(10)	8 900(4)	2 214(5)
N(12)	3 222(10)	9 013(4)	754(5)
N(13)	1 133(11)	8 930(4)	2 942(5)
N(14)	2 726(10)	8 827(4)	41(5)
O(11)	3 628(8)	9 439(3)	3 106(4)
O(12)	397(10)	8 399(4)	592(5)
C(11)	2 310(13)	9 227(5)	3 426(7)
C(12)	1 231(13)	8 519(5)	−27(7)
C(13)	6 901(16)	8 531(6)	1 144(8)
C(14)	6 713(17)	8 813(6)	2 914(9)
C(15)	3 427(15)	10 507(6)	616(8)
C(16)	670(16)	10 148(6)	1 565(8)
C(17)	2 091(14)	9 311(5)	4 315(7)
C(18)	3 377(17)	9 429(7)	4 839(9)
C(19)	3 157(19)	9 515(7)	5 711(10)
C(110)	1 743(17)	9 461(7)	6 025(9)
C(111)	464(20)	9 345(8)	5 528(10)
C(112)	672(17)	9 252(6)	4 651(9)
C(113)	577(13)	8 325(5)	−868(7)
C(114)	1 468(14)	8 492(5)	−1 537(7)
C(115)	833(17)	8 304(6)	−2 310(9)
C(116)	−726(18)	7 952(7)	−2 418(9)
C(117)	−1 586(17)	7 789(7)	−1 743(9)
C(118)	−939(15)	7 975(6)	−958(7)
C(119)	3 447(13)	10 859(5)	2 363(7)
C(120)	2 985(18)	10 796(7)	3 158(9)
C(121)	3 548(19)	11 260(7)	3 825(9)
C(122)	4 527(18)	11 779(7)	3 638(9)
C(123)	4 947(18)	11 825(7)	2 864(9)
C(124)	4 458(16)	11 368(6)	2 224(8)
C(125)	4 643(12)	7 806(5)	2 050(6)
C(126)	5 549(14)	7 412(5)	2 316(7)
C(127)	4 893(14)	6 824(6)	2 343(7)
C(128)	3 350(15)	6 599(5)	2 124(7)
C(129)	2 465(15)	6 981(6)	1 848(8)
C(130)	3 116(13)	7 575(5)	1 818(7)
H(N11)	1 058(13)	8 680(5)	1 612(6)
(*b*) Molecule 2			
Mo(2)	6 362(1)	4 966(1)	2 976(1)
Cl(2)	4 280(3)	5 494(1)	3 423(2)
P(21)	4 279(4)	4 356(1)	1 967(2)
P(22)	7 988(4)	5 672(1)	4 088(2)
N(21)	8 180(10)	4 729(4)	2 428(5)
N(22)	6 252(10)	4 380(4)	3 611(5)
N(23)	8 995(11)	5 036(4)	1 818(6)
N(24)	6 302(11)	3 960(4)	4 039(5)
O(21)	7 101(8)	5 562(3)	2 090(4)
O(22)	8 580(10)	3 820(4)	3 385(5)
C(21)	8 288(13)	5 479(5)	1 688(7)
C(22)	7 557(14)	3 689(5)	3 880(7)
C(23)	2 511(17)	4 017(6)	2 467(9)
C(24)	3 606(18)	4 783(7)	1 233(9)
C(25)	7 237(16)	5 561(6)	5 111(8)
C(26)	9 979(16)	5 535(6)	4 110(8)
C(27)	8 899(13)	5 867(5)	1 056(7)
C(28)	8 342(15)	6 382(6)	1 044(8)
C(29)	8 933(17)	6 774(6)	456(9)
C(210)	10 061(17)	6 619(6)	−95(8)
C(211)	10 631(16)	6 114(6)	−84(8)
C(212)	10 042(15)	5 736(5)	525(7)
C(213)	7 585(13)	3 201(5)	4 417(7)
C(214)	6 734(14)	3 162(5)	5 100(7)
C(215)	6 781(15)	2 700(6)	5 565(8)
C(216)	7 634(16)	2 277(6)	5 297(8)
C(217)	8 501(16)	2 319(6)	4 618(8)
C(218)	8 526(14)	2 790(5)	437(7)
C(219)	8 222(13)	6 466(5)	4 016(6)
C(220)	9 162(15)	6 692(6)	3 410(7)
C(221)	8 393(16)	7 314(6)	3 317(8)
C(222)	8 638(16)	7 648(6)	3 848(8)
C(223)	7 721(16)	7 457(6)	4 434(8)
C(224)	7 472(15)	6 829(6)	4 540(8)
C(225)	4 907(13)	3 731(5)	1 362(7)
C(226)	4 652(16)	3 595(6)	529(8)
C(227)	5 159(17)	3 097(7)	94(9)
C(228)	5 883(17)	2 745(6)	478(9)
C(229)	6 207(17)	2 893(6)	1 305(8)
C(230)	5 715(15)	3 380(6)	1 753(8)

