Metal–Carbonyl and Metal–Nitrosyl Complexes. Part XIII.[1] *X*-Ray Study of the Molecular Structures of π-Cyclopentadienyl- and π-(Methylcyclopentadienyl)-*trans*-iododicarbonyl(trimethyl phosphite)molybdenum

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The molecular geometries of π-cyclopentadienyl- and π-(methylcyclopentadienyl)-*trans*-iododicarbonyl(trimethyl phosphite)molybdenum [(I) and (II)] have been determined by *X*-ray crystal-structure analysis. The Mo–P distances [2·406(9) and 2·388(8) Å] are significantly shorter than in π-cyclopentadienyl-*trans*-iododicarbonyl(triphenylphosphine)molybdenum (III) [2·481(5) Å], whereas the Mo–I distances [2·836(4) and 2·850(3) Å in (I) and (II); 2·858(3) Å in (III)] are essentially constant. Both (I) and (II) crystallize in the orthorhombic space group $P2_12_12_1$, with $Z = 4$ in unit cells of dimensions: (I), $a = 10·75$, $b = 16·60$, $c = 8·57$ (all ±0·01) Å; (II), $a = 16·317(6)$, $b = 11·323(3)$, $c = 8·740(2)$ Å. Photographic data were used for (I) and diffractometer data for (II). The structures were solved by Patterson and Fourier methods and refined by least squares to *R* 7·8% [(I), 906 reflections] and 5·9% [(II), 1847 reflections].

THOUGH many tertiary-phosphine (PR_3) complexes of transition metals have featured in *X*-ray crystallographic studies,[2] relatively few phosphite [$P(OR)_3$] complexes have been examined. Where comparisons can be made, however, it appears that a metal–phosphite M–P bond is significantly shorter than the analogous metal–phosphine bond. Since we had previously determined the molecular geometry of π-cyclopentadienyl-*trans*-iododicarbonyl(triphenylphosphine)molybdenum (III),[3] we undertook *X*-ray studies of π-cyclopentadienyl- and π-methylcyclopentadienyl-*trans*-iododicarbonyl(trimethyl phosphite)molybdenum (I) and (II) in order to compare molybdenum–phosphite and –phosphine bonds in very similar molecular environments. The atomic co-ordinates were derived by Fourier and least-squares methods and are shown in Tables 1 and 2.

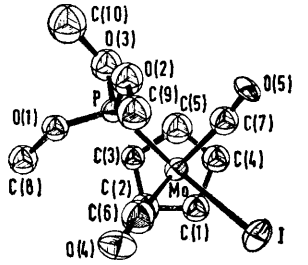

FIGURE 1 The molecular structure of $(\pi\text{-}C_5H_5)Mo(CO)_2[P(OMe)_3]I$ (I), viewed along the normal to the C_5H_5-plane

Views of the molecular structures are provided in Figures 1 and 2, and the molecular dimensions are listed in Tables 3 and 4.

The Mo–P bond lengths are 2·406(9) in (I), 2·388(8) in (II), and 2·481(5) Å in (III), *i.e.* the molybdenum–phosphite bond is *ca.* 0·1 Å shorter than the molybdenum–phosphine bond. The Cr–P bonds in pentacarbonyl(triphenyl phosphite)chromium and pentacarbonyl(triphenylphosphine)chromium have lengths of 2·309 and 2·422 Å,[4] so that here also there is a difference of *ca.* 0·1 Å. Precise comparisons of this sort cannot be made in other cases, but several pertinent results can be cited. The Fe–P mean bond distance in $(\pi\text{-}C_5H_5)Fe[P(OPh)_3]_2I$ is 2·15 Å [5] whereas that in $Fe_3(CO)_{11}(PPh_3)$ [6] and $Fe_3(CO)_9(PMe_2Ph)_3$ [7] is 2·24 Å, and the Ir–P mean bond length of

