Crystal and Molecular Structure of Octacarbonyl-μ-(1,2,3,4-tetraphenylbut-2-ene-1,1,4,4-tetrayl)-*triangulo*-triosmium $(Ph_4C_4)Os_3(CO)_8$

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The title compound crystallizes in the monoclinic system, space-group $P2_1/n$, $Z = 4$, $a_0 = 9{\cdot}36(2)$, $b_0 = 33{\cdot}77(6)$, $c_0 = 10{\cdot}76(2)$ Å, $\beta = 98^\circ\ 47'(5')$. An *X*-ray crystal-structure analysis has been made by use of 2178 non-zero reflexions collected with an automatic diffractometer; the structure was solved by Patterson and Fourier methods and refined by least-squares techniques to *R* 0·12. The molecule is built up by a cluster of three osmium atoms, at the corners of an almost equilateral triangle, and by the organic ligand; the osmium atoms are linked with two [Os(1)] or three [Os(2) and Os(3)] carbonyl groups. The chelation between the two parts of the molecule is partially attained through μ-bonds; the possible existence of a three-centre C · · · H · · · Os bond or of an Os–H hydride bond is discussed.

DURING research on metal carbonyls, especially acetylenic derivatives of $Os_3(CO)_{12}$,[1-3] we carried out an *X*-ray study of $(Ph_4C_4)Os_3(CO)_8$. So far, for similar osmium complexes, there is only one complete *X*-ray analysis of $Os_3(CO)_{12}$[4] and incomplete analyses of $(C_6H_8)Os_2(CO)_6$[5] and of $(Ph_4C_4)Os_3(CO)_9$.[2]

EXPERIMENTAL

The compound was prepared as described in ref. 1 and recrystallized from n-heptane as yellow lamellar {010} crystals, slightly elongated in the *z* direction, and suitable for *X*-ray study. No pleochroism or cleavage was detected.

Crystal Data.—$C_{36}H_{20}O_8Os_3$, $M = 1151{\cdot}13$, Monoclinic prismatic, $a_0 = 9{\cdot}36(2)$, $b_0 = 33{\cdot}77(6)$, $c_0 = 10{\cdot}76(2)$ Å, $\beta = 98^\circ\ 47'\ (5')$ [extrapolated *vs.* $1/2\{(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)\}$], $U = 3364{\cdot}8$ Å^3, $D_m = 2{\cdot}13$,* $Z = 4$, $D_c = 2{\cdot}27$, $F(000) = 2112$. Space-group $P2_1/n$ (No. 14) from systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 216$ cm^{-1}.

Unit-cell dimensions were determined from preliminary Weissenberg photographs.

Intensity Measurements.—Intensities were measured by a General Electric automatic three-circle diffractometer equipped with a NaCl(Tl) scintillation counter. A crystal of dimensions 0·20 × 0·02 × 0·30 mm was mounted with its *z* axis coincident with the ϕ axis of the goniostat; integrated intensities were collected by the θ—2θ scanning method (scanning speed, 1° min^{-1}; background, 0·5° on both sides of each peak). Owing to the low diffracting power of the crystal, the measurements were restricted to reflexions with $2\theta \leqslant 90^\circ$; of the 2669 collected reflexions 491 were rejected because of the low magnitude of their intensities.

A standard reflexion (271) was checked every 40 reflexions (*ca.* every 2½ h); its value, on a relative scale, decreased from 5240 to 3200 during the 7 days of the measurements; this was due to the deterioration of the crystal which at the end showed a light brown colour and slightly increased unit-cell parameters: *ca.* 1% a_0 and c_0, and *ca.* 2% b_0.

All the reflexions were put on the same relative scale by a plot of the intensity of the standard reflexion *vs.* time. Because of the low accuracy of the experimental data and of the small dimensions of the crystal, no absorption

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* D_m was obtained by flotation and the low value is attributed to the poor (lamellar) quality of the sample used.

[1] G. Cetini, O. Gambino, G. A. Vaglio, and R. P. Ferrari, *Atti Accad. Sci. Torino*, 1969, **103**, 495.

[2] G. Ferraris and G. Gervasio, *Atti Accad. Sci. Torino*, 1971, **105**, 303.