RESULTS AND DISCUSSION

The structure contains two crystallographically independent molecules which differ mainly in the orientations of the phenyl groups present. Figure 1 is a diagram of molecule 1 showing the atomic numbering; the numbering for molecule 2 is obtained by changing the first digit of each number from 1 to 2. Bond lengths involving the azenide ligands are given in Figure 2 and other relevant parameters in Table 3. The results of some least-

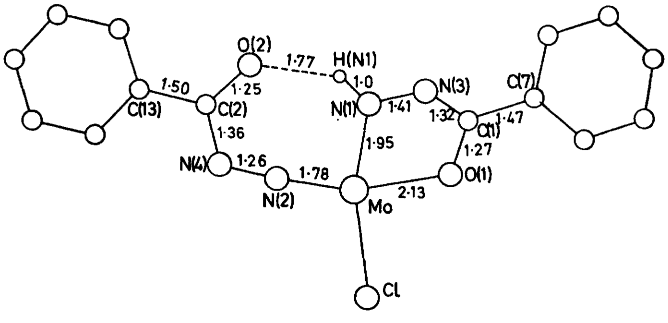

FIGURE 2 Bond lengths in the diazene and diazenide (averaged over the two independent molecules)

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

squares-plane calculations are given in Table 4. Although no hydrogen atom could be found in the neighbourhood of N(21) or O(22), there are no other significant indications that the two molecules are different and we feel they should be considered chemically equivalent, both being represented as [MoCl(NHNCOPh)(NNCOPh)-$(PMe_2Ph)_2$]. Accordingly, the parameters in Figure 2 are averages from the two molecules.