TABLE 1

Atomic co-ordinates (as fractions of the cell edges) and thermal parameters (Å^2) for (I) with standard deviations in parentheses

	x	*y*	*z*	*B*
C(1)	0·4088(33)	0·5193(21)	0·7269(45)	4·54(64)
C(2)	0·4997(43)	0·5224(21)	0·6046(42)	5·46(79)
C(3)	0·4651(29)	0·4554(17)	0·5079(36)	3·50(52)
C(4)	0·3167(37)	0·4541(21)	0·7033(43)	4·52(73)
C(5)	0·3529(42)	0·4154(25)	0·5693(57)	5·80(89)
C(6)	0·6988(43)	0·4066(26)	0·8000(56)	5·75(96)
C(7)	0·4480(32)	0·2958(21)	0·8481(45)	4·27(66)
C(8)	0·7772(36)	0·3783(21)	0·4105(45)	4·54(69)
C(9)	0·7311(42)	0·2007(27)	0·8040(53)	5·43(83)
C(10)	0·5764(56)	0·2002(37)	0·3462(70)	7·84(133)
O(1)	0·7415(19)	0·3035(12)	0·5046(23)	3·56(40)
O(2)	0·6361(27)	0·2063(18)	0·6655(32)	5·28(54)
O(3)	0·5252(28)	0·2656(15)	0·4523(35)	5·37(55)
O(4)	0·7950(28)	0·4161(16)	0·8295(36)	†
O(5)	0·4046(43)	0·2415(20)	0·8835(38)	†
P	0·6083(8)	0·2922(5)	0·5857(10)	†
Mo	0·5154(2)	0·3953(1)	0·7450(3)	†
I	0·5127(3)	0·4328(2)	1·0679(3)	

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

	β_{11}	β_{22}	β_{33}
O(4)	1212(310)	489(112)	1930(531)
O(5)	3532(700)	735(156)	1862(636)
P	876(73)	265(23)	1156(256)
Mo	777(17)	319(6)	901(222)
I	1720(41)	648(12)	911(225)
	β_{12}	β_{12}	β_{23}
O(4)	−125(136)	−570(300)	30(180)
O(5)	−1355(288)	1584(478)	−381(225)
P	−32(38)	−46(77)	−10(44)
Mo	−57(11)	−13(29)	−37(14)
I	−221(20)	114(30)	−120(17)

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TABLE 2

Atomic co-ordinates (as fractions of the cell edges) and thermal parameters (Å^2) for (II) with standard deviations in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached

	x	y	z	B
C(1)	−0·7053(21)	0·3942(32)	0·5245(43)	3·87(69)
C(2)	−0·6570(22)	0·3656(34)	0·6559(46)	4·46(76)
C(3)	−0·6875(21)	0·2671(29)	0·7284(38)	3·61(63)
C(4)	−0·7671(18)	0·3060(29)	0·5150(38)	3·50(55)
C(5)	−0·7613(22)	0·2311(33)	0·6425(43)	4·49(74)
C(6)	−0·5354(20)	0·2693(30)	0·3995(38)	3·80(63)
C(7)	−0·6444(21)	0·0346(30)	0·4476(38)	3·51(58)
C(8)	−0·4455(22)	0·1946(35)	0·9005(40)	4·15(69)
C(9)	−0·4396(25)	0·0081(38)	0·4646(50)	5·56(91)
C(10)	−0·6217(23)	−0·0249(32)	0·8224(45)	4·39(72)
C(11)	−0·6996(24)	0·4949(36)	0·4103(47)	4·66(82)
O(1)	−0·5046(15)	0·2212(23)	0·7775(26)	4·48(48)
O(2)	−0·4456(14)	0·0973(20)	0·5817(26)	3·79(43)
O(3)	−0·5484(16)	0·0072(23)	0·7482(31)	4·69(52)
O(4)	−0·4815(14)	0·3121(28)	0·3469(30)	†
O(5)	−0·6571(15)	−0·0607(22)	0·4245(30)	†
P	−0·5336(5)	0·1293(7)	0·6562(9)	†
Mo	−0·6376(1)	0·2091(2)	0·4942(3)	†
I	−0·6784(2)	0·2057(3)	0·1771(2)	†
H(2)	−0·5999	0·4155	0·6991	5·3
H(3)	−0·6628	0·2149	0·8226	2·6
H(4)	−0·8130	0·2974	0·4296	3·3
H(5)	−0·8050	0·1658	0·6781	4·3
H(8*a*)	−0·4039	0·2941	0·8929	4·3
H(8*b*)	−0·4760	0·1471	0·9821	4·3
H(8*c*)	−0·4039	0·0956	0·8929	4·3
H(9*a*)	−0·3798	−0·0588	0·4911	5·4
H(9*b*)	−0·4760	−0·0588	0·4911	5·4
H(9*c*)	−0·4471	0·0000	0·3750	5·4
H(10*a*)	−0·6016	−0·1029	0·8750	4·4
H(10*b*)	−0·6779	0·0515	0·7411	4·4
H(10*c*)	−0·6442	0·0147	0·8929	4·4
H(11*a*)	−0·6731	0·5515	0·4732	4·8
H(11*b*)	−0·7500	0·6029	0·3750	4·8
H(11*c*)	−0·6490	0·4044	0·3571	4·8