[3] O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organometallic Chem.*, 1971, **30**, 381.

[4] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

[5] R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc.*, 1963, 380.

correction was made. The calculation of the atomic scattering factors, including, for osmium, the real and imaginary correction for anomalous scattering, was done by linear interpolation of the values from ref. 6.

Solution and Refinement of the Structure.—From a three-dimensional Patterson function the co-ordinates of the three independent osmium atoms were obtained. A series of difference syntheses was then calculated phased on the known atoms; the resulting atom positions obtained were refined by least-squares methods. During the process of structure solution a three-dimensional model and calculations of bond and angle values were found very useful.

TABLE 1

Fractional atomic co-ordinates and vibrational parameters (Å^2), with the estimated standard deviations in parentheses

	x/a_0	y/b_0	z/c_0	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os(1)	−0·11374(10)	0·16211(3)	−0·02170(10)	2·30(5)	5·31(7)	4·26(6)	0·18(5)	−0·19(4)	−0·19(6)
Os(2)	0·11260(11)	0·20993(4)	−0·09620(12)	2·98(5)	5·96(8)	5·18(7)	−0·14(5)	0·19(5)	0·22(7)
Os(3)	0·15576(10)	0·15524(4)	0·11923(10)	2·19(5)	5·43(7)	4·09(7)	−0·24(5)	−0·26(4)	−0·08(6)

	x/a_0	y/b_0	z/c_0	B		x/a_0	y/b_0	z/c_0	B
C(1)	−0·0557(52)	0·1325(15)	0·1651(50)	5·2(1·2)	C(23)	−0·1058(57)	0·1452(17)	0·2767(56)	4·0(1·4)
C(2) *	−0·1034(51)	0·0954(15)	0·0826(48)	14·3(1·1)	C(24)	−0·0203(54)	0·1430(15)	0·3933(52)	5·3(1·2)
C(3)	−0·0545(83)	0·0907(24)	−0·0201(75)	3·6(2·1)	C(25)	−0·0801(57)	0·1509(17)	0·5086(53)	6·7(1·4)
C(4)	0·0641(50)	0·1195(15)	−0·0395(45)	4·0(1·1)	C(26)	−0·2386(47)	0·1591(15)	0·5099(44)	4·9(1·1)
C(5)	0·1601(41)	0·1208(13)	−0·1599(39)	2·8(0·9)	C(27)	−0·3175(56)	0·1610(18)	0·3823(54)	5·2(1·3)
C(6)	0·2146(60)	0·0845(18)	−0·2141(53)	5·6(1·4)	C(28)	−0·2598(52)	0·1524(16)	0·2686(49)	4·2(1·1)
C(7)	0·2844(58)	0·0924(18)	−0·3100(55)	5·5(1·3)	C(29)	−0·2710(42)	0·1524(13)	−0·1346(39)	2·7(0·9)
C(8)	0·3009(56)	0·1263(18)	−0·3423(52)	5·1(1·3)	C(30)	−0·2035(53)	0·2048(17)	0·0363(50)	5·9(1·2)
C(9)	0·2660(45)	0·1620(15)	−0·3117(42)	4·2(1·0)	C(31)	0·2359(76)	0·1198(22)	0·2156(74)	5·8(1·9)
C(10)	0·1942(68)	0·1603(22)	−0·1939(63)	6·7(1·7)	C(32)	0·1943(80)	0·1938(23)	0·1988(77)	8·6(2·1)
C(11)	−0·1108(52)	0·0700(16)	−0·1205(50)	6·9(1·2)	C(33)	0·3481(47)	0·1615(14)	0·0656(41)	4·8(1·0)
C(12)	−0·1474(47)	0·0811(14)	−0·2590(44)	3·3(1·0)	C(34)	0·0618(79)	0·2533(25)	0·0266(76)	6·4(2·1)
C(13)	−0·2121(70)	0·0518(22)	−0·3423(64)	7·2(1·7)	C(35)	0·0169(42)	0·2321(13)	−0·2342(40)	2·8(0·9)
C(14)	−0·2072(83)	0·0123(26)	−0·3150(80)	6·3(2·1)	C(36)	0·3072(76)	0·2314(23)	−0·1352(71)	14·4(2·1)
C(15)	−0·1752(79)	−0·0004(24)	−0·1886(80)	9·6(2·1)	O(1)	−0·3822(51)	0·1517(15)	−0·2071(47)	8·6(1·3)
C(16)	−0·1098(55)	0·0301(17)	−0·1080(52)	3·9(1·2)	O(2)	−0·2387(48)	0·2297(14)	0·0941(44)	7·0(1·2)
C(17)	−0·2334(55)	0·0780(17)	0·1295(54)	4·5(1·3)	O(3)	0·2915(46)	0·0947(14)	0·2970(44)	6·0(1·1)
C(18)	−0·1921(66)	0·0599(19)	0·2326(62)	7·4(1·5)	O(4)	0·1989(43)	0·2205(13)	0·2916(41)	7·7(1·1)
C(19)	−0·2955(89)	0·0299(25)	0·2657(81)	10·2(8·1)	O(5)	0·4562(36)	0·1666(10)	0·0370(31)	4·0(0·7)
C(20)	−0·4341(84)	0·0253(24)	0·1781(78)	9·0(2·0)	O(6)	0·0362(51)	0·2782(16)	0·0659(46)	11·2(1·3)
C(21)	−0·4810(85)	0·0470(24)	0·0676(78)	10·4(2·1)	O(7)	−0·0280(40)	0·2575(14)	−0·3264(40)	8·1(1·2)
C(22)	−0·3472(69)	0·0748(19)	0·0491(63)	6·7(1·6)	O(8)	0·4171(40)	0·2473(14)	−0·1216(40)	6·0(1·1)

