Crystal and Molecular Structure of Heptacarbonyl-μ_3-diphenylacetylene-μ-(1,2,3,4-tetraphenylbutadiene-1,4-diyl)-*triangulo*-triosmium

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Crystals of the title compound are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 14{\cdot}395(6)$, $b = 18{\cdot}895(11)$, $c = 9{\cdot}451(5)$ Å, $\alpha = 92{\cdot}53(3)$, $\beta = 103{\cdot}25(7)$, $\gamma = 113{\cdot}81(5)$°. The structure was solved by Patterson and Fourier syntheses, and refined by least-squares methods to R 0·078 for 4053 non-zero reflexions measured on a diffractometer. The molecule is built up by a cluster of three osmium atoms, at the corners of a nearly equilateral triangle, and by two organic ligands; the osmium atoms are bonded to two [Os(1) and Os(3)] or three [Os(2)] carbonyl groups. While the chelation between Ph_4C_4 and the cluster is attained *via* σ-bonds and the donation of π-electrons of the osmacyclopentadiene ring, Ph_2C_2 appears to be four-electron donor on the whole cluster. The shortest Os–Os bond [2·680(2) Å] faces the Ph_4C_4 ligand.

As part of a series of studies [1-3] on derivatives of $Os_3(CO)_{12}$ we carried out an X-ray study of $(Ph_4C_4)(Ph_2C_2)Os_3(CO)_7$ (I) in order to compare its molecular configuration with that of $(Ph_4C_4)Os_3(CO)_8$ (II),[2] in which a puzzling interaction between a phenyl group and an osmium atom has been detected. By comparison with (II) and on the basis of physicochemical measurements, two configurations for (I) have been suggested,[3] in which diphenylacetylene bridges either two osmium atoms [Os(2) and Os(3)], or the cluster as a whole.

EXPERIMENTAL

$Ph_6C_6Os_3(CO)_7$ was prepared as described in ref. 3 and recrystallized from n-heptane (at room temperature) as red-orange lamellar {110} crystals elongated in the z direction.

Crystal Data.—$C_{49}H_{30}O_7Os_3$, $M = 1301{\cdot}369$, Triclinic, $a = 14{\cdot}395(6)$, $b = 18{\cdot}895(11)$, $c = 9{\cdot}451(5)$ Å, $\alpha = 92{\cdot}53(3)$, $\beta = 103{\cdot}25(7)$, $\gamma = 113{\cdot}81(5)$°, $U = 2262{\cdot}2$ Å^3, $D_m = 1{\cdot}90$ (flotation), $Z = 2$, $D_c = 1{\cdot}91$, $F(000) = 1186$. $\mu = 161$ cm^{-1} for Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å. Space group $P\bar{1}$.

Since no significant difference was detected between the amplitudes of several Bijvoet pairs, space group $P\bar{1}$ was assumed and the choice was confirmed by the subsequent structural analysis. Unit-cell parameters and their σ were obtained by a least-squares procedure using the values of 30 θ (>24°) measured on a single-crystal diffractometer ($\lambda\alpha_1 = 1{\cdot}54051$ Å, $\lambda\alpha = 1{\cdot}54178$ Å).

Intensity Measurements.—Intensities were measured on a General Electric automatic three-circle diffractometer, by use of nickel-filtered radiation Cu-K_α, on a crystal ($0{\cdot}04 \times 0{\cdot}02 \times 0{\cdot}44$ mm) mounted with its z axis coincident with the instrumental ϕ axis. Integrated intensities ($2\theta \leqslant 100°$ because of the low diffracting power of the crystal) were collected by the θ—2θ scanning method (2° min^{-1}, 0·5° background on both sides of each peak); 731 of the 4784 measured reflexions were rejected because they were not statistically reliable.

A standard reflexion (222) was checked every 40 reflexions; its relative intensity showed a non-linear decrease from 3260 to 2720 during the eight days of the measurements. This effect, due to a slight deterioration of the crystal, was taken into account by a time-dependent scale-factor. Crystal deterioration and the narrowing of 2θ range are likely to have lowered the accuracy of the experimental data; because of this and also the small crystal size, no absorption or extinction corrections were applied.

Atomic scattering factors, including for osmium $\Delta f'$ and $\Delta f''$, were taken from ref. 4. The programs used, except a slightly modified full-matrix ORFLS,[5] are local versions of standard programs.