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

	β_{11}	β_{22}	β_{33}
O(4)	385(102)	2010(377)	2208(434)
O(5)	486(130)	790(220)	1661(411)
P	237(27)	476(56)	908(97)
Mo	233(6)	550(14)	665(22)
I	558(11)	1243(26)	720(22)

	β_{12}	β_{13}	β_{23}
O(4)	−340(172)	77(178)	1272(382)
O(5)	−57(133)	−248(187)	−254(252)
P	64(36)	−43(44)	−4(68)
Mo	1(12)	−5(13)	4(27)
I	−104(19)	−72(14)	42(29)

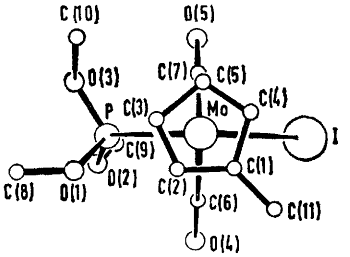

FIGURE 2 The molecular structure of (π-MeC$_5$H$_4$)Mo(CO)$_2$-[P(OMe)$_3$]I (II), viewed along the normal to the C$_5$H$_4$-plane

TABLE 3

Molecular dimensions of (I)

(*a*) Bond lengths (Å)

Mo–I	2·836(4)	P–O(3)	1·515(31)
Mo–P	2·406(9)	O(1)–C(8)	1·529(42)
Mo–C(6)	2·035(46)	O(2)–C(9)	1·568(53)
Mo–C(7)	2·008(36)	O(3)–C(10)	1·519(66)
Mo–C(1)	2·362(35)	O(4)–C(6)	1·075(55)
Mo–C(2)	2·435(36)	O(5)–C(7)	1·059(51)
Mo–C(3)	2·326(31)	C(1)–C(2)	1·433(55)
Mo–C(4)	2·375(39)	C(1)–C(4)	1·481(51)
Mo–C(5)	2·329(47)	C(2)–C(3)	1·436(47)
P–O(1)	1·602(22)	C(3)–C(5)	1·473(55)
P–O(2)	1·610(31)	C(4)–C(5)	1·371(60)

(*b*) Valency angles (°)

I–Mo–P	135·6(0·2)	O(2)–P–O(3)	99·9(1·5)
I–Mo–C(6)	76·3(1·3)	P–O(1)–C(8)	123·2(2·0)
I–Mo–C(7)	75·4(1·1)	P–O(2)–C(9)	119·6(2·5)
P–Mo–C(6)	78·2(1·3)	P–O(3)–C(10)	116·5(3·0)
P–Mo–C(7)	79·3(1·1)	Mo–C(6)–O(4)	176·9(3·8)
C(6)–Mo–C(7)	108·9(1·6)	Mo–C(7)–O(5)	169·9(3·6)
Mo–P–O(1)	122·2(0·8)	C(2)–C(1)–C(4)	112·4(3·2)
Mo–P–O(2)	117·8(1·1)	C(1)–C(2)–C(3)	102·5(3·2)
Mo–P–O(3)	113·0(1·1)	C(2)–C(3)–C(5)	110·8(3·2)
O(1)–P–O(2)	97·0(1·3)	C(1)–C(4)–C(5)	105·5(3·4)
O(1)–P–O(3)	103·5(1·4)	C(3)–C(5)–C(4)	108·6(3·5)