* Fractional co-ordinates maintained constant during the isotropic refinement.

Owing to the poor accuracy of the light-atom positions, because of the overwhelming contribution to the structure-factors from the three osmium atoms and of the low accuracy of the intensity measurements, only the three heavy atoms were refined anisotropically. The refinement was considered complete when all the shifts of the parameters were smaller than their estimated standard deviations.

A final difference Fourier map showed no abnormality; hydrogen-atom positions were not detectable. The final R value, for the 2178 reflexions used throughout the refinement, is 0·12; weighted value R' 0·11.*

The program used for the least-squares refinement was that of ref. 7 with minor modifications. The weighting scheme was ($|F_o|$ 0·17 times the absolute value): $w_{hkl} = 64/(0{\cdot}01|F_o|^2 + 2|F_o| + 20)$ for $|F_o| \geqslant 20$ and $w_{hkl} = 0{\cdot}00225|F_o|^2 + 0{\cdot}1$ for $|F_o| < 20$.

The constants in these expressions were modified during the refinement in order to maintain $\Sigma w\Delta^2$ at a satisfactorily constant value for the amplitudes batched in various groups.

The final fractional co-ordinates and the thermal parameters are listed in Table 1; anisotropic parameters for osmium atoms are the B_{ij} coefficients of the function:

$$\exp\left(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*\right)$$

DISCUSSION

Description of the Structure.—The molecular configuration revealed by the present X-ray study is shown in Figure 1; it is quite different from that found[8] for the analogous iron compound. The molecule is built

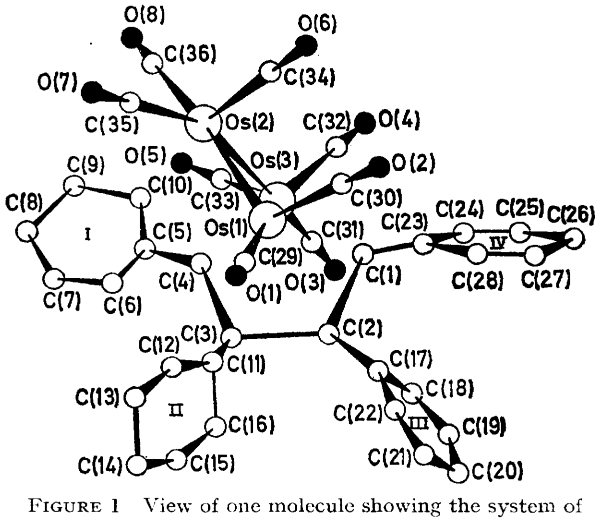

FIGURE 1 View of one molecule showing the system of atom labelling used

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* $|F_o|$ and F_c values are listed in Supplementary Publication No. 20338 (14 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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

[7] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, A Fortran Crystallographic Least-Squares Program, ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

[8] R. P. Dodge and V. Schomaker, *J. Organometallic Chem.*, 1965, **3**, 274.

up by an organic ligand and a cluster of three osmium atoms at the corners of a nearly equilateral triangle; osmium atoms are linked with two [Os(1)] or three [Os(2) and Os(3)] carbonyl groups. The chelation between the two parts of the molecule is attained through various bonds discussed later.

