

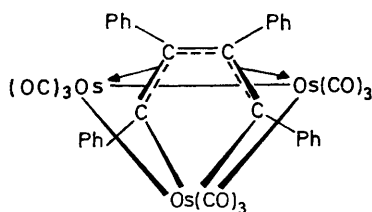
Crystal and Molecular Structure of Nonacarbonyl- μ -(1,2,3,4-tetraphenylbutadiene-1,4-diyl)-triangulo-triosmium, $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_9$

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Crystals of the title compound occur in two forms: (i) M-form, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 12.148(5)$, $b = 9.796(4)$, $c = 29.565(16)$ Å, $\beta = 91.79(5)^\circ$; and (ii) O-form, orthorhombic, space group $Iba2$, $Z = 8$, $a = 38.45(8)$, $b = 18.59(4)$, $c = 9.80(2)$ Å. The structures of both modifications were solved by Patterson and Fourier syntheses, and refined by least-squares methods to R 0.095 (4807 reflexions, M-form) and 0.080 (1916 reflexions, O-form); they have the same molecular structure. The molecule is built up of the organic ligand Ph_4C_4 , with a cluster of three osmium atoms at the corners of an isosceles triangle, bonded to two, three, or four carbonyl groups. Co-ordination between Ph_4C_4 and the cluster is attained *via* σ -bonds and the donation of four π -electrons of the osmacyclopentadiene ring. The cluster and the ligand configurations are discussed in relation to those of similar compounds.

AFTER a preliminary paper¹ on the heavy-atom localization of a monoclinic form (M-form) of $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_9$, a close examination of the crystallization products also revealed the presence of an orthorhombic form (O-form). As part of a structural research on acetylenic derivatives of metal carbonyls,¹⁻⁴ an X-ray study of the two modifications of the title compound was carried out in order to detect possible differences in their molecular structures and to compare them with that of the parent² $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_8$. On the basis of ref. 1 and of other physicochemical measurements Gambino *et al.*⁵ had suggested the following alternative molecular configurations:

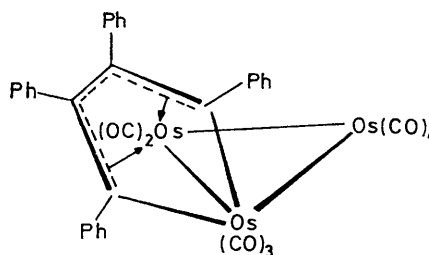


(I)

EXPERIMENTAL

$(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_9$ was prepared as described in ref. 5 and recrystallized from n-heptane (room temperature or -20°C); quick evaporation favours the M- and slow evaporation the O-form.

Crystals of the M-form are short prismatic [010] with well developed {001}, {010}, {201}, and {103}; those of the O-form are acicular [001], with {010} more developed than {100} and a cleavage, probably {100}, along the z axis. Both the forms are amethyst-violet and marked pleochroism is observed for crystals of the O-form, which are thinner than those of the M-form: the transmitted light is amethyst-violet or indigo for vibrations along [001] or [100], respectively.



(II)

¹ G. Ferraris and G. Gervasio, *Atti Accad. Sci. Torino*, 1971, **105**, 303.

² G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1972, 1057.

³ G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1973, 1933.

⁴ G. Gervasio and G. Ferraris, *Cryst. Struct. Comm.*, 1973, **2**, 447.

⁵ O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organometallic Chem.*, 1971, **30**, 381.

Intensity Measurements.—Integrated intensities (θ — 2θ scan, 0.5° in 2θ were scanned on both sides of each peak in order to obtain a measure of the background) were collected on a General Electric automatic three-circle diffractometer, by use of nickel-filtered $\text{Cu-K}\alpha$ radiation on crystals mounted with their elongation direction (y or z) coincident with the instrumental ϕ axis. A standard reflexion for each compound was monitored every 40 reflexions and a non-linear decrease of the intensities was detected during the measurements. This effect, presumably due to some deterioration of the crystals, was taken into account by use of a time-dependent scale factor. Time-consuming absorption and extinction corrections, which, because of this effect, are unlikely to improve the standard of the final results, were not applied. Atomic scattering factors, including $\Delta f'$ and $\Delta f''$ for osmium, were taken from ref. 6. The programs used are those of the 'X-Ray '70' system,⁷ except for a few ancillary ones.

Crystal Data.—(i) *M-Form*. $\text{C}_{37}\text{H}_{20}\text{O}_9\text{Os}_3$, $M = 1179.13$, Monoclinic, $a = 12.148(5)$, $b = 9.796(4)$, $c = 29.565(16)$ Å, $\beta = 91.79(5)^\circ$, $U = 3516.6$ Å³, $D_m = 2.21$ (floatation), $Z = 4$, $D_c = 2.23$, $F(000) = 2168$. $\mu(\text{Cu-K}\alpha) = 207$ cm⁻¹. Space group $P2_1/c$ (No. 14).