TABLE 3

Important bond lengths and angles

	M = 1 (molecule 1)	M = 2 (molecule 2)
(*a*) Bond lengths (Å)		
Mo(M)–P(M1)	2.542(4)	2.545(3)
Mo(M)–P(M2)	2.525(4)	2.522(3)
Mo(M)–Cl(M)	2.454(3)	2.429(3)
Mo(M)–O(M1)	2.131(7)	2.130(7)
Mo(M)–N(M1)	1.946(8)	1.945(9)
Mo(M)–N(M2)	1.770(8)	1.793(9)
N(M1)–N(M3)	1.41(1)	1.40(1)
N(M3)–C(M1)	1.32(1)	1.33(2)
C(M1)–O(M1)	1.29(1)	1.25(1)
N(M2)–N(M4)	1.24(1)	1.27(1)
N(M4)–C(M2)	1.35(1)	1.37(2)
C(M2)–O(M2)	1.27(1)	1.22(1)
C(M1)–C(M7)	1.46(2)	1.48(2)
C(M2)–C(M13)	1.48(2)	1.52(2)
P(M1)–C(M3)	1.82(1)	1.82(1)
P(M1)–C(M4)	1.82(1)	1.82(2)
P(M1)–C(M25)	1.80(1)	1.81(1)
P(M2)–C(M5)	1.83(1)	1.82(1)
P(M2)–C(M6)	1.82(1)	1.82(2)
P(M2)–C(M19)	1.79(1)	1.82(1)
N(M1)–H(NM1)	1.01(10)	
O(M2)–H(NM1)	1.77(10)	
(*b*) Bond angles (°)		
P(M1)–Mo(M)–N(M1)	105.3(3)	97.9(2)
P(M1)–Mo(M)–N(M2)	95.7(3)	93.5(3)
P(M1)–Mo(M)–Cl(M)	80.0(1)	83.3(1)
P(M1)–Mo(M)–O(M1)	86.3(2)	89.8(2)
P(M1)–Mo(M)–P(M2)	160.9(1)	168.5(1)
P(M2)–Mo(M)–Cl(M)	80.9(1)	85.3(3)
P(M2)–Mo(M)–N(M1)	93.1(3)	93.4(2)
P(M2)–Mo(M)–N(M2)	89.2(3)	88.9(3)
P(M2)–Mo(M)–O(M1)	94.9(2)	91.3(2)
Cl(M)–Mo(M)–N(M1)	162.2(3)	163.6(3)
Cl(M)–Mo(M)–N(M2)	107.0(3)	106.3(3)
Cl(M)–Mo(M)–O(M1)	91.4(2)	91.0(2)
N(M1)–Mo(M)–N(M2)	89.6(4)	90.0(4)
N(M1)–Mo(M)–O(M1)	72.2(3)	72.7(3)
N(M2)–Mo(M)–O(M1)	161.6(3)	163.0(4)
N(M3)–N(M1)–Mo(M)	124(1)	123(1)
N(M3)–N(M1)–H(NM1)	127(6)	
Mo(M)–N(M1)–H(NM1)	108(6)	
N(M1)–N(M3)–C(M1)	108(1)	109(1)
N(M3)–C(M1)–O(M1)	120(1)	120(1)
N(M3)–C(M1)–C(M7)	119(1)	120(1)
O(M1)–C(M1)–C(M7)	121(1)	120(1)
C(M1)–O(M1)–Mo(M)	116(1)	116(1)
Mo(M)–N(M2)–N(M4)	174(1)	175(1)
N(M2)–N(M4)–C(M2)	116(1)	114(1)
N(M4)–C(M2)–O(M2)	123(1)	126(1)
N(M4)–C(M2)–C(M13)	117(1)	112(1)
O(M2)–C(M2)–C(M13)	120(1)	122(1)
C(M2)–O(M2)–H(NM1)	122(3)	
O(M2)–H(NM1)–N(M1)	166(9)	
Mo(M)–P(M1)–C(M3)	112(1)	113(1)
Mo(M)–P(M1)–C(M4)	112(1)	114(1)
Mo(M)–P(M1)–C(M25)	118(1)	113(1)
C(M3)–P(M1)–C(M4)	106(1)	105(1)
C(M3)–P(M1)–C(M25)	104(1)	104(1)
C(M4)–P(M1)–C(M25)	104(1)	106(1)
P(M1)–C(M25)–C(M26)	120(1)	123(1)
P(M1)–C(M25)–C(M30)	122(1)	119(1)
Mo(M)–P(M2)–C(M5)	112(1)	112(1)
Mo(M)–P(M2)–C(M6)	113(1)	111(1)
Mo(M)–P(M2)–C(M19)	115(1)	117(1)
C(M5)–P(M2)–C(M6)	105(1)	105(1)
C(M5)–P(M2)–C(M19)	105(1)	107(1)
C(M6)–P(M2)–C(M19)	106(1)	105(1)
P(M2)–C(M19)–C(M20)	117(1)	118(1)
P(M2)–C(M19)–C(M24)	124(1)	122(1)

TABLE 4

Mean planes through various sets of atoms

(*i*) Displacements (Å) of atoms from the planes

	A(M = 1)	A(M = 2)
Mo(M1)	0.023	0.007
N(M1)	−0.032	−0.009
N(M3)	0.022	0.007
O(M1)	−0.022	−0.006
C(M1)	0.008	0.002

	B(M = 1)	B(M = 2)
Mo(M1)	0.026	0.003
N(M2)	−0.041	−0.006
N(M4)	−0.003	0.001
O(M2)	−0.024	−0.002
C(M2)	0.042	0.004

	D(M = 1)	D(M = 2)
N(M3)	−0.001	−0.001
O(M1)	−0.001	−0.001
C(M1)	0.002	0.002
C(M7)	−0.001	−0.001

	E(M = 1)	E(M = 2)
Mo(M1)	0.028	0.010
N(M1)	−0.010	−0.078
N(M2)	−0.028	−0.025
N(M3)	0.037	−0.042
N(M4)	0.015	−0.031
O(M1)	−0.034	0.055
O(M2)	−0.052	0.066
C(M1)	0.005	0.025
C(M2)	0.039	0.020