Solution and Refinement of the Structure.—Starting from the three independent osmium atoms, whose co-ordinates were obtained from a Patterson synthesis, the complete solution was attained by a sequence of difference-Fourier syntheses. Least-squares refinement, with anisotropic thermal parameters for the osmium atoms only, was considered complete when the shifts of the parameters were smaller than their estimated standard deviations. R value, for the 4053 reflexions listed in Supplementary Publication No. SUP 20738 (19 pp, 1 microfiche),* is 0·078; weighted value R' 0·085. The weighting scheme was ($|F_o|$ 0·24 times the absolute scale): $w = 67/(0{\cdot}04F_o^2 + 2|F_o| + 18)$ for $|F_o| \geqslant 18$; $w = 0{\cdot}055|F_o| + 0{\cdot}01$ for $|F_o| < 18$. The constants in these expressions were modified during the refinement in order to maintain $\Sigma w\Delta^2$ satisfactorily constant for the amplitudes batched in various groups. A score of the strongest reflexions, suspected of severe extinction, were given zero weight. A final difference-Fourier synthesis showed a satisfactorily balanced distribution of positive and negative ripples.

Final fractional co-ordinates and thermal parameters are listed in Table 1. Least-squares planes were calculated by the method of ref. 6.

RESULTS AND DISCUSSION

The present X-ray study shows that the correct molecular configuration (Figure 1) is that in which

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[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] R. P. Ferrari, G. A. Vaglio, O. Gambino, and G. Cetini, *Inorg. Chim. Acta*, 1973, **7**, 193.

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

[5] 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.

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

diphenylacetylene bridges the cluster as a whole. The complete molecule is built up by two organic ligands and a cluster of three osmium atoms which are at the corners of a nearly equilateral triangle; this has its shortest side, Os(1)–Os(3) (Table 2), facing Ph_4C_4 and the osmium atoms are bonded to two [Os(1) and Os(3)] or three [Os(2)] carbonyl groups.

TABLE 1

Fractional atomic co-ordinates and vibrational parameters (Å²), with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	*B*/Å²
Os(1)	0·16131(8)	0·23780(7)	0·14327(12)	*
Os(2)	−0·03441(9)	0·15805(6)	0·19902(13)	*
Os(3)	0·13073(8)	0·27596(6)	0·39942(12)	*
C(1)	0·2443(17)	0·2292(12)	0·3989(23)	2·3(0·4)
C(2)	0·3131(20)	0·2615(15)	0·3173(28)	4·0(0·5)
C(3)	0·3175(17)	0·3344(12)	0·2626(24)	2·7(0·4)
C(4)	0·2388(20)	0·3553(15)	0·2971(27)	3·8(0·5)
C(5)	0·2407(20)	0·4317(15)	0·2577(28)	4·2(0·5)
C(6)	0·2209(33)	0·4470(25)	0·1162(47)	5·5(0·9)
C(7)	0·2406(31)	0·5242(24)	0·0939(44)	6·0(0·9)
C(8)	0·2642(35)	0·5782(26)	0·2194(50)	6·2(1·0)
C(9)	0·2734(29)	0·5663(22)	0·3637(41)	5·2(0·8)
C(10)	0·2631(30)	0·4898(22)	0·3769(41)	4·6(0·8)
C(11)	0·4112(22)	0·3894(16)	0·2177(30)	3·9(0·5)
C(12)	0·4728(35)	0·4635(26)	0·2993(49)	3·6(1·0)
C(13)	0·5567(31)	0·5090(23)	0·2591(43)	4·9(0·8)
C(14)	0·5887(35)	0·4885(26)	0·1433(49)	6·1(1·0)
C(15)	0·5327(37)	0·4119(28)	0·0679(53)	4·9(1·1)
C(16)	0·4418(30)	0·3607(22)	0·1068(41)	6·4(0·8)
C(17)	0·3967(27)	0·2328(20)	0·3104(38)	4·6(0·7)
C(18)	0·4880(28)	0·2596(20)	0·4293(39)	5·9(0·7)
C(19)	0·5688(28)	0·2358(21)	0·4263(40)	7·1(0·8)
C(20)	0·5557(28)	0·1826(21)	0·3056(39)	6·6(0·8)
C(21)	0·4685(27)	0·1569(20)	0·1897(38)	7·3(0·7)
C(22)	0·3849(25)	0·1802(19)	0·1897(35)	5·5(0·7)
C(23)	0·2449(20)	0·1659(15)	0·4808(28)	3·6(0·5)
C(24)	0·2298(23)	0·0918(17)	0·4100(32)	5·3(0·6)
C(25)	0·2421(28)	0·0366(21)	0·5064(40)	6·4(0·8)
C(26)	0·2835(35)	0·0583(21)	0·6547(40)	6·3(0·8)
C(27)	0·3006(27)	0·1321(20)	0·7233(38)	7·3(0·8)
C(28)	0·2843(23)	0·1855(17)	0·6335(32)	5·1(0·6)
C(29)	0·0184(16)	0·2899(12)	0·2320(23)	2·2(0·4)
C(30)	0·0273(17)	0·2666(13)	0·1026(24)	3·4(0·4)
C(31)	−0·0228(20)	0·2830(15)	−0·0458(29)	4·7(0·5)
C(32)	−0·0202(24)	0·3574(18)	−0·0573(33)	5·2(0·7)
C(33)	−0·0600(27)	0·3748(20)	−0·1990(39)	7·3(0·8)
C(34)	−0·0990(35)	0·3189(27)	−0·3129(50)	8·6(1·1)
C(35)	−0·1007(30)	0·2468(23)	−0·3146(42)	8·0(0·9)
C(36)	−0·0583(27)	0·2263(20)	−0·1722(39)	6·3(0·8)
C(37)	−0·0653(20)	0·3223(15)	0·2431(28)	3·8(0·5)
C(38)	−0·1717(20)	0·2844(14)	0·1586(27)	4·1(0·5)
C(39)	−0·2393(19)	0·3179(14)	0·1657(27)	4·6(0·5)
C(40)	−0·2003(21)	0·3899(16)	0·2586(29)	6·0(0·6)
C(41)	−0·0926(22)	0·4331(16)	0·3354(31)	5·6(0·6)
C(42)	−0·0291(21)	0·3954(15)	0·3286(29)	4·5(0·5)
C(43)	0·0676(18)	0·2021(14)	0·5174(26)	4·6(0·5)
C(44)	0·1399(17)	0·3525(13)	0·5491(25)	3·5(0·4)
C(45)	−0·0239(18)	0·0661(14)	0·2705(25)	3·6(0·5)
C(46)	−0·1493(22)	0·1443(16)	0·2792(30)	6·0(0·6)
C(47)	−0·1266(22)	0·0945(16)	0·0121(30)	6·4(0·6)
C(48)	0·1882(20)	0·2678(15)	−0·0396(31)	5·3(0·5)
C(49)	0·1148(23)	0·1346(18)	0·0621(33)	6·0(0·6)
O(1)	0·0438(14)	0·1590(10)	0·6007(20)	5·1(0·4)
O(2)	0·1505(13)	0·3990(10)	0·6416(19)	4·9(0·3)
O(3)	−0·0195(15)	0·0139(11)	0·3221(21)	5·7(0·4)
O(4)	−0·2146(16)	0·1353(11)	0·3304(21)	6·2(0·4)
O(5)	−0·1919(19)	0·0491(14)	−0·0757(27)	9·5(0·6)
O(6)	0·2037(16)	0·2892(12)	−0·1420(24)	6·3(0·4)
O(7)	−0·1009(16)	−0·0729(12)	−0·0013(22)	6·8(0·5)