(*c*) Deviations (Å) of the atoms from the mean plane of the π-cyclopentadienyl ring

C(1)	0·012	C(5)	−0·002
C(2)	−0·013	I	3·106
C(3)	0·009	Mo	2·023
C(4)	−0·007	P	2·921

TABLE 4

Molecular dimensions of (II)

(*a*) Bond lengths (Å)

Mo–I	2·850(3)	O(1)–C(8)	1·474(43)
Mo–P	2·388(8)	O(2)–C(9)	1·441(49)
Mo–C(6)	1·983(34)	O(3)–C(10)	1·408(46)
Mo–C(7)	2·020(34)	O(4)–C(6)	1·105(42)
Mo–C(1)	2·384(36)	O(5)–C(7)	1·117(42)
Mo–C(2)	2·288(39)	C(1)–C(2)	1·430(54)
Mo–C(3)	2·298(34)	C(1)–C(4)	1·421(47)
Mo–C(4)	2·387(30)	C(2)–C(3)	1·376(51)
Mo–C(5)	2·411(37)	C(3)–C(5)	1·476(50)
P–O(1)	1·559(26)	C(4)–C(5)	1·404(50)
P–O(2)	1·618(24)	C(1)–C(11)	1·518(55)
P–O(3)	1·617(27)		

(*b*) Valency angles (°)

I–Mo–P	137·5(0·2)	P–O(1)–C(8)	123·9(2·3)
I–Mo–C(6)	78·2(1·0)	P–O(2)–C(9)	120·2(2·2)
I–Mo–C(7)	77·2(1·0)	P–O(3)–C(10)	125·2(2·3)
P–Mo–C(6)	77·3(1·0)	Mo–C(6)–O(4)	173·9(3·2)
P–Mo–C(7)	77·8(1·0)	Mo–C(7)–O(5)	172·4(3·0)
C(6)–Mo–C(7)	107·3(1·4)	C(2)–C(1)–C(4)	106·2(3·1)
Mo–P–O(1)	111·5(1·0)	C(2)–C(1)–C(11)	131·6(3·3)
Mo–P–O(2)	118·5(0·9)	C(4)–C(1)–C(11)	122·2(3·2)
Mo–P–O(3)	120·8(1·0)	C(1)–C(2)–C(3)	110·7(3·2)
O(1)–P–O(2)	98·8(1·3)	C(2)–C(3)–C(5)	106·5(3·0)
O(1)–P–O(3)	106·1(1·4)	C(1)–C(4)–C(5)	109·3(3·0)
O(2)–P–O(3)	98·1(1·3)	C(3)–C(5)–C(4)	107·0(3·0)

(*c*) Deviations (Å) of the atoms from the mean plane through atoms C(1)—(5) of the π-methylcyclopentadienyl ring

C(1)	−0·018	C(11)	−0·086
C(2)	−0·001	I	3·185
C(3)	0·018	Mo	2·017
C(4)	0·030	P	2·761
C(5)	−0·030		

2·25 Å in IrCl[P(OPh)$_2$(OC$_6$H$_4$)]$_2$[P(OPh)$_3$] [8] is *ca.* 0·15 Å shorter than that found in various six-co-ordinate triphenylphosphine–iridium complexes.[9] Moreover, the Rh–P bond length (2·14 Å) in di-μ-chloro-bis(triphenyl

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phosphite)(cyclo-octa-1,5-diene)dirhodium[10] is appreciably shorter than the mean (2·32 Å) in $RhH(CO)(PPh_3)_3$.[11] It is also relevant that the Co–P bond distances in $HCo[P(OEt)_2Ph]_4$[12] are 0·06—0·10 Å shorter than those in $HCo(N_2)(PPh_3)_3$.[13] All these results are consistent with the π-bonding capability of the phosphite ligand being greater than that of the phosphine ligand.