Unit-cell parameters and their σ were obtained by a least-squares procedure by use of 32 values of θ ($\geq 40^\circ$) measured on a single crystal diffractometer ($\lambda_{\text{Cu}} = 1.54051$, $\lambda_{\text{Os}} = 1.54178$ Å).

Intensities were recorded for a crystal ($0.17 \times 0.32 \times 0.72$ mm) mounted along its y axis, with 2° min⁻¹ scanning speed and $2\theta \leq 130^\circ$. The intensity of a standard reflexion (2,2,10) dropped from 2060 to 1500 during the 15 days of measurements. 371 Of the 5178 measured reflexions were rejected as being unobserved [$I < 2\sigma(I)$] or badly measured owing to instrumental failures.

(ii) *O-Form*. $\text{C}_{37}\text{H}_{20}\text{O}_9\text{Os}_3$, $M = 1179.13$, Orthorhombic, $a = 38.45(8)$, $b = 18.59(4)$, $c = 9.80(2)$ Å, $U = 7004.9$ Å³, $D_m = 2.21$ (floatation), $Z = 8$, $D_c = 2.24$, $F(000) = 4336$. $\mu(\text{Cu-K}\alpha) = 208$ cm⁻¹. Space group $Iba2$ (No. 45). The alternative space group $Ibam$ (No. 72) was rejected on the basis of the distribution of peaks in the Harker sections and of the satisfactory refinement of the structure in the acentric space group. Unit-cell parameters were obtained by extrapolation *vs.* $1/2 \{(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)\}$ of values measured on Weissenberg photographs.

Intensities were recorded for a crystal ($0.04 \times 0.03 \times 0.36$ mm) mounted along its z axis, with 1° min⁻¹ scanning speed and $2\theta \leq 100^\circ$. The intensity of a standard reflexion (10,5,1) decreased from 22 400 to 18 000 during the 6 days of the measurements. Owing to the scanty relative intensities (small dimensions of the crystal) and to the limited number of reflexions collected (20 limitation) the criterion for determining unobserved reflexions was not very severe [$I < \sigma(I)$] and only 28 of the 1944 measured reflexions were rejected.

Solution and Refinement of the Structure.—Starting from the three independent osmium atoms, whose co-ordinates were obtained from Patterson syntheses, the complete solution of the two structures was attained by a sequence of difference-Fourier syntheses. Least-squares refinements were by diagonal-matrix BLOKLS⁷ with anisotropic

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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

thermal parameters for osmium atoms only; the convergence was considered complete when the shifts of the parameters were smaller than their estimated σ . The introduction of the anomalous scattering was allowed to test the polarity for the O-form, which is acentric; the R values (0.080 and 0.092 for hkl and hkl indexing respectively) showed that the former was the correct polarity. R and R' (weighted) values are 0.095 and 0.096 for the M- and 0.080 and 0.069 for the O-form. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21017 (46 pp., 1 microfiche).^{*} The weighting scheme was: $w = 1/[1 + (|F_o| - B)^2/A^2]$, where the constants A and B (35.0 and 35.0 for the M- and 200.0 and 100.0 for the O-form) were modified during the refinement in order to maintain the average value of $w\Delta^2$ roughly constant for the amplitudes batched in various groups.

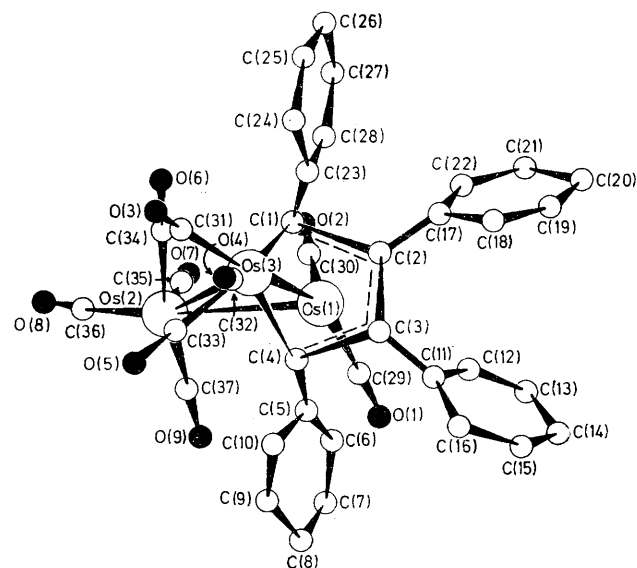
Final difference-Fourier syntheses showed scattered ripples (± 1 e Å⁻³) with some concentrations near the osmium atoms.

Final fractional co-ordinates and thermal parameters are listed in Tables 1 and 2 for the two forms; anisotropic parameters for osmium atoms are the B_{ij} coefficients of

the function: $\exp(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*)$.

RESULTS AND DISCUSSION

The present X-ray analysis shows the same overall molecular structure, which corresponds to the hypothetical structure (II),⁵ for both the M- and the O-form.



