Molybdenum(IV) Oxo-complexes. Part II.[1] Crystal and Molecular Structure of Dichlorotris(diethylphenylphosphine)oxomolybdenum(IV), *cis-mer*-[$MoOCl_2(PEt_2Ph)_3$].

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The molecular geometry of the title compound has been determined by *X*-ray crystal-structure analysis from diffractometer data. The crystals are monoclinic, space-group $P2_1/c$, $a = 12{\cdot}238(6)$, $b = 14{\cdot}818(10)$, $c = 21{\cdot}687(10)$ Å, $\beta = 121{\cdot}28(3)°$, $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0·081 for 2283 reflections.

The crystals are built of monomeric molecular units, with distorted octahedral co-ordination around the molybdenum atom. The molybdenum–ligand bond distances are: Mo–O 1·801(9), Mo–Cl (*trans* to O) 2·424(4), Mo–Cl (*trans* to P) 2·482(4), Mo–P (*trans* to Cl) 2·522(4), and Mo–P (*trans* to P) 2·580(5) and 2·553(5) Å.

THE blue and green forms of the complex *mer*-[$MoOCl_2(PMe_2Ph)_3$] are believed to be geometrical isomers with the oxygen atom *trans* to chlorine or phosphorus, respectively.[2] However, the spectral properties of the two isomers are so similar that it seemed desirable to subject their solids to an *X*-ray diffraction study of the molecular structures. In Part I we have shown that the molecular geometry of the blue form agrees with that predicted from spectroscopic data. Unfortunately, we were unable, at the time, to investigate the structure of the green isomer, for the attempts to obtain crystals suitable for *X*-ray analysis were not successful. Following the suggestion of Butcher and Chatt [2] that all green compounds of the series *mer*-[$MoOX_2L_3$] (where X = halogen or pseudo-halogen, and L = monotertiary phosphine) have the same configuration around the molybdenum atom, we have determined the crystal structure of the green complex *mer*-[$MoOCl_2(PEt_2Ph)_3$] (I).

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[1] Part I, Lj. Manojlović-Muir, *J. Chem. Soc.* (*A*), 1971, 2796.

[2] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

EXPERIMENTAL

The crystals are emerald-green, needle-like, prisms. They are stable in dry air, but decompose rapidly in solvents containing oxygen or moisture.[2]

Crystal Data.—$C_{30}H_{45}Cl_2MoOP_3$, $M = 681{\cdot}5$, monoclinic, $a = 12{\cdot}238(6)$*, $b = 14{\cdot}818(10)$, $c = 21{\cdot}687(10)$ Å, $\beta = 121{\cdot}28(3)°$, $U = 3361$ Å^3, $D_m = 1{\cdot}37$ (by flotation in aqueous zinc chloride), $Z = 4$, $D_c = 1{\cdot}346$, $F(000) = 1416$, Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 7·2 cm^{-1}. Space-group $P2_1/c$.

Measurements.—For the diffraction measurements, a crystal of dimensions 0·010 × 0·018 × 0·056 cm was mounted on a Hilger and Watts' Y290 four-circle diffractometer, controlled by a PDP 8 computer; the orientation of the crystal was such as to make b^* nearly coincident with the ϕ axis of the instrument. Molybdenum radiation was used, in conjunction with a zirconium filter and a pulse-height analyser. The unit-cell parameters, initially determined from X-ray photographs, were adjusted by a least-squares treatment of the setting angles of twelve manually centred reflections. The intensity measurements were made using the θ—2θ scan technique, with a scan step in 2θ of 0·02° and a counting time for each step of 1 s. Each reflection was scanned through a 2θ range of 1·60° (centred on the Mo-K_α peak), and the local background was counted for 20 s at each end of the scan range. To check the crystal and electronic stability, the intensities of two strong reflections were monitored periodically throughout the data collection, but no significant changes in their values were observed.

All independent reflections in the sphere with 2θ(Mo-K_α) $\leqslant 44{\cdot}0°$ were measured, and their integrated intensities, I, and corresponding variances, $\sigma^2(I)$, were derived as described previously.[1] The empirical factor, q, in the expression for $\sigma^2(I)$ was assigned a value of 0·04. Of 4019 measured reflections only 2283, for which $I \geqslant 3\sigma(I)$, were employed in the subsequent analysis. Their I and $\sigma(I)$ values were corrected for Lorentz and polarization effects, but not for absorption.