The Mo–P–O and O–P–O angles in the trimethyl phosphite ligands have mean values of 117·3 and 100·6°. The C–P–C angles in triphenylphosphine complexes are also substantially smaller than tetrahedral, *e.g.* 103·4° in $(\pi\text{-}C_5H_5)Mo(CO)_2(COMe)(PPh_3)$[14] and 103·9° in $[(Ph_3P)_2Cu]BH_4$,[15] but larger than the O–P–O angles in the phosphite complexes. These results suggest that the *s* component of the phosphorus orbital directed towards an atom is reduced as the electronegativity of the atom is increased.[16] The P–O bond lengths in the phosphite ligands (mean 1·59 Å) must have some double-bond character, for they are shorter than the P–C bonds (1·83 Å) in triphenylphosphine[17] by an amount which cannot be accounted for by the difference between the covalent radii of oxygen (0·66 Å) and carbon (0·77 Å) atoms.

TABLE 5

Intermolecular separations (< 3·8 Å) in the crystal structure of (I)

$C(1) \cdots O(2^{III})$	3·27	$C(10) \cdots C(4^{II})$	3·66
$O(1) \cdots O(3^{II})$	3·28	$O(2) \cdots C(5^{II})$	3·68
$C(1) \cdots C(9^{III})$	3·38	$O(4) \cdots C(3^{I})$	3·68
$O(4) \cdots C(2^{I})$	3·39	$C(6) \cdots C(8^{I})$	3·70
$O(5) \cdots C(8^{II})$	3·49	$C(8) \cdots O(3^{II})$	3·77
$O(4) \cdots C(8^{I})$	3·57	$C(2) \cdots O(5^{III})$	3·78
$C(10) \cdots C(5^{II})$	3·61		

The superscripts refer to the following transformations of the atomic co-ordinates:

I $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$ III $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$

II $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$

TABLE 6

Intermolecular separations (< 3·8 Å) in the crystal structure of (II)

$O(2) \cdots C(4^{I})$	3·22	$O(4) \cdots C(5^{I})$	3·63
$O(1) \cdots O(3^{III})$	3·36	$O(1) \cdots C(10^{III})$	3·64
$C(9) \cdots C(4^{I})$	3·52	$C(11) \cdots C(8^{III})$	3·67
$O(4) \cdots O(5^{II})$	3·58	$O(4) \cdots C(9^{II})$	3·74
$C(8) \cdots O(5^{II})$	3·58	$C(8) \cdots O(3^{III})$	3·77

The superscripts refer to the following transformations of the atomic co-ordinates:

I $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ III $-1 - x, \frac{1}{2} + y, \frac{3}{2} - z$

II $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

The mean Mo–CO distance in (I) and (II) is 2·011(15) Å, whereas in (III) it is 1·983(14) Å. Though the difference cannot properly be regarded as significant, nevertheless the change is in the direction demanded by the increased M → P, and hence decreased M → CO, π-bonding in the phosphite complexes. The Mo–I distance is essentially unaffected by interchange of the phosphite and phosphine ligands.

The mean I–Mo–P and OC–Mo–CO angles in (I) and (II) are 136·6 and 108·1°, and the corresponding angles in (III) are 140·9 and 105·3°. For comparison, the P–Mo–P and OC–Mo–NCO angles in $(\pi\text{-}C_5H_5)Mo(PPh_3)_2(CO)NCO$ are 133 and 112°,[18] the P–Mo–COMe and OC–Mo–CO angles in $(\pi\text{-}C_5H_5)Mo(CO)_2(COMe)(PPh_3)$ are 133 and 108°,[14] and the OC–Mo–C_3F_7 and OC–Mo–CO-(*trans*) angles in $(\pi\text{-}C_5H_5)Mo(CO)_3(C_3F_7)$ are 132 and 117°.[19] These results suggest that as one *trans*-angle at the metal is reduced in size the other increases, though it is by no means clear whether the effect is electronic or steric in origin. The *cis*-valency angles in all these complexes lie in the range 73—80°.

The Mo–C(π-C_5H_5) distances in (I) range from 2·326 to 2·435, mean 2·365 Å. The distances in (II) range from 2·288 to 2·411, mean 2·354 Å. The mean Mo–C(π-C_5H_5) distance is 2·333 Å in (III) and 2·347 Å in $(\pi\text{-}C_5H_5)Mo(CO)_2(COMe)(PPh_3)$.