View of one molecule showing the atom labelling system

The molecule (Figure), is built up of the organic ligand Ph_4C_4 and a cluster of three osmium atoms at the corners of an isosceles triangle; Os(1), Os(2), and Os(3) are bonded to two, four, and three carbonyl groups respectively (Table 3). The organic ligand faces the short Os(1)–Os(3) side of the cluster as in the similar

⁷ 'X-Ray '67' system of programs, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, Revised 1970, University of Maryland Technical Report TR 67 55.

compounds $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_8$ ² and $(\text{Ph}_4\text{C}_4)(\text{Ph}_2\text{C}_2)\text{Os}_3(\text{CO})_7$ ³

The plane of the cluster is nearly perpendicular (86° for both forms) to the plane [(2) and (2'), Table 4]

The planes (4)—(7) and (4')—(7') (Table 4) of the phenyl groups form angles of $83, 75, 61, \text{ and } 53^\circ$, and $75, 62, 62, \text{ and } 53^\circ$ with the respective planes [(2) and (2')] of the chelant carbons. The small and not

TABLE 1
Fractional atomic co-ordinates and vibrational parameters (\AA^2), with estimated standard deviations in parentheses, for the monoclinic (M) form

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	0.28223(5)	0.19563(7)	0.11373(2)	1.56(2)	3.39(3)	1.71(3)	0.37(2)	-1.16(66)	0.05(2)
Os(2)	0.24906(6)	0.16098(9)	0.02234(2)	2.72(3)	5.02(4)	1.95(3)	0.73(3)	-1.11(78)	-0.65(3)
Os(3)	0.17185(5)	0.40104(8)	0.06878(2)	1.98(3)	3.84(3)	1.86(3)	0.70(2)	-0.75(67)	0.43(2)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
C(1)	0.3000(14)	0.4217(17)	0.1198(6)	3.3(0.3)	C(24)	0.3791(29)	0.6580(34)	0.1138(12)	7.2(0.7)
C(2)	0.2758(15)	0.3790(18)	0.1626(7)	3.2(0.3)	C(25)	0.4685(30)	0.7420(40)	0.1156(13)	8.0(0.8)
C(3)	0.1775(16)	0.3024(19)	0.1666(7)	3.9(0.3)	C(26)	0.5712(30)	0.7030(35)	0.1117(13)	7.2(0.7)
C(4)	0.1117(14)	0.2880(18)	0.1242(6)	3.3(0.3)	C(27)	0.5902(27)	0.5658(33)	0.1105(12)	7.7(0.7)
C(5)	-0.0019(14)	0.2215(17)	0.1267(6)	2.9(0.3)	C(28)	0.5035(27)	0.4761(34)	0.1079(11)	6.7(0.7)
C(6)	-0.0190(16)	0.0953(20)	0.1433(7)	4.1(0.3)	C(29)	0.2518(20)	0.0234(25)	0.1318(9)	4.7(0.4)
C(7)	-0.1253(19)	0.0341(24)	0.1458(8)	5.4(0.4)	C(30)	0.4286(12)	0.1517(15)	0.1073(5)	2.7(0.2)
C(8)	-0.2135(27)	0.1111(35)	0.1257(12)	6.8(0.7)	C(31)	0.2470(15)	0.4954(19)	0.0228(6)	3.5(0.3)
C(9)	-0.2012(22)	0.2284(28)	0.1091(9)	6.2(0.5)	C(32)	0.1072(16)	0.5555(20)	0.0907(7)	3.8(0.3)
C(10)	-0.0920(20)	0.2954(24)	0.1067(9)	4.7(0.4)	C(33)	0.0539(19)	0.3633(24)	0.0286(8)	4.3(0.4)
C(11)	0.1411(19)	0.2519(24)	0.2103(8)	4.7(0.4)	C(34)	0.3840(16)	0.2635(20)	0.0156(7)	4.0(0.3)
C(12)	0.2046(24)	0.1526(30)	0.2369(10)	5.7(0.5)	C(35)	0.3234(23)	0.0090(28)	0.0098(10)	6.6(0.5)
C(13)	0.1797(36)	0.1248(45)	0.2801(16)	9.0(1.0)	C(36)	0.1929(18)	0.1937(21)	-0.0374(8)	4.1(0.4)
C(14)	0.0870(40)	0.1640(48)	0.2945(17)	9.8(1.1)	C(37)	0.1163(15)	0.0625(18)	0.0414(6)	3.8(0.3)
C(15)	0.0149(30)	0.2555(38)	0.2752(13)	7.5(0.8)	O(1)	0.2324(11)	-0.0893(22)	0.1442(8)	7.7(0.5)
C(16)	0.0467(21)	0.3046(25)	0.2285(9)	5.7(0.5)	O(2)	0.5188(15)	0.1166(18)	0.1036(6)	5.7(0.4)
C(17)	0.3436(19)	0.4079(24)	0.2040(8)	4.4(0.4)	O(3)	0.2875(17)	0.5669(21)	-0.0048(7)	6.6(0.4)
C(18)	0.3055(22)	0.5158(28)	0.2325(10)	5.5(0.5)	O(4)	0.0700(16)	0.6634(19)	0.1059(7)	6.7(0.4)
C(19)	0.3370(27)	0.5456(34)	0.2726(12)	6.7(0.6)	O(5)	-0.0250(13)	0.3324(16)	0.0046(6)	5.3(0.3)
C(20)	0.4599(31)	0.4856(39)	0.2825(14)	9.0(0.8)	O(6)	0.4666(15)	0.3234(18)	0.0120(6)	6.3(0.4)
C(21)	0.5090(33)	0.3947(39)	0.2547(14)	9.0(0.8)	O(7)	0.3653(27)	-0.1040(32)	-0.0013(12)	10.8(0.8)
C(22)	0.4385(29)	0.3474(35)	0.2142(13)	8.1(0.7)	O(8)	0.1641(15)	0.2279(18)	-0.0732(6)	6.1(0.3)
C(23)	0.3993(15)	0.5198(18)	0.1135(6)	3.5(0.3)	O(9)	0.0448(16)	-0.0015(20)	0.0505(7)	6.4(0.4)