* Anisotropic coefficients for osmium are the B_{ij} coefficients of the function: $\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja^*_ia^*_j\right)$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	2·73(5)	3·65(6)	2·76(5)	0·96(2)	0·26(2)	0·10(2)
Os(2)	2·65(5)	2·95(5)	3·53(6)	0·71(2)	0·12(4)	−0·02(2)
Os(3)	2·59(5)	2·63(5)	2·58(5)	0·75(2)	0·22(2)	0·22(2)

When the present compound is compared with compound (II) [2] the following points seem to be of particular significance. Whilst the C(1)–C(4) bond is still roughly perpendicular to Os(1)–Os(3), the disappearance of a bond of any kind between Ph(I) and Os(2) [2] allows a rotation, around Os(1)–Os(3), of the Ph_4C_4 group in order to accommodate the Ph_2C_2 group. The reciprocal position of the Ph_4C_4 phenyl groups is appreciably affected; the angles of phenyl groups (I)—(IV) with plane (2) (Table 3) of the chelate carbon atoms are now 66, 85, 56, and 59°. Both the group of four chelate carbon atoms and the five-atom moiety including also Os(3) are still satisfactorily planar [planes (2) and (3), Table 3]; these two planes form with the plane of the osmium atoms [plane (1)] angles of 79 and 81°, respectively. The three Os–Os bond lengths are significantly shorter than in (II), and Os(1)–Os(3) (2·680 Å) is the shortest of all such distances in published structures involving Os_3 clusters (see refs. 1, 2, and 7—10); there is, however, a value of 2·67 Å quoted in ref. 11.