Structure Analysis.—The position of the molybdenum atom was determined from a three-dimensional Patterson function, and the positions of the other non-hydrogen atoms from subsequent difference syntheses. The structural model was refined by full-matrix least-squares. The function minimized, the expressions for the least-squares weights, w, and the weighted agreement factor, R', and also the computer programs used were as described in Part I.[1] The atomic scattering factors were taken from ref. 3, except those for molybdenum[4] and hydrogen.[5] The anomalous dispersion was accounted for in the structure-factor calculations, using Cromer's values[6] of $\Delta f'$ and $\Delta f''$ for molybdenum, chlorine, and phosphorus.

The refinement of the positional and isotropic thermal parameters of all non-hydrogen atoms brought R to 0·136. An allowance was then made for the anisotropic thermal vibrations of molybdenum, chlorine, phosphorus, and oxygen atoms and R decreased to 0·087. Benzene ring hydrogen atoms and those belonging to five (of the six) methylene groups were located in a low-angle difference synthesis based on data with $\sin\theta/\lambda \leqslant 0{\cdot}35$ Å^{-1}. All hydrogen atoms of these two types were included in the structure-factor calculations, but their parameters, derived from the known stereochemistry of the phenyl and methylene groups, were not refined. The refinement converged at R 0·081 and R' 0·081.

The final atomic parameters are shown in Table 1. In the last cycle of refinement all parameters shifted by $<0{\cdot}5\sigma$. The standard deviation of an observation of unit weight was 1·9. The adequacy of the weighting scheme was confirmed by an analysis of the variation of the mean $w\Delta^2$ (where $\Delta = |F_o| - |F_c|$) with $|F_o|$ and $\sin\theta/\lambda$. The extreme function values of 1·3 and −1·4 eÅ^{-3} in the final

TABLE 1

Final fractional co-ordinates (× 10^4) and thermal parameters of atoms

Atom	x	y	z	B/Å^2
Mo	1192·5(10)	2051·3(9)	3132·0(6)	*
Cl(1)	1665(4)	0458(3)	3377(2)	*
Cl(2)	2318(3)	2252(3)	4460(2)	*
P(1)	0070(3)	1489(3)	1848(2)	*
P(2)	3412(4)	2331(3)	3300(2)	*
P(3)	−0815(3)	1872(3)	3202(2)	*
O	0766(7)	3210(6)	2862(5)	*
C(1)	1053(13)	1113(10)	1493(7)	4·6(3)
C(2)	1871(13)	0408(10)	1826(7)	4·9(3)
C(3)	2643(14)	0075(11)	1588(8)	5·8(4)
C(4)	2585(16)	0467(13)	0993(9)	6·7(4)
C(5)	1785(16)	1144(12)	0652(9)	6·5(4)
C(6)	0981(14)	1467(11)	0888(8)	5·8(4)
C(7)	−1105(15)	2264(12)	1155(9)	6·2(4)
C(8)	−0745(17)	3181(13)	1097(9)	7·7(5)
C(9)	−0918(13)	0484(10)	1687(7)	4·7(3)
C(10)	−1577(16)	0041(12)	0928(9)	6·7(4)
C(11)	4592(13)	1482(10)	3694(8)	4·6(3)
C(12)	5068(17)	1211(13)	4404(10)	7·8(5)
C(13)	5997(19)	0452(14)	4742(10)	8·6(5)
C(14)	6395(16)	0090(13)	4378(10)	7·2(4)
C(15)	5960(17)	0300(13)	3713(10)	7·1(4)
C(16)	4996(15)	0941(12)	3319(8)	6·1(4)
C(17)	3511(17)	2654(13)	2507(9)	7·2(4)
C(18)	2771(28)	3475(22)	2121(16)	14·5(9)
C(19)	4097(20)	3309(15)	3892(11)	9·2(5)
C(20)	5469(30)	3551(23)	4119(17)	16·0(10)
C(21)	−2316(11)	2242(9)	2411(6)	3·2(3)
C(22)	−2453(12)	3068(10)	2177(7)	4·4(3)
C(23)	−3569(15)	3473(12)	1591(9)	6·2(4)
C(24)	−4575(14)	2841(12)	1226(8)	6·0(4)
C(25)	−4471(15)	2008(12)	1404(9)	6·4(4)
C(26)	−3313(13)	1631(10)	2027(8)	5·0(3)
C(27)	−1157(13)	0763(11)	3415(8)	5·3(3)
C(28)	−0222(16)	0475(12)	4203(9)	7·3(4)
C(29)	−0778(14)	2621(10)	3877(8)	5·3(3)
C(30)	−1986(16)	2573(12)	3963(9)	6·8(4)