TABLE 2
Fractional atomic co-ordinates and vibrational parameters (\AA^2), with estimated standard deviations in parentheses, for the orthorhombic (O) form

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	0.11588(3)	0.26337(6)	0.20669(19)	2.31(5)	3.61(5)	3.08(45)	0.24(4)	0.23(5)	0.19(6)
Os(2)	0.07528(3)	0.14936(8)	0.27794(20)	2.82(5)	4.97(6)	5.02(64)	-0.39(5)	0.37(6)	0.98(7)
Os(3)	0.10049(3)	0.17029(7)	0.0	2.67(5)	4.21(6)	4.14(56)	0.01(5)	-0.50(6)	-0.37(6)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
C(1)	0.1053(7)	0.2778(14)	0.0043(37)	4.0(0.6)	C(24)	0.0820(9)	0.3413(18)	-0.2146(48)	6.2(0.8)
C(2)	0.1350(5)	0.3175(11)	0.0242(24)	2.1(0.4)	C(25)	0.0596(12)	0.3849(25)	-0.2971(61)	8.7(1.1)
C(3)	0.1613(8)	0.2644(16)	0.0662(35)	4.5(0.6)	C(26)	0.0272(9)	0.4123(19)	-0.2424(43)	6.3(0.8)
C(4)	0.1518(7)	0.1917(14)	0.0753(30)	3.3(0.5)	C(27)	0.0223(10)	0.3934(21)	-0.1026(46)	6.8(0.9)
C(5)	0.1782(7)	0.1402(15)	0.1075(30)	3.9(0.6)	C(28)	0.0473(7)	0.3526(14)	-0.0235(33)	4.0(0.6)
C(6)	0.2011(7)	0.1428(14)	0.2202(33)	3.7(0.5)	C(29)	0.1389(8)	0.2683(17)	0.3707(38)	5.0(0.7)
C(7)	0.2297(8)	0.0938(15)	0.2373(31)	4.5(0.6)	C(30)	0.0855(9)	0.3291(17)	0.2850(43)	5.4(0.7)
C(8)	0.2344(8)	0.0401(16)	0.1544(35)	5.1(0.7)	C(31)	0.0542(9)	0.1669(17)	-0.0603(38)	4.9(0.7)
C(9)	0.2109(9)	0.0322(18)	0.0382(41)	6.3(0.8)	C(32)	0.1146(9)	0.1665(19)	-0.1693(43)	6.3(0.8)
C(10)	0.1831(7)	0.0820(15)	0.0170(36)	4.4(0.6)	C(33)	0.1007(8)	0.0715(17)	0.0346(34)	4.4(0.7)
C(11)	0.1987(6)	0.2883(13)	0.0962(28)	3.0(0.5)	C(34)	0.0376(9)	0.2055(19)	0.2350(40)	6.1(0.8)
C(12)	0.2265(8)	0.2615(16)	0.0075(39)	5.0(0.7)	C(35)	0.0690(7)	0.1534(13)	0.4591(29)	3.5(0.5)
C(13)	0.2600(9)	0.2794(18)	0.0358(40)	5.9(0.8)	C(36)	0.0524(11)	0.0627(24)	0.2561(53)	8.6(1.1)
C(14)	0.2673(8)	0.3257(16)	0.1388(38)	4.8(0.7)	C(37)	0.1182(9)	0.1126(18)	0.3292(39)	5.7(0.7)
C(15)	0.2438(9)	0.3559(19)	0.2287(41)	6.2(0.8)	O(1)	0.1549(7)	0.2747(13)	0.4791(30)	6.8(0.6)
C(16)	0.2083(8)	0.3355(15)	0.1900(37)	4.6(0.6)	O(2)	0.0670(6)	0.3744(13)	0.3325(27)	6.4(0.5)
C(17)	0.1452(7)	0.3912(14)	-0.0043(34)	3.8(0.5)	O(3)	0.0248(7)	0.1632(13)	-0.0931(30)	7.1(0.6)
C(18)	0.1707(9)	0.4100(19)	-0.1109(41)	6.3(0.8)	O(4)	0.1286(6)	0.1653(12)	-0.2760(31)	7.0(0.6)
C(19)	0.1798(10)	0.4829(23)	-0.1313(48)	7.9(1.0)	O(5)	0.1030(6)	0.0087(16)	0.0436(28)	6.8(0.6)
C(20)	0.1674(11)	0.5327(23)	-0.0429(53)	8.9(1.2)	O(6)	0.0118(6)	0.2387(13)	0.1850(32)	7.4(0.6)
C(21)	0.1382(11)	0.5195(25)	0.0413(57)	9.5(1.3)	O(7)	0.0571(8)	0.1788(15)	0.5765(33)	8.2(0.7)
C(22)	0.1295(8)	0.4473(17)	0.0760(37)	5.1(0.7)	O(8)	0.0393(8)	0.0054(21)	0.2764(44)	10.7(0.8)
C(23)	0.0765(7)	0.3261(15)	-0.0874(33)	4.0(0.6)	O(9)	0.1428(7)	0.0793(14)	0.3710(33)	7.7(0.7)