Whilst the bonds C(1)–C(4) and Os(1)–Os(3) are roughly mutually perpendicular, the osmium triangle is rotated around Os(1)–Os(3) towards phenyl group (I) [Ph(I)] in such a way that the latter is nearly perpendicular (87°) to the osmium plane and the group Ph(I),C(4),-Os(2) is planar. The equation of this plane (1) is: * $7{\cdot}23X + 0{\cdot}23Y + 5{\cdot}48Z = 0{\cdot}33$, $\chi^2 = 2{\cdot}9$, and the distances (Å) from it of relevant atoms are C(4) −0·069(8), C(5) −0·02(7), C(6) 0·06(10), C(7) 0·04(10), C(8) −0·01(10), C(9) −0·08(8), C(10) 0·04(10), and Os(2) 0·001(2).

TABLE 2

Interatomic distances and angles, with their standard deviations in parentheses, in the osmium co-ordination polyhedra

(*a*) Distances (Å)

Os(1)–Os(2)	2·874(2)
Os(1)–Os(3)	2·747(1)
Os(2)–Os(3)	2·944(2)
Os(1)–C(1)	2·24(5)
Os(1)–C(2)	2·51(5)
Os(1)–C(3)	2·47(8)
Os(1)–C(4)	2·23(5)
Os(1)–C(29)	1·79(4)
Os(1)–C(30)	1·83(6)
Os(2) · · · C(10)	2·18(7)
Os(2)–C(34)	2·08(8)
Os(2)–C(35)	1·78(4)
Os(2)–C(36)	2·06(7)
Os(3)–C(1)	2·25(5)
Os(3)–C(4)	2·16(5)
Os(3)–C(31)	1·68(8)
Os(3)–C(32)	1·57(8)
Os(3)–C(33)	1·98(4)
C(29)–O(1)	1·20(6)
C(30)–O(2)	1·12(7)
C(31)–O(3)	1·27(9)
C(32)–O(4)	1·34(9)
C(33)–O(5)	1·12(6)
C(34)–O(6)	0·99(10)
C(35)–O(7)	1·33(6)
C(36)–O(8)	1·15(8)

(*b*) Angles (°)