* These atoms were assigned anisotropic temperature factors of the form: $\exp[-10^{-5}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The final values of the β_{ij} parameters are:

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	582(11)	723(9)	220(4)	−3(9)	111(5)	−66(5)
Cl(1)	1165(46)	672(28)	303(13)	157(28)	236(20)	44(16)
Cl(2)	821(40)	1199(39)	230(12)	199(31)	41(18)	−178(18)
P(1)	819(42)	687(29)	197(12)	142(26)	179(19)	42(15)
P(2)	773(41)	576(29)	425(16)	−28(26)	248(21)	−67(17)
P(3)	660(35)	619(28)	190(11)	63(24)	136(16)	24(14)
O	444(81)	652(67)	347(32)	59(55)	124(42)	86(37)

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* Throughout the paper limits of error are estimated standard deviations. They are derived from the appropriate least-squares matrix or, in the case of mean values, from the range of individual measurements, and are given in the units of the least significant digit of the quantities to which they refer.

[3] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

difference synthesis were close to the position of the molybdenum atom. The average peak-height of the carbon atoms in the final electron-density synthesis was 4·5 eÅ^{-3}. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20287 (8 pp., 1 microfiche).*

TABLE 2

Molecular geometry of *cis-mer*-[$MoOCl_2(PEt_2Ph)_3$]

(*a*) Bond lengths (Å)

Mo–Cl(1)	2·424(4)	C(29)–C(30)	1·58(3)
Mo–Cl(2)	2·482(4)	C(1)–C(2)	1·37(2)
Mo–P(1)	2·522(4)	C(2)–C(3)	1·38(3)
Mo–P(2)	2·580(5)	C(3)–C(4)	1·39(3)
Mo–P(3)	2·553(5)	C(4)–C(5)	1·33(2)
Mo–O	1·801(9)	C(5)–C(6)	1·41(3)
P(1)–C(1)	1·82(2)	C(6)–C(1)	1·37(3)
P(1)–C(7)	1·84(2)	C(11)–C(12)	1·39(3)
P(1)–C(9)	1·83(2)	C(12)–C(13)	1·49(3)
P(2)–C(11)	1·77(1)	C(13)–C(14)	1·25(4)
P(2)–C(17)	1·85(2)	C(14)–C(15)	1·29(3)
P(2)–C(19)	1·83(2)	C(15)–C(16)	1·41(2)
P(3)–C(21)	1·83(1)	C(16)–C(11)	1·40(3)
P(3)–C(27)	1·81(2)	C(21)–C(22)	1·30(2)
P(3)–C(29)	1·82(2)	C(22)–C(23)	1·43(2)
C(7)–C(8)	1·45(3)	C(23)–C(24)	1·42(2)
C(9)–C(10)	1·55(2)	C(24)–C(25)	1·28(3)
C(17)–C(18)	1·49(4)	C(25)–C(26)	1·47(2)
C(19)–C(20)	1·53(4)	C(26)–C(21)	1·40(2)
C(27)–C(28)	1·54(2)		

(*b*) Bond angles (°)