formed by C(1)—(4). These carbon atoms are practically coplanar with Os(3); we note that the value of a χ^2 calculation is doubtful in this case because the Os(3) contribution is too large.⁸

significant differences among the lengths of the three bonds C(1)—C(2), C(2)—C(3), and C(3)—C(4)

⁸ D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, 1953, 6, 698.

TABLE 3

Interatomic distances (Å) and angles (°), with standard deviations in parentheses, involving the osmium atoms in the two forms

(a) Distances								
	O	M		O	M		O	M
Os(1)—Os(2)	2.732(2)	2.741(2)	Os(2)—C(34)	1.83(4)	1.94(2)	C(29)—O(1)	1.23(5)	1.19(3)
Os(1)—Os(3)	2.729(2)	2.739(1)	Os(2)—C(35)	1.79(3)	1.79(3)	C(30)—O(2)	1.20(4)	1.16(2)
Os(2)—Os(3)	2.917(2)	2.894(1)	Os(2)—C(36)	1.85(4)	1.90(2)	C(31)—O(3)	1.18(4)	1.19(3)
Os(1)—C(1)	2.04(4)	2.23(2)	Os(2)—C(37)	1.85(3)	1.98(2)	C(32)—O(4)	1.18(5)	1.24(3)
Os(1)—C(2)	2.18(2)	2.31(2)	Os(3)—C(1)	2.01(3)	2.14(2)	C(33)—O(5)	1.17(4)	1.21(3)
Os(1)—C(3)	2.22(3)	2.30(2)	Os(3)—C(4)	2.14(3)	2.13(2)	C(34)—O(6)	1.27(4)	1.17(3)
Os(1)—C(4)	2.31(3)	2.29(2)	Os(3)—C(31)	1.88(3)	1.90(2)	C(35)—O(7)	1.32(4)	1.27(4)
Os(1)—C(29)	1.84(4)	1.81(3)	Os(3)—C(32)	1.75(4)	1.83(2)	C(36)—O(8)	1.19(6)	1.15(3)
Os(1)—C(30)	1.86(4)	1.84(2)	Os(3)—C(33)	1.87(3)	1.87(2)	C(37)—O(9)	1.20(4)	1.11(3)
(b) Angles								
	O	M		O	M		O	M
Os(1)—Os(3)—Os(2)	57.6(1)	58.1(1)	C(29)—Os(1)—Os(2)	95(1)	99(1)	C(1)—Os(3)—C(33)	167(1)	172(1)
Os(1)—Os(2)—Os(3)	57.7(1)	58.1(1)	C(29)—Os(1)—Os(3)	142(1)	136(1)	C(4)—Os(3)—Os(1)	55(1)	54(1)
Os(2)—Os(1)—Os(3)	64.7(1)	63.8(1)	C(29)—Os(1)—C(30)	85(2)	91(1)	C(4)—Os(3)—Os(2)	90(1)	94(1)
C(1)—Os(1)—Os(2)	104(1)	102(1)	C(30)—Os(1)—Os(2)	93(1)	89(1)	C(4)—Os(3)—C(31)	171(1)	171(1)
C(1)—Os(1)—Os(3)	47(1)	50(1)	C(30)—Os(1)—Os(3)	126(1)	125(1)	C(4)—Os(3)—C(32)	93(1)	90(1)
C(1)—Os(1)—C(2)	38(1)	35(1)	C(34)—Os(2)—Os(1)	87(1)	86(1)	C(4)—Os(3)—C(33)	97(1)	96(1)
C(1)—Os(1)—C(3)	63(1)	63(1)	C(34)—Os(2)—Os(3)	88(1)	85(1)	C(31)—Os(3)—Os(1)	117(1)	118(1)
C(1)—Os(1)—C(4)	70(1)	71(1)	C(34)—Os(2)—C(35)	95(2)	89(1)	C(31)—Os(3)—Os(2)	88(1)	83(1)
C(1)—Os(1)—C(29)	160(1)	157(1)	C(34)—Os(2)—C(36)	95(2)	96(1)	C(31)—Os(3)—C(32)	90(2)	94(1)
C(1)—Os(1)—C(30)	101(2)	98(1)	C(34)—Os(2)—C(37)	167(2)	169(1)	C(31)—Os(3)—C(33)	92(1)	91(1)
C(2)—Os(1)—Os(2)	140(1)	135(1)	C(35)—Os(2)—Os(1)	107(1)	104(1)	C(32)—Os(3)—Os(1)	132(1)	130(1)
C(2)—Os(1)—Os(3)	76(1)	73(1)	C(35)—Os(2)—Os(3)	164(1)	162(1)	C(32)—Os(3)—Os(2)	170(1)	171(1)