	F(M = 1)	F(M = 2)
N(M4)	−0.001	0.001
O(M2)	−0.001	0.002
C(M2)	0.002	−0.005
C(M13)	−0.001	0.001

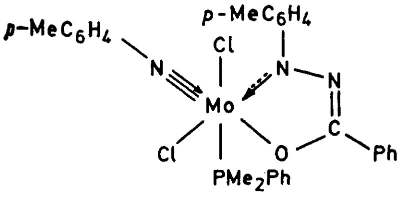
(*ii*) Equations of planes

A(1) $-4.383x + 21.704y - 3.007z = 17.981$
A(2) $4.270x + 9.720y - 10.235z = 10.583$
B(1) $-4.594x + 21.488y - 2.943z = 17.711$
B(2) $3.641x + 10.851y + 10.450z = 10.812$
C(1) $-4.690x + 21.241y - 3.836z = 17.311$
D(1) $-4.229x + 21.840y - 3.129z = 18.107$
D(2) $4.229x + 9.824y + 10.232z = 10.607$
E(1) $-4\ 465x + 21.605y + 3.133z = 17.832$
E(2) $3.953x + 10.778y + 10.033z = 10.844$
F(1) $-4.414x + 21.725y - 1.614z = 17.927$
F(2) $-3.620x + 11.190y + 10.250z = 10.852$

This structure analysis has confirmed the presence of one chelating and one unidentate ligand and of the presence of the proton on the chelating ligand as required by the diamagnetism of the complex.

One particularly interesting feature of complexes of these ' aroyldiazene ' ligands is that in most cases various canonical forms can be written to represent their mode of bonding and often the bond lengths found do indeed indicate that a resonance structure must be considered. An example of this is given by the complex [$MoCl_2$-$(NC_6H_4Me\text{-}p)(p\text{-}MeC_6H_4N_2COPh)(PMe_2Ph)$] described and discussed in Part 1 of this series, where (B) was considered to make the most important contribution to the overall electronic structure.

Comparison of the relevant bond lengths in the present complex and in (B) shows much similarity but also some small differences. Let us first consider the chelate rings in the two complexes. The two N–N distances

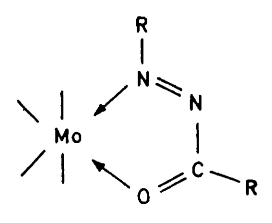


(B)

must be considered equal, within the limits of experimental error, as must the two C=N and two C–O bond lengths. The differences between the Mo–N distances is just significant, with the value in the present complex shorter by 0.04 Å than in (B). In contrast, the Mo–N distance in the present complex is 0.025 Å longer than in (B). This may be an indication that the π interaction in the Mo–N bond is a little stronger in the present case, due either to changes in electron density on the metal or to the effect of the different substituents on the relevant nitrogen atoms. Nevertheless, the chelate ring can almost certainly be given the same representation as in (B) and is thus a chelating benzoyldiazene ligand. That the chelate ring contains significant delocalisation is apparent from its complete planarity, the maximum deviation for either molecule being 0.03 Å (Table 4).

For the two unidentate ligands there are obvious differences. In the present complex the ligand must be considered as a diazenide, in view of the very short N=N bond length. However, the linearity of the N=N–Mo unit implies that π bonding between the nitrogen and metal is strong and so the bonding can be represented by N=N$\overset{\rightarrow}{-}$Mo, with the ligand a three-electron donor. This contrasts with the four-electron donor function of the imide ligand in (B), and as would be expected the N–Mo bond length in the present complex is longer than in (B) (1.781 vs. 1.726 Å), although the difference is perhaps not as large as one might expect. The different electron contributions from these two unidentate ligands is balanced by having one chloride and two phosphines in the present complex and two chlorides and one phosphine in (B), so that equivalent electron configurations are maintained. If we accept the mode of bonding discussed above for the chelate, the metal has an 18-electron configuration in both complexes although the formal oxidation states are IV in the present complex and VI in (B).

The possibility of some small contribution from a neutral form of the chelate ligand (C), giving an oxidation state for the metal reduced by two was discussed for (B) and of course the same possibility occurs here. The only pieces of evidence for this, however, are the slightly shorter than expected O–C and N–N single bonds and slightly longer C=N double bonds found in both complexes, but these deviations from expected values are barely significant.