P(1)–Mo–P(2)	98·0(2)	C(27)–P(3)–C(29)	105·1(8)
P(1)–Mo–P(3)	92·4(1)	P(1)–C(1)–C(2)	118·2(14)
P(1)–Mo–Cl(1)	81·5(1)	P(1)–C(1)–C(6)	123·9(12)
P(1)–Mo–Cl(2)	167·6(2)	P(2)–C(11)–C(12)	120·6(15)
P(1)–Mo–O	93·2(3)	P(2)–C(11)–C(16)	125·0(11)
P(2)–Mo–P(3)	169·6(1)	P(3)–C(21)–C(22)	120·7(9)
P(2)–Mo–Cl(1)	90·7(2)	P(3)–C(21)–C(26)	120·4(10)
P(2)–Mo–Cl(2)	84·7(2)	P(1)–C(7)–C(8)	120·6(11)
P(2)–Mo–O	90·0(3)	P(1)–C(9)–C(10)	118·2(13)
P(3)–Mo–Cl(1)	90·7(2)	P(2)–C(17)–C(18)	114·8(21)
P(3)–Mo–Cl(2)	85·1(1)	P(2)–C(19)–C(20)	116·2(21)
P(3)–Mo–O	89·6(3)	P(3)–C(27)–C(28)	113·3(10)
Cl(1)–Mo–Cl(2)	86·4(2)	P(3)–C(29)–C(30)	115·6(10)
Cl(1)–Mo–O	174·7(3)	C(1)–C(2)–C(3)	122·0(16)
Cl(2)–Mo–O	98·9(3)	C(2)–C(3)–C(4)	119·0(15)
Mo–P(1)–C(1)	117·9(4)	C(3)–C(4)–C(5)	120·1(21)
Mo–P(1)–C(7)	116·2(6)	C(4)–C(5)–C(6)	120·6(20)
Mo–P(1)–C(9)	113·9(5)	C(5)–C(6)–C(1)	120·4(14)
Mo–P(2)–C(11)	119·4(6)	C(6)–C(1)–C(2)	117·8(17)
Mo–P(2)–C(17)	118·9(6)	C(11)–C(12)–C(13)	122·4(21)
Mo–P(2)–C(19)	107·0(9)	C(12)–C(13)–C(14)	117·5(20)
Mo–P(3)–C(21)	116·2(5)	C(13)–C(14)–C(15)	122·4(19)
Mo–P(3)–C(27)	117·8(6)	C(14)–C(15)–C(16)	124·9(22)
Mo–P(3)–C(29)	111·2(6)	C(15)–C(16)–C(11)	118·1(16)
C(1)–P(1)–C(7)	104·7(8)	C(16)–C(11)–C(12)	113·8(15)
C(1)–P(1)–C(9)	100·7(8)	C(21)–C(22)–C(23)	127·7(13)
C(7)–P(1)–C(9)	101·1(7)	C(22)–C(23)–C(24)	111·9(14)
C(11)–P(2)–C(17)	101·7(9)	C(23)–C(24)–C(25)	123·2(13)
C(11)–P(2)–C(19)	105·3(8)	C(24)–C(25)–C(26)	122·8(14)
C(17)–P(2)–C(19)	102·7(11)	C(25)–C(26)–C(21)	115·4(13)
C(21)–P(3)–C(27)	105·0(6)	C(26)–C(21)–C(22)	118·8(10)
C(21)–P(3)–C(29)	99·5(6)		

(*c*) Selected intramolecular contacts (Å)

O ··· Cl(2)	3·29	Cl(2) ··· P(2)	3·41
O ··· P(1)	3·18	Cl(2) ··· P(3)	3·41
O ··· P(2)	3·15	Cl(2) ··· C(19)	3·39
O ··· P(3)	3·11	Cl(2) ··· C(29)	3·36
Cl(1) ··· Cl(2)	3·36	P(1) ··· P(2)	3·85
Cl(1) ··· P(1)	3·23	P(1) ··· P(3)	3·66
Cl(1) ··· P(2)	3·56	P(2) ··· C(1)	3·90
Cl(1) ··· P(3)	3·54	P(3) ··· C(9)	3·82
Cl(1) ··· C(2)	3·50	C(1) ··· C(17)	3·50
Cl(1) ··· C(9)	3·38	C(2) ··· C(16)	3·59
Cl(1) ··· C(27)	3·53	C(3) ··· C(16)	3·58
Cl(1) ··· C(28)	3·58	C(7) ··· C(22)	3·58

TABLE 2 (*Continued*)

(*d*) Mean planes through various sets of atoms

(i) Displacements (Å) of atoms from the planes. Atoms not included in the derivation of planes are italicized

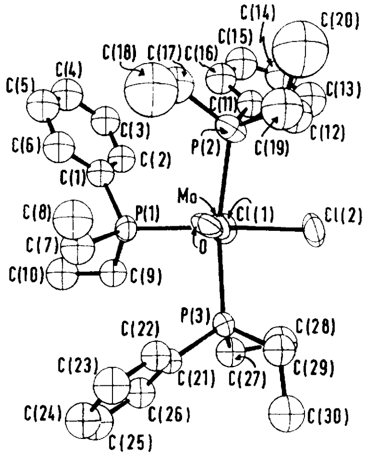
Plane (A)		Plane (B)		Plane (C)	
P(1)	−0·029	P(1)	−0·128	O	−0·187
O	0·029	P(2)	0·139	Cl(1)	−0·136
Cl(1)	0·028	P(3)	0·146	P(2)	0·160
Cl(2)	−0·027	Cl(2)	−0·157	P(3)	0·163
Mo	0·029	*Mo*	0·123	*Mo*	−0·070