Os(1)–Os(3)–Os(2)	60·5(1)
Os(1)–Os(2)–Os(3)	56·4(1)
Os(2)–Os(1)–Os(3)	63·1(1)
C(1)–Os(1)–Os(3)	52(1)
C(1)–Os(1)–C(2)	38(2)
C(1)–Os(1)–C(3)	62(2)
C(1)–Os(1)–C(29)	126(2)
C(1)–Os(1)–C(30)	96(2)
C(2)–Os(1)–C(4)	59(2)
C(2)–Os(1)–C(29)	96(2)
C(3)–Os(1)–C(4)	37(2)
C(3)–Os(1)–C(29)	89(2)
C(4)–Os(1)–Os(2)	75(2)
C(4)–Os(1)–Os(3)	50(1)
C(4)–Os(1)–C(29)	112(2)
C(4)–Os(1)–C(30)	158(2)
C(29)–Os(1)–Os(2)	119(1)
C(30)–Os(1)–Os(2)	93(2)
C(30)–Os(1)–Os(3)	108(2)
C(10) · · · Os(2)–Os(1)	92(2)
C(10) · · · Os(2)–Os(3)	83(2)
C(10) · · · Os(2)–C(34)	169(3)
C(10) · · · Os(2)–C(35)	95(2)
C(10) · · · Os(2)–C(36)	78(3)
C(34)–Os(2)–Os(1)	88(2)
C(34)–Os(2)–Os(3)	88(2)
C(34)–Os(2)–C(35)	96(3)
C(34)–Os(2)–C(36)	100(3)
C(35)–Os(2)–Os(1)	100(1)
C(35)–Os(2)–Os(3)	156(1)
C(35)–Os(2)–C(36)	92(3)
C(36)–Os(2)–Os(1)	165(2)
C(36)–Os(2)–Os(3)	111(2)
C(1)–Os(3)–Os(1)	52(1)
C(1)–Os(3)–C(4)	74(2)
C(1)–Os(3)–C(31)	87(3)
C(1)–Os(3)–C(32)	117(4)
C(4)–Os(3)–Os(1)	52(1)
C(4)–Os(3)–Os(2)	75(1)
C(4)–Os(3)–C(31)	100(3)
C(4)–Os(3)–C(32)	144(4)
C(4)–Os(3)–C(33)	96(2)
C(31)–Os(3)–C(32)	117(4)
C(32)–Os(3)–Os(1)	105(3)
C(32)–Os(3)–Os(2)	69(4)
C(33)–Os(3)–Os(2)	74(1)
C(33)–Os(3)–C(31)	85(3)
C(33)–Os(3)–C(32)	77(4)
Os(1)–C(29)–O(1)	170(1)
Os(1)–C(30)–O(2)	166(5)
Os(2)–C(34)–O(6)	166(8)
Os(2)–C(35)–O(7)	163(4)
Os(2)–C(36)–O(8)	160(6)
Os(3)–C(31)–O(3)	175(7)
Os(3)–C(32)–O(4)	160(6)
Os(3)–C(33)–O(5)	177(1)

The four chelate carbon atoms lie in plane (2) of equation $5{\cdot}95X - 19{\cdot}08Y + 4{\cdot}54Z = -2{\cdot}09$, $\chi^2 = 0{\cdot}4$, and relevant distances (Å) from this plane are: C(1) −0·02(9), C(2) 0·03(9), C(3) −0·05(10), and C(4) 0·02(8).

These four atoms and Os(3) form a rough pentagonal group [plane (3)] whose equation is $4{\cdot}59X - 24{\cdot}03Y + 4{\cdot}07Z = -2{\cdot}69$, $\chi^2 = 17{\cdot}3$; relevant distances (Å) from it are: C(1) −0·21(9), C(2) 0·16(9), C(3) 0·09(10), C(4) −0·17(8), and Os(3) 0·004(2). The inclinations of planes (2) and (3) with respect to the plane of the osmium atoms are 68 and 64°.

We can argue the existence of a Ph(I) · · · Os(2) bond on the basis both of the short contact C(10) · · · Os(2) [2·18(7) Å] and of the planarity of the Ph(I),C(4),-Os(2) group [plane (1)], however the nature of this bond is not quite clear.

TABLE 3

Interatomic distances and angles, with their standard deviations in parentheses, in the organic ligand

(*a*) Distances (Å)

C(1)–C(2)	1·56(4)
C(2)–C(3)	1·27(9)
C(3)–C(4)	1·51(9)
C(4)–C(5)	1·69(6)
C(5)–C(6)	1·48(7)
C(6)–C(7)	1·33(8)
C(7)–C(8)	1·21(9)
C(8)–C(9)	1·31(8)
C(9)–C(10)	1·52(10)
C(10)–C(5)	1·43(9)
C(3)–C(11)	1·33(10)
C(11)–C(12)	1·53(7)
C(12)–C(13)	1·41(9)
C(13)–C(14)	1·37(10)
C(14)–C(15)	1·41(10)
C(15)–C(16)	1·42(10)
C(16)–C(11)	1·36(8)
C(2)–C(17)	1·51(7)
C(17)–C(18)	1·27(9)
C(18)–C(19)	1·48(10)
C(19)–C(20)	1·49(10)
C(20)–C(21)	1·41(10)
C(21)–C(22)	1·41(10)
C(22)–C(17)	1·47(9)
C(1)–C(23)	1·42(8)
C(23)–C(24)	1·38(8)
C(24)–C(25)	1·46(8)
C(25)–C(26)	1·51(7)
C(26)–C(27)	1·46(7)
C(27)–C(28)	1·44(8)
C(28)–C(23)	1·45(7)