(C)

The remaining metal–ligand distances, the interbond angles at the metal, and the interligand non-bonded contacts in the present complex also raise some interesting points. In view of their mutual *trans* arrangement it is surprising to find that the two Mo–P bond lengths are different, showing the same variation in the two molecules. The only logical explanation for this is the orientation of the PMe$_2$Ph groups containing P(M1), the more distant atom, which is very similar in the two molecules and which brings the two attached methyl groups close to the Cl atom (Cl · · · Me *ca.* 3.5 Å). Other features are rather difficult to explain. For example, the two P atoms are positioned such that the P–Mo–Cl angles are <90° (in spite of the short Cl · · · Me contacts just mentioned) giving Cl · · · P distances of *ca.* 3.2—3.3 Å. In contrast, the supplementary N(M1)–Mo–P angles are all >90° (93—105°) and correspond to N · · · P distances of 3.2—3.3 Å also. Here, one is tempted to suggest that the ' van der Waals radius ' of the nitrogen atom is larger in the direction of the N · · · P vector due to its lone pair of electrons, which, occupying an essentially pure *p* orbital, will increase the electron density in this direction. Surprisingly, however, the Mo–N(M2) bond to the unidentate ligand, which is expected to have more electron density, and the lone pairs on the *sp*-hybridised N(M2) atom, one of which will also be in a ' repelling ' orientation, do not seem to have as much effect since the N(M2)–Mo–P and N(M2)–Mo–(M1) angles are 89—96°. The N(M2)–Mo–Cl angle in each molecule is large (106, 107°) but this is partly helped by the movement of O(M1) in the chelate ring away from a symmetrical axial position due to the restricted chelate bite.

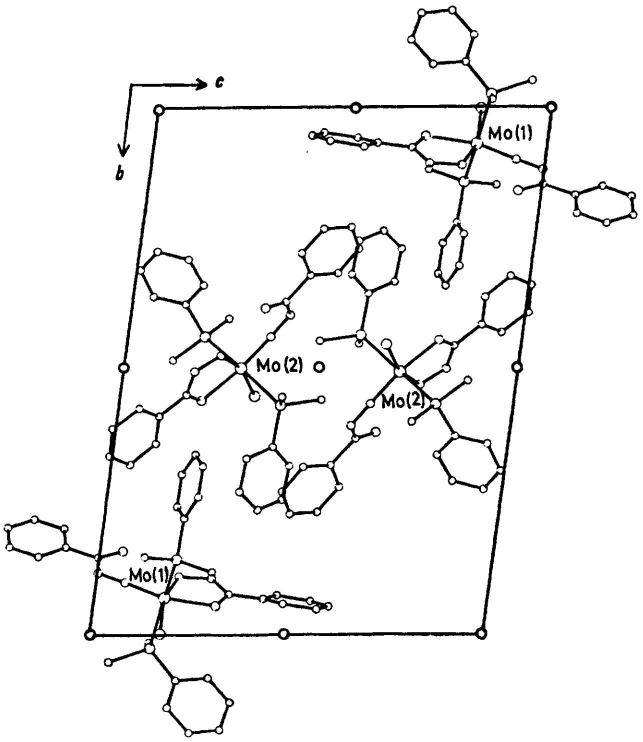


FIGURE 3 Packing diagram for [MoCl(N$_2$COPh)(NHNCOPh)(PMe$_2$Ph)$_2$]

One other feature, which must play a significant part in deciding the overall molecular conformations, is the contact of *ca.* 2.8 Å between O(M2) and N(M1), the carbonyl oxygen on the unidentate ligand and the protonated nitrogen in the chelate ring. In view of this contact and the appropriate coplanarity of the N(M2)-N(M4)C(M2)O(M2) unit with the chelate ring (see Table 4), this must be considered a hydrogen bond, and it is because of the great similarity between the two independent molecules in this context that we believe the two molecules are chemically equivalent, although we could not locate the proton in molecule 2. Finally, we mention that bond lengths and angles in the remaining portions of the molecule are, within experimental error, equal to standard values.

Figure 3 shows the unit-cell contents as viewed down the *b* axis, and the structure can be seen to pack as discrete monomeric units. The packing of the molecule is primarily determined by interactions of the bulky phenyl rings. Excluding possible hydrogen contacts, there are only five intermolecular contacts <3.6 Å. The smallest distance of 3.48 Å is between the atom C(6) of a phenyl ring and a methyl carbon atom C(8′).

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