Plane (D)		Plane (E)		Plane (F)	
C(1)	−0·017	C(11)	−0·042	C(21)	−0·025
C(2)	0·003	C(12)	−0·004	C(22)	0·026
C(3)	0·009	C(13)	0·041	C(23)	−0·006
C(4)	−0·007	C(14)	−0·026	C(24)	−0·016
C(5)	−0·006	C(15)	−0·027	C(25)	0·016
C(6)	0·018	C(16)	0·059	C(26)	0·003
P(1)	−0·005	*P(2)*	0·022	*P(3)*	−0·049

(ii) Equations of planes

$$\begin{array}{lrcl}
(A) & -12{\cdot}135x - 1{\cdot}913y + 10{\cdot}997z & = & 1{\cdot}634 \\
(D) & 5{\cdot}829x + 9{\cdot}677y + 5{\cdot}551z & = & 2{\cdot}503 \\
(E) & 8{\cdot}437x + 9{\cdot}848y - 2{\cdot}421z & = & 4{\cdot}397 \\
(F) & -9{\cdot}400x + 3{\cdot}409y + 19{\cdot}725z & = & 7{\cdot}672
\end{array}$$

Throughout the refinement, the thermal parameters of some carbon atoms were rather large. For C(18) and C(20) the final *B* values are so high as to suggest a slight positional disorder, but no evidence for such disorder could be found in any of the difference syntheses. Furthermore, in the molecular model refined no allowance has been made for the anisotropic thermal vibration of the carbon atoms. The range of the chemically equivalent C(sp^2)–C(sp^2) bonds is greater than can be accounted for in terms of the least-squares standard deviations (Table 2). However, although the structural model of the groups attached to the phosphorus atoms is somewhat approximate, the parameters of the molybdenum atom and of the atoms bonded to molybdenum are unlikely to be systematically in error, for they are not strongly correlated with those of the carbon atoms. Moreover, the amplitudes of vibration of the molybdenum, chlorine, phosphorus, and oxygen atoms are normal (Figure, Table 3).



The molecular structure of *cis-mer*-[$MoOCl_2(PEt_2Ph)_3$]. The thermal motion ellipsoids enclose 50% of probability

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No 20.

TABLE 3

Root-mean-square amplitudes of vibration (Å) along principal axes of thermal ellipsoids

Atom	Axis (1)	Axis (2)	Axis (3)
Mo	0·172	0·220	0·289
Cl(1)	0·221	0·261	0·292
Cl(2)	0·172	0·243	0·395
P(1)	0·183	0·217	0·283
P(2)	0·206	0·245	0·295
P(3)	0·176	0·212	0·264
O	0·155	0·250	0·291

DISCUSSION

The crystal structure of *cis-mer*-[$MoOCl_2(PEt_2Ph)_3$] (I) is built of monomeric molecular units. All intermolecular interactions are of the van der Waals type (Table 4).

TABLE 4

Intermolecular distances $\leqslant$3·80 Å

C(13) ··· C(13^{I})	3·44	C(10) ··· C(5^{V})	3·74
O ··· C(9^{II})	3·49	C(10) ··· C(4^{V})	3·75
C(28) ··· C(28^{III})	3·50	Cl(2) ··· C(24^{VI})	3·75
O ··· C(10^{II})	3·54	C(8) ··· C(28^{II})	3·77
C(20) ··· C(30^{IV})	3·61	C(20) ··· C(4^{VII})	3·79
C(13) ··· C(12^{I})	3·70	C(23) ··· C(15^{II})	3·79
C(23) ··· Cl(1^{II})	3·73	C(18) ··· C(27^{II})	3·79

The superscripts refer to the following transformations of the atomic co-ordinates x, y, z:

I $1 - x, -y, 1 - z$
II $-x, \frac{1}{2} + y, \frac{1}{2} - z$
III $-x, -y, 1 - z$
IV $1 + x, y, z$
V $-x, -y, -z$
VI $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
VII $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

The molecular structure of the complex (Figure) differs significantly from that deduced from spectroscopic data.[2] As expected, the co-ordination polyhedron around the molybdenum atom is a highly distorted octahedron and the arrangement of the phosphine ligands is meridional. Surprisingly, the oxygen atom is *trans* to chlorine. The configuration of ligands around the molybdenum atom is therefore the same as in the blue isomer of *cis-mer*-[$MoOCl_2(PMe_2Ph)_3$] [1] (II). However, the details of the molecular geometries of these closely related complexes show some unexpected differences.