(*b*) Angles (°)

Os(1)–C(1)–Os(3)	76(2)
Os(1)–C(1)–C(2)	81(3)
Os(1)–C(1)–C(23)	124(4)
Os(3)–C(1)–C(2)	110(3)
Os(3)–C(1)–C(23)	120(4)
C(2)–C(1)–C(23)	128(5)
Os(1)–C(2)–C(1)	62(3)
Os(1)–C(2)–C(3)	74(4)
Os(1)–C(2)–C(17)	122(3)
C(1)–C(2)–C(3)	119(5)
C(1)–C(2)–C(17)	107(4)
C(3)–C(2)–C(17)	131(6)
Os(1)–C(3)–C(2)	77(4)
Os(1)–C(3)–C(4)	63(3)
Os(1)–C(3)–C(11)	117(5)
C(2)–C(3)–C(4)	114(6)
C(2)–C(3)–C(11)	129(7)
C(4)–C(3)–C(11)	116(6)
Os(1)–C(4)–Os(3)	77(2)
Os(1)–C(4)–C(3)	80(4)
Os(1)–C(4)–C(5)	123(3)
Os(3)–C(4)–C(3)	117(4)
Os(3)–C(4)–C(5)	113(3)
C(3)–C(4)–C(5)	128(5)
C(4)–C(5)–C(6)	123(4)
C(4)–C(5)–C(10)	113(4)
C(6)–C(5)–C(10)	124(5)
C(5)–C(6)–C(7)	112(5)
C(6)–C(7)–C(8)	121(6)
C(7)–C(8)–C(9)	139(6)
C(8)–C(9)–C(10)	110(5)
C(9)–C(10)–C(5)	113(5)
C(9)–C(10) · · · Os(2)	127(4)
Os(2) · · · C(10)–C(5)	119(4)
C(3)–C(11)–C(12)	132(5)
C(3)–C(11)–C(16)	117(6)
C(12)–C(11)–C(16)	110(5)
C(11)–C(12)–C(13)	117(5)
C(12)–C(13)–C(14)	123(6)
C(13)–C(14)–C(15)	120(8)
C(14)–C(15)–C(16)	112(7)
C(15)–C(16)–C(11)	132(6)
C(2)–C(17)–C(18)	109(5)
C(2)–C(17)–C(22)	122(5)
C(18)–C(17)–C(22)	127(6)
C(17)–C(18)–C(19)	115(6)
C(18)–C(19)–C(20)	117(7)
C(19)–C(20)–C(21)	127(7)
C(20)–C(21)–C(22)	109(7)
C(21)–C(22)–C(17)	124(6)
C(1)–C(23)–C(24)	122(5)
C(1)–C(23)–C(28)	117(5)
C(24)–C(23)–C(28)	120(5)
C(23)–C(24)–C(25)	121(5)
C(24)–C(25)–C(26)	123(5)
C(25)–C(26)–C(27)	111(4)
C(26)–C(27)–C(28)	126(5)
C(27)–C(28)–C(23)	119(5)

If we suppose that Ph(I) is a normal phenyl group, plane (1) and the values of the angles C(9)–C(10) · · · Os(2) [127(4)°] and C(5)–C(10) · · · Os(2) [119(4)°] require that the hydrogen atom bound to C(10) is on the

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* All the equations of planes, in fractional co-ordinates and referred to the cell axes, have been computed by the method of ref. 9. $\chi^2 = \Sigma(d/\sigma)^2$ and gives the statistical significance of the planarity.[10]

[9] V. Schomaker, J. Waser, R. E. Marsch, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

[10] D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, 1953, **6**, 698.