C(2)—Os(1)—C(3)	39(1)	36(1)	C(35)—Os(2)—C(36)	95(2)	97(1)	C(32)—Os(3)—C(33)	97(2)	93(1)
C(2)—Os(1)—C(4)	67(1)	64(1)	C(35)—Os(2)—C(37)	82(1)	94(1)	C(33)—Os(3)—Os(1)	119(1)	121(1)
C(2)—Os(1)—C(29)	122(1)	122(1)	C(36)—Os(2)—Os(1)	157(2)	159(1)	C(33)—Os(3)—Os(2)	72(1)	78(1)
C(2)—Os(1)—C(30)	104(1)	107(1)	C(36)—Os(2)—Os(3)	99(2)	101(1)	Os(1)—C(29)—O(1)	177(3)	179(2)
C(3)—Os(1)—Os(2)	140(1)	135(1)	C(36)—Os(2)—C(37)	98(2)	94(1)	Os(1)—C(30)—O(2)	176(3)	176(2)
C(3)—Os(1)—Os(3)	73(1)	74(1)	C(37)—Os(2)—Os(1)	81(1)	83(1)	Os(3)—C(31)—O(3)	177(3)	173(2)
C(3)—Os(1)—C(4)	36(1)	37(1)	C(37)—Os(2)—Os(3)	90(1)	89(1)	Os(3)—C(32)—O(4)	171(3)	176(2)
C(3)—Os(1)—C(29)	99(1)	96(1)	C(1)—Os(3)—Os(1)	48(1)	53(1)	Os(3)—C(33)—O(5)	173(3)	176(2)
C(3)—Os(1)—C(30)	138(1)	137(1)	C(1)—Os(3)—Os(2)	98(1)	100(1)	Os(2)—C(34)—O(6)	170(3)	179(2)
C(4)—Os(1)—Os(2)	92(1)	94(1)	C(1)—Os(3)—C(4)	74(1)	76(1)	Os(2)—C(35)—O(7)	157(2)	173(3)
C(4)—Os(1)—Os(3)	49(1)	49(1)	C(1)—Os(3)—C(31)	97(1)	96(1)	Os(2)—C(36)—O(8)	163(5)	172(2)
C(4)—Os(1)—C(29)	103(1)	98(1)	C(1)—Os(3)—C(32)	92(2)	89(1)	Os(2)—C(37)—O(9)	169(3)	175(2)
C(4)—Os(1)—C(30)	170(2)	170(1)						

TABLE 4

Equations of weighted planes, in the form $AX + BY + CZ = D$, in fractional co-ordinates, referred to the cell axes. Distances (Å × 10²) of relevant atoms from the planes are given below the respective atoms for monoclinic and orthorhombic (with apex) form; $\chi^2 = \Sigma(d/\sigma)^2$ and gives the statistical significance of the planarity (ref. 8)

Plane	Atoms				A	B	C	D	χ^2
	Os(1)	Os(2)	Os(3)						
(1)					10.62	4.49	-5.56	2.45	
(1')					31.48	-9.89	2.11	1.48	
(2)	C(1)	C(2)	C(3)	C(4)					
(2')	-1	2	-2	1	-5.92	8.38	5.68	2.45	2.6
	-0.1	0.2	-0.2	0.1	9.75	-2.51	-9.39	0.29	0.02
(3)	C(1)	C(2)	C(3)	C(4)	Os(3)				
(3')	-8	6	3	-6	6	-5.75	8.23	8.24	2.81
	-7	4	4	-6	6	11.91	-1.40	-9.29	0.90
(4)	C(1)	C(23)	C(24)	C(25)	C(26)	C(27)	C(28)		
(4')	9	-3	-8	4	3	4	-9	0.93	-0.26
	1	-2	-2	2	-0.4	-1	2	18.45	15.51
	C(2)	C(17)	C(18)	C(19)	C(20)	C(21)	C(22)		
(5)	-2	3	-2	-1	5	-7	3	-6.02	-6.80
(5')	3	0.1	-4	-4	13	-9	1	27.76	-1.63
	C(3)	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)		
(6)	4	-3	-7	8	2	-0.1	0.3	6.04	7.45
(6')	-3	-1	3	-1	-1	-3	5	3.94	14.39
	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)		
(7)	-0.5	2	-2	2	-1	1	-1	-2.11	4.12
(7')	5	-2	-5	3	2	0.3	-3	23.91	10.43
								26.47	4.25
								-5.36	5.17