The Mo–O bond length is 1·801(9), whereas in (II) it is only 1·676(7) Å. However, the Mo–O stretching frequency in (I) of 940 is close to that in (II) of 954 cm^{-1}, and they are both in the range expected for Mo–O multiple bonds.[2] Furthermore, the comparable Mo–O distance of 1·834(9) Å in *trans*-[$MoO_2(CN)_4$]$^{4-}$ is believed to indicate considerable multiple-bonding character.[7]

The Mo–Cl (*trans* to O) distance is 2·424(4), and the corresponding one in (II) is 2·551(3) Å. The shortening of this bond in (I) appears to be related to the longer Mo–O distance, which implies a smaller donation of charge density from oxygen to molybdenum, compared with (II), and consequently weaker electrostatic repulsion of the *trans* chlorine atom.[8-11] The Mo–Cl (*trans* to P) distance of 2·482(4) is comparable with the analogous one in (II) of 2·464(3) Å and, likewise, it reflects the *trans*-influence (*ca.* 0·1 Å) of a co-ordinated tertiary phosphine in octahedral complexes.[12]

The Mo–P (*trans* to Cl) bond is 2·522(4) Å, and the mean length of the Mo–P (*trans* to P) bonds is 2·567(14) Å. These values may be compared with the corresponding ones in (II) of 2·500(3) and 2·550(9) Å, and with the mean W–P (*trans* to P) distance of 2·550(3) Å in [$WCl_4(PMe_2Ph)_2$].[12]

The geometry of the phosphine ligands is comparable with that in (II). The mean P–C(sp^2) and P–C(sp^3) distances of 1·805(20) and 1·831(6) Å, respectively, are consistent with those found in other co-ordinated tertiary phosphines.[13] The mean C(sp^2)–C(sp^2) and C(sp^3)–C(sp^3) distances are 1·375(15) and 1·525(19) Å, respectively. All phenyl rings are planar within the limits of experimental error (Table 2). On average, the Mo–P–C angles are somewhat larger, and the C–P–C angles somewhat smaller than the tetrahedral value. Such a pattern is commonly observed in co-ordinated phosphines.[13,14] An interesting feature, however, is the increase of the angles subtended at methylene carbon atoms by 3—10° from the tetrahedral value.

The orientation of the organic substituents on the phosphorus atoms with respect to the co-ordination polyhedron around molybdenum (Figure) is different from that in (II). This may be a consequence of the different steric requirements of the PMe_2Ph and PEt_2Ph ligands. As a result, the C_s molecular symmetry of (II) is not preserved in (I).

The only meridional plane in the octahedron around molybdenum, which can be considered planar, is that defined by the atoms O, Cl(1), Cl(2), and P(1). In this plane, electrostatic repulsion between anionic ligands appears to be the dominant factor in determining the angular distortions from ideal octahedral geometry (see Part I). The non-bonding O ··· Cl(2) and Cl(1) ··· Cl(2) contacts of 3·29 and 3·36 Å respectively are comparable with those of 3·33 and 3·41 Å in (II). In (I), where the Mo–O bond is longer than in (II), such contacts are achieved with much smaller angular distortions. Thus, the O–Mo–Cl(2) and Cl(1)–Mo–P(1) angles are, respectively, 98·9(3) and 81·5(1)° in (I) and 105·7(3) and 76·9(1)° in (II). In both complexes the acute Cl(1)–Mo–P(1) angles are coupled with very short Cl(1) ··· P(1) contacts. In (I), however, this contact is 3·23 Å, compared with 3·14 Å in (II), and some of the strain in this part of the molecule is relieved,

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despite the shorter Mo–Cl (*trans* to O) bond. In the crowded P(1), P(2), P(3), Cl(2) plane the distortions are mainly due to the steric requirements of the bulky phosphine ligands, as indicated by some short contacts between carbon atoms of different phosphine ligands (Table 2).

The factor which causes the differences in the molecular geometries of these closely related complexes still remains obscure. It could be that the two geometries reflect different steric requirements and electronic properties of the PEt_2Ph and PMe_2Ph ligands. However, according to Butcher and Chatt's spectroscopic investigation of these and related complexes,[2] the configuration of the green isomer of (II) is the same as that of (I). Recently, Chatt and Dilworth have succeeded in isolating crystals of the green isomer of (II), and an *X*-ray crystal structure analysis of this complex is now in progress.

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