C(10) · · · Os(2) direction; this seems an unlikely situation since La Placa *et al.*[11] have found Mn–H to be 1·60(2) Å and, considering the Os–CO and Mn–CO bond lengths, we must expect an Os–H bond not shorter than 1·6 Å. To remove this difficulty we could suppose C(10) being in resonance between an sp^3 and sp^2 configuration with its hydrogen atom no longer on the C(10) · · · Os(2) direction; this hypothesis would be in agreement with the distribution of the bond and angle values in Ph(I) (Tables 2 and 3). A third possibility is that the hydrogen atom is directly bound to Os(2) and C(10) · · · Os(2) is a σ bond. Unfortunately, both the two cases of a three-centre bond[12] (first two hypotheses) and that of a hydride bond (third hypothesis) are in agreement with the absorption at τ 25·5 in the n.m.r. spectrum.[13]

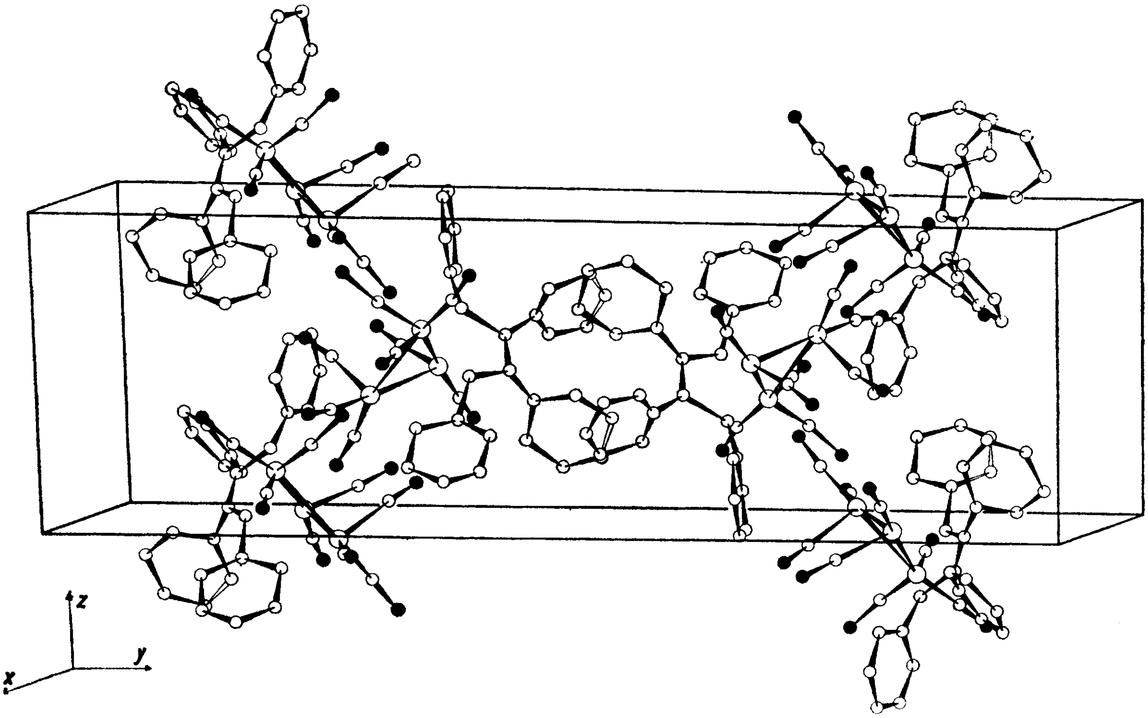

FIGURE 2 Clinographic projection, along the *x* axis, of the content of one unit cell.

The equations of the planes of the phenyl groups, including their extra carbon atoms are:

Plane (4): Ph(I) $7{\cdot}16X + 1{\cdot}38Y + 5{\cdot}75Z = 0{\cdot}43; \; \chi^2 = 1{\cdot}2$

Plane (5): Ph(II) $9{\cdot}08X - 4{\cdot}64Y - 3{\cdot}71Z = -0{\cdot}82; \; \chi^2 = 2{\cdot}7$

Plane (6): Ph(III) $-3{\cdot}86X + 25{\cdot}89Y + 5{\cdot}91Z = 3{\cdot}54; \; \chi^2 = 11{\cdot}0$

Plane (7): Ph(IV) $2{\cdot}06X + 32{\cdot}79Y - 1{\cdot}38Z = 4{\cdot}08; \; \chi^2 = 2{\cdot}1$

The deviations from planarity are not significant, except for plane (6); however, if we exclude C(2), the corresponding equation is:

Plane (8): $-4{\cdot}63X + 23{\cdot}30Y + 6{\cdot}43Z = 3{\cdot}76; \; \chi^2 = 0{\cdot}2$

Both steric hindrance and the requirement of a bond between Ph(I) and Os(2) are responsible for remarkable angles of twist for the phenyl groups; in fact the angles of planes (4)—(8) with the plane of the chelate carbon atoms [plane (2)] are 38, 59, 60, 57, and 62°.