TABLE 5

Interatomic distances (Å) and angles (°), with standard deviations in parentheses, involving the organic ligand in the two forms

(a) Distances								
	O	M		O	M		O	M
C(1)-C(2)	1.37(3)	1.37(3)	C(8)-C(9)	1.46(5)	1.26(4)	C(19)-C(20)	1.36(7)	1.19(5)
C(1)-C(23)	1.69(4)	1.56(3)	C(9)-C(10)	1.43(5)	1.48(4)	C(20)-C(21)	1.41(7)	1.36(6)
C(2)-C(3)	1.47(4)	1.42(3)	C(11)-C(12)	1.46(4)	1.46(4)	C(21)-C(22)	1.42(6)	1.52(5)
C(2)-C(17)	1.45(3)	1.48(3)	C(11)-C(16)	1.32(4)	1.38(3)	C(23)-C(24)	1.30(6)	1.38(4)
C(3)-C(4)	1.40(4)	1.47(3)	C(12)-C(13)	1.36(5)	1.35(5)	C(23)-C(28)	1.37(4)	1.35(4)
C(3)-C(11)	1.53(4)	1.46(3)	C(13)-C(14)	1.36(5)	1.27(7)	C(24)-C(25)	1.43(6)	1.36(5)
C(4)-C(5)	1.43(4)	1.53(2)	C(14)-C(15)	1.38(5)	1.37(6)	C(25)-C(26)	1.45(6)	1.31(5)
C(5)-C(6)	1.41(4)	1.35(3)	C(15)-C(16)	1.47(5)	1.52(5)	C(26)-C(27)	1.43(6)	1.36(5)
C(5)-C(10)	1.41(4)	1.42(3)	C(17)-C(18)	1.48(5)	1.44(4)	C(27)-C(28)	1.45(5)	1.37(5)
C(6)-C(7)	1.44(4)	1.43(3)	C(17)-C(22)	1.44(4)	1.32(4)			
C(7)-C(8)	1.30(4)	1.43(4)	C(18)-C(19)	1.41(6)	1.48(4)			

(b) Angles								
	O	M		O	M		O	M
Os(1)-C(1)-Os(3)	85(1)	77(1)	Os(1)-C(4)-C(3)	69(2)	72(1)	C(14)-C(15)-C(16)	110(3)	114(3)
Os(1)-C(1)-C(2)	76(2)	75(1)	Os(1)-C(4)-C(5)	133(2)	131(1)	C(15)-C(16)-C(11)	128(3)	118(2)
Os(1)-C(1)-C(23)	136(2)	132(1)	Os(3)-C(4)-C(3)	113(2)	115(1)	C(2)-C(17)-C(18)	123(3)	116(2)
Os(3)-C(1)-C(2)	128(2)	117(1)	Os(3)-C(4)-C(5)	127(2)	126(1)	C(2)-C(17)-C(22)	118(3)	124(2)
Os(3)-C(1)-C(23)	117(2)	121(1)	C(3)-C(4)-C(5)	118(2)	118(2)	C(18)-C(17)-C(22)	120(3)	119(3)
C(2)-C(1)-C(23)	110(2)	119(2)	C(4)-C(5)-C(6)	126(3)	124(2)	C(17)-C(18)-C(19)	119(3)	115(2)
Os(1)-C(2)-C(1)	66(2)	69(1)	C(4)-C(5)-C(10)	118(3)	116(2)	C(18)-C(19)-C(20)	118(4)	125(3)
Os(1)-C(2)-C(3)	72(2)	72(2)	C(6)-C(5)-C(10)	116(3)	119(2)	C(19)-C(20)-C(21)	122(4)	124(4)
Os(1)-C(2)-C(17)	133(2)	130(1)	C(5)-C(6)-C(7)	123(3)	124(2)	C(20)-C(21)-C(22)	119(4)	115(3)
C(1)-C(2)-C(3)	104(2)	116(2)	C(6)-C(7)-C(8)	121(3)	115(2)	C(21)-C(22)-C(17)	117(3)	120(3)
C(1)-C(2)-C(17)	135(2)	125(2)	C(7)-C(8)-C(9)	119(3)	123(3)	C(1)-C(23)-C(24)	121(3)	118(2)
C(3)-C(2)-C(17)	120(2)	118(2)	C(8)-C(9)-C(10)	121(3)	123(3)	C(1)-C(23)-C(28)	119(3)	123(2)
Os(1)-C(3)-C(2)	69(2)	72(1)	C(9)-C(10)-C(5)	120(3)	116(2)	C(24)-C(23)-C(28)	120(3)	119(2)
Os(1)-C(3)-C(4)	75(2)	71(1)	C(3)-C(11)-C(12)	118(3)	122(2)	C(23)-C(24)-C(25)	124(4)	117(3)
Os(1)-C(3)-C(11)	128(2)	129(1)	C(3)-C(11)-C(16)	126(3)	119(2)	C(24)-C(25)-C(26)	120(5)	125(4)
C(2)-C(3)-C(4)	119(2)	114(2)	C(12)-C(11)-C(16)	116(3)	118(2)	C(25)-C(26)-C(27)	112(4)	117(3)
C(2)-C(3)-C(11)	120(2)	122(2)	C(11)-C(12)-C(13)	119(3)	121(3)	C(26)-C(27)-C(28)	124(3)	120(3)
C(4)-C(3)-C(11)	121(3)	123(2)	C(12)-C(13)-C(14)	120(3)	119(4)	C(27)-C(28)-C(23)	119(3)	121(3)
Os(1)-C(4)-Os(3)	75(1)	76(1)	C(13)-C(14)-C(15)	127(3)	128(5)			