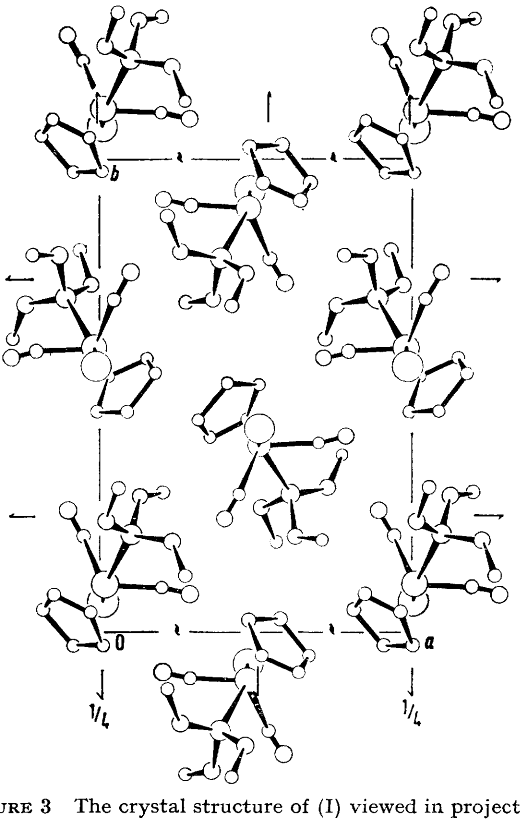

FIGURE 3 The crystal structure of (I) viewed in projection along the *c* axis

The arrangements of the molecules in the crystals are shown in Figures 3 and 4, and the intermolecular

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approach distances are listed in Tables 5 and 6. None of the distances is abnormal.

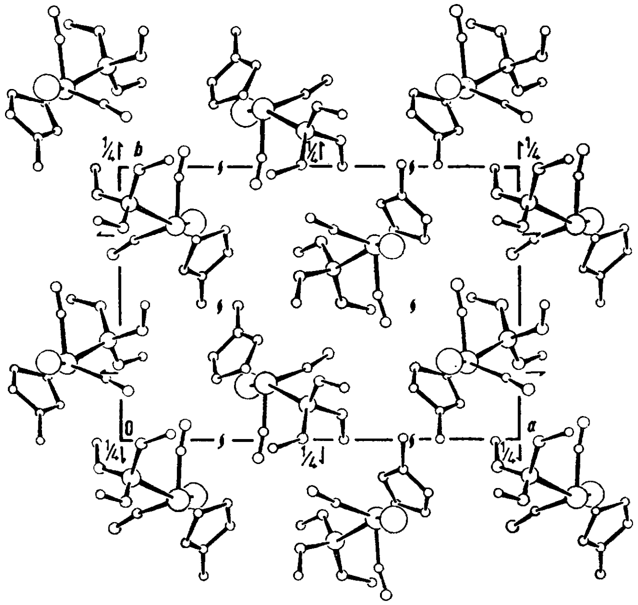

FIGURE 4 The crystal structure of (II) viewed in projection along *c* axis

EXPERIMENTAL

(i) π-*Cyclopentadienyl*-trans-*iododicarbonyl*(*trimethyl phosphite*)*molybdenum*, (I)

Crystal Data.—$C_{10}H_{14}IMoO_5P$, $M = 468{\cdot}1$, Orthorhombic, $a = 10{\cdot}75$, $b = 16{\cdot}60$, $c = 8{\cdot}57$ (all $\pm 0{\cdot}01$) Å, $U = 1528$ Å^3, $D_m = 1{\cdot}99$, $Z = 4$, $D_c = 2{\cdot}03$, $F(000) = 896$. Space group $P2_12_12_1$ (D_2^4). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = $246{\cdot}5$ cm^{-1}.

Crystallographic Measurements.—Cell dimensions were derived from precession photographs taken with Mo-K_α radiation. Intensity data were recorded as layers *hk*0—7 on multiple-film equi-inclination Weissenberg photographs taken with nickel-filtered Cu-K_α radiation, and the intensities of 906 independent reflections above background were measured by means of a Joyce–Deeley integrating microdensitometer. The crystal employed was $1{\cdot}0 \times 0{\cdot}15 \times 0{\cdot}15$ mm, and absorption corrections appropriate to a cylindrical crystal were applied.