Since the standard deviations for the bonds and angles of the light atoms are quite large, a thorough discussion of the molecular structure on the basis of bond order is not easily feasible. Anyway, in order to settle the bond configuration around Os(1), we can suppose that while Os(1)–C(1), Os(1)–C(4), Os(3)–C(1), Os(3)–C(4), C(1)–C(2), and C(3)–C(4) are single bonds, C(2)–C(3) is a double bond (Tables 2 and 3); owing to the short contacts of Os(1) with C(2) and C(3) the existence of a μ-bond[14] between C(2)=C(3) and Os(1) seems plausible. It would result, therefore, that Os(1) has a seven-fold co-ordination according to a very distorted octahedron with a face centred by such a bond.

On the other hand, emphasizing the role of the values of the bond angles with respect to those of the bond distances (Tables 2 and 3), we cannot exclude for Os(1) a co-ordination number of six, in such a way that two corners of the resulting octahedron are towards the middle of the two (now double) bonds C(1)=C(2) and C(3)=C(4); the other four corners would be occupied by Os(2), Os(3), C(29), and C(30).

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[11] S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, 1969, **8**, 1928.

[12] R. E. Rundle, *J. Phys. Chem.*, 1957, **61**, 45.

[13] R. P. Ferrari, G. A. Vaglio, O. Gambino, M. Valle, and G. Cetini, to be published.

[14] P. L. Pauson, *Proc. Chem. Soc.*, 1960, 297.

On the hypothesis of a three-centre bond, around Os(2) there are, octahedrally distributed, three carbonyls, two osmium atoms, and C(10); if instead there is a hydride Os–H bond, we should find seven atoms around Os(2) (Table 2).

Os(3) is seven-co-ordinated according to a distorted pentagonal bipyramid where C(4) and C(32) are the vertices facing the pentagonal section (Table 2).

TABLE 4

Principal intramolecular contacts ($\leqslant$3·2 Å)

Os(2) ··· C(4)	3·16(5)	C(1) ··· C(31)	2·73(9)
Os(2) ··· C(3)	3·13(4)	C(1) ··· C(32)	3·10(9)
Os(2) ··· C(32)	3·20(8)	C(4) ··· C(31)	2·96(9)
Os(2) ··· C(33)	3·06(5)	C(4) ··· C(33)	3·07(7)
Os(3) ··· C(23)	3·20(6)		

Whatever the true co-ordination for Os(1) and Os(2) might be, the resulting molecular structure is in agreement with the measured diamagnetic properties [13] of the compound. The molecule is very overcrowded and there are several short contacts concerning the phenyl groups, or phenyl and carbonyl groups; the values for the intramolecular contacts <3·2 Å are reported in Table 4.

Figure 2 shows, in clinographic projection along the x axis, the packing of the molecules in a unit cell. Among the molecules there are several notable contacts and those <3·3 Å are listed in Table 5. Through some of these contacts, the molecules form chains twisting along the z axis, and these chains are linked along the x axis to produce layers parallel to (010); between these layers there are no contacts <3·3 Å.

TABLE 5

Principal intermolecular contacts ($\leqslant$3·3 Å)

C(8) ··· O(1^{I})	3·21(7)	O(1) ··· O(6^{V})	3·26(6)
C(9) ··· O(1^{I})	3·33(6)	O(2) ··· O(7^{II})	2·99(6)
C(26) ··· O(6^{II})	3·11(7)	O(2) ··· O(8^{II})	3·27(6)
C(27) ··· O(6^{II})	3·29(8)	O(4) ··· O(7^{III})	3·11(6)
C(32) ··· O(7^{III})	3·12(8)	O(4) ··· O(8^{II})	3·12(6)
C(33) ··· O(7^{III})	3·12(7)	O(5) ··· O(7^{III})	2·95(6)
C(36) ··· O(2^{IV})	3·16(9)	O(7) ··· O(8^{V})	3·14(6)

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

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

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