(Table 5) are in agreement with a configuration =C(1)-C(2)-C(3)-C(4)= for the organic ligand. On the basis of bond lengths and angles, the organic ligand should act as a four-electron donor on Os(1) (π co-ordination) and form two σ -bonds: C(1)-Os(3) and C(4)-Os(3). The behaviour of the organic ligand appears constant in these and in other similar molecules^{2,3} with the possible exception of $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_8$, where the existence of the localized double bond C(2)-C(3) cannot be excluded² and where an interaction, not fully understood, between Ph(I) and Os(2) was found.

A comparison of the four independent Os_3 clusters* observed in $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_8$,² $(\text{Ph}_4\text{C}_4)(\text{Ph}_2\text{C}_2)\text{Os}_3(\text{CO})_7$,³ and $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_9$ with that found in $\text{Os}_3(\text{CO})_{12}$ ⁹ establishes (i) a small but significant departure from an equilateral triangle and (ii) a shorter mean Os-Os distance. Further, (iii) the side which interacts with Ph_4C_4 is shorter than the mean Os-Os length; except for that in $(\text{Ph}_4\text{C}_4)(\text{Ph}_2\text{C}_2)\text{Os}_3(\text{CO})_7$, the length of the chelated side corresponds closely to that for Os-Os (2.75 Å) in $(\text{C}_6\text{H}_8)\text{Os}_2(\text{CO})_6$.¹⁰

Some of the largest differences between angles in the two structures [*i.e.* Os-C-O angles involving O(6), O(7), O(8) and O(9)] occur for atoms engaged in short intermolecular contacts (Tables 6 and 7); these are

* The labelling of the osmium atoms is the same in the four discussed molecules with respect to the co-ordination with Ph_4C_4 ; the lengths of Os(1)-Os(2), Os(1)-Os(3), Os(2)-Os(3) are 2.874(2), 2.747(1), and 2.944(2) Å in $(\text{Ph}_4\text{C}_4)\text{Os}_3(\text{CO})_8$ and 2.814(2), 2.680(2), and 2.744(2) Å in $(\text{Ph}_4\text{C}_4)(\text{Ph}_2\text{C}_2)\text{Os}_3(\text{CO})_7$.

TABLE 6

Principal intermolecular contacts (≤ 3.3 Å) for the monoclinic form

O(1) ... C(24 ^I)	3.19(4)	O(4) ... O(8 ^{III})	3.16(3)
O(1) ... O(4 ^I)	3.30(3)	O(5) ... C(32 ^{III})	3.16(3)
O(2) ... C(8 ^{II})	3.30(4)	O(5) ... C(33 ^{III})	3.16(3)
O(3) ... O(5 ^{III})	3.34(3)	O(6) ... O(7 ^V)	2.99(4)
O(3) ... O(6 ^{IV})	3.19(3)	O(9) ... C(37 ^{VI})	3.35(3)
O(4) ... O(5 ^{III})	3.30(3)	O(9) ... O(9 ^{VI})	3.15(3)

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

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

TABLE 7

Principal intermolecular contacts (≤ 3.3 Å) for the orthorhombic form

O(1) ... O(4 ^I)	3.30(4)	O(5) ... O(9 ^{IV})	2.81(4)
O(3) ... C(34 ^{III})	3.04(5)	O(6) ... O(7 ^V)	3.07(4)
O(3) ... O(6 ^{III})	2.95(4)	O(7) ... C(32 ^I)	3.34(5)
O(4) ... O(7 ^{III})	3.11(4)	O(8) ... O(8 ^{VI})	3.03(4)
O(5) ... C(37 ^{IV})	3.14(5)		

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

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

shorter, on average, in the O- than in the M-form and, except for C(24), concern only carbonyl groups.

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⁹ E. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

¹⁰ R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc.*, 1963, 380.