Structure Analysis.—Initial co-ordinates for the iodine and molybdenum atoms were deduced from a three-dimensional Patterson function, and an electron-density distribution phased by these atoms (R 40·1%) yielded positions for the phosphorus, carbon, and oxygen atoms of the trimethyl phosphite and carbonyl ligands. Three rounds of least-squares adjustment of the co-ordinates and isotropic thermal parameters of these atoms (with unit weights) converged at R 12·8%. A difference-Fourier electron-density distribution revealed the five carbon atoms of the cyclopentadienyl ring, and several further rounds of least-squares refinement gave R 9·6%.

At this stage corrections for anomalous dispersion were incorporated in the least-squares programme, with values of $\Delta f'$ and $\Delta f''$ for iodine, molybdenum, and phosphorus taken from ref. 20, and structure factors calculated on the basis of co-ordinates x, y, z and $\bar{x}, \bar{y}, \bar{z}$ favoured the former set. Anisotropic temperature factors were assigned successively to the iodine atom, the molybdenum and phosphorus atoms, and the carbonyl oxygen atoms, and a weighting scheme was adopted of the form $\sqrt{w} = (A + B|F_o| + C|F_o|^2)^{-1}$ where A, B, and C were chosen so that $w\Delta^2$ was approximately constant when averaged over various ranges of $|F_o|$. The calculations finally converged at R 7·8%, with A 0·018, B −3·28, and C 19·36.

The calculations employed the '*X*-Ray '63' system [21] at the Atlas Computer Laboratory. Observed and calculated structure factors for (I) and (II) are listed in Supplementary Publication No. SUP 20443 (20 pp., 1 microfiche).*

(ii) π-*Methylcyclopentadienyl*-trans-*iododicarbonyl*(*trimethyl phosphite*)*molybdenum*, (II)

Crystal Data.—$C_{11}H_{16}IMoO_5P$, $M = 481{\cdot}1$, Orthorhombic, $a = 16{\cdot}317(6)$, $b = 11{\cdot}323(3)$, $c = 8{\cdot}740(2)$ Å, $U = 1615$ Å^3, $D_m = 1{\cdot}99$, $Z = 4$, $D_c = 1{\cdot}98$, $F(000) = 928$. Space group $P2_12_12_1$ (D_2^4). Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = $28{\cdot}4$ cm^{-1}.

Crystallographic Measurements.—Cell dimensions were initially determined from precession photographs and subsequently adjusted by least-squares treatment of the θ, χ, ϕ setting angles of twelve reflections measured on a Hilger and Watts' Y 290 automatic diffractometer controlled by a PDP 8 computer. The intensities were measured by the θ—2θ step scan procedure with zirconium-filtered Mo-K_α radiation. Background counts were taken at each end of the scan range. The intensities of two standard reflections were monitored after every 40 intensity measurements, and the results used to place the reflections on a common scale; the changes in the standard intensities during data collection were small (<5%). Reflections with $h, k, l \geqslant 0$ were surveyed out to $\theta \leqslant 30°$. Lorentz-polarization corrections were applied, but absorption was neglected. 1847 reflections with $I/\sigma(I) > 3{\cdot}0$ were obtained.

Structure Analysis.—Initial co-ordinates were obtained by Patterson and Fourier methods. The atomic parameters were subsequently adjusted by a series of least-squares calculations with allowance for anomalous dispersion. The weighting scheme used was $w = 1/\sigma^2(|F_o|)$. Structure factors calculated with co-ordinates x, y, z and $\bar{x}, \bar{y}, \bar{z}$ showed that the second set was correct in this case. With an anisotropic temperature factor assigned to the iodine atom the calculations converged at R 7·4%. When anisotropic temperature factors were extended to the molybdenum and phosphorus atoms, subsequent refinement reduced R to 6·4%, and when the carbonyl oxygen atoms were similarly treated R was further reduced to 6·2%.

The sixteen hydrogen atoms in the molecule were located in a difference electron-density distribution, and included in subsequent calculations at fixed positions. One additional round of least-squares adjustment of the atomic parameters of the non-hydrogen atoms gave R 5·9%, and the analysis was terminated.

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

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