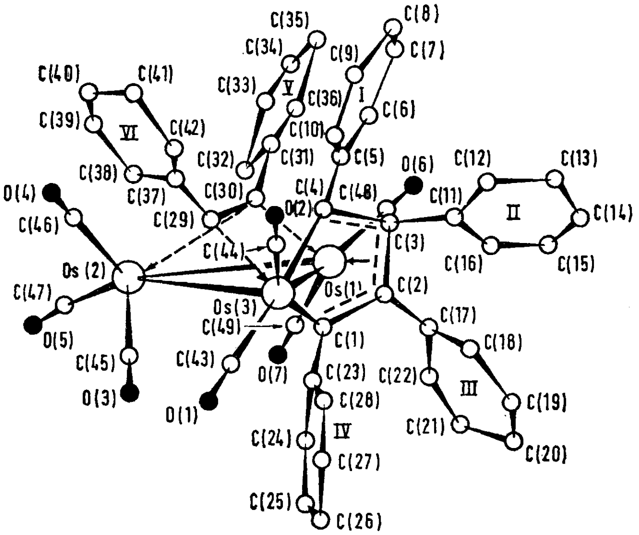

FIGURE 1 View of one molecule showing the atom labelling system

The C(29)–C(30) bond of diphenylacetylene (Table 4) is roughly parallel to Os(1)–Os(3) and its mid-point is nearly above the centre of gravity of the osmium cluster. C(37), C(29), C(30), and C(31) lie in a plane

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TABLE 2

Interatomic distances (Å) and angles (°) involving the osmium atoms and the carbonyl groups with standard deviations in parentheses

(*a*) Distances

Os(1)–Os(2)	2·814(2)	Os(1)–C(30)	2·16(2)	Os(2)–C(47)	1·94(3)	C(44)–O(2)	1·15(3)
Os(1)–Os(3)	2·680(2)	Os(1)–C(48)	1·92(3)	Os(3)–C(1)	2·14(2)	C(45)–O(3)	1·14(3)
Os(2)–Os(3)	2·744(2)	Os(1)–C(49)	1·85(3)	Os(3)–C(4)	2·15(3)	C(46)–O(4)	1·12(4)
Os(1)–C(1)	2·47(2)	Os(2)–C(29)	2·28(2)	Os(3)–C(29)	2·08(2)	C(47)–O(5)	1·11(4)
Os(1)–C(2)	2·27(3)	Os(2)–C(30)	2·22(2)	Os(3)–C(43)	1·91(2)	C(48)–O(6)	1·10(4)
Os(1)–C(3)	2·25(2)	Os(2)–C(45)	1·94(3)	Os(3)–C(44)	1·92(2)	C(49)–O(7)	1·20(4)
Os(1)–C(4)	2·30(3)	Os(2)–C(46)	1·91(3)	C(43)–O(1)	1·17(3)		

(*b*) Angles

Os(1)–Os(3)–Os(2)	62·5(1)	C(4)–Os(3)–Os(1)	56(1)	C(29)–Os(2)–Os(1)	68(1)	C(46)–Os(2)–Os(3)	102(1)
Os(1)–Os(2)–Os(3)	57·6(1)	C(4)–Os(3)–C(29)	83(1)	C(29)–Os(2)–C(30)	34(1)	C(46)–Os(2)–Os(1)	157(1)
Os(2)–Os(1)–Os(3)	59·9(1)	C(4)–Os(3)–C(43)	165(1)	C(29)–Os(2)–C(45)	150(1)	C(46)–Os(2)–C(47)	93(1)
C(1)–Os(1)–Os(3)	49(1)	C(4)–Os(3)–C(44)	97(1)	C(29)–Os(2)–C(46)	91(1)	C(47)–Os(2)–Os(3)	162(1)
C(1)–Os(1)–Os(2)	87(1)	C(29)–Os(3)–Os(2)	54(1)	C(29)–Os(2)–C(47)	121(1)	C(47)–Os(2)–Os(1)	105(1)
C(1)–Os(1)–C(2)	33(1)	C(29)–Os(3)–Os(1)	73(1)	C(29)–Os(3)–C(43)	112(1)	C(1)–Os(3)–Os(2)	96(1)
C(1)–Os(1)–C(3)	62(1)	C(4)–Os(1)–Os(3)	50(1)	C(29)–Os(3)–C(44)	97(1)	C(1)–Os(3)–Os(1)	60(1)
C(1)–Os(1)–C(4)	67(1)	C(4)–Os(1)–Os(2)	105(1)	C(43)–Os(3)–Os(2)	76(1)	C(1)–Os(3)–C(4)	76(1)
C(1)–Os(1)–C(30)	118(1)	C(4)–Os(1)–C(30)	82(1)	C(43)–Os(3)–Os(1)	124(1)	C(1)–Os(3)–C(29)	133(1)
C(1)–Os(1)–C(48)	144(1)	C(4)–Os(1)–C(48)	102(1)	C(43)–Os(3)–C(44)	85(1)	C(1)–Os(3)–C(43)	91(1)
C(1)–Os(1)–C(49)	98(1)	C(4)–Os(1)–C(49)	165(1)	C(44)–Os(3)–Os(2)	134(1)	C(1)–Os(3)–C(44)	126(1)
C(2)–Os(1)–Os(3)	75(1)	C(30)–Os(1)–Os(3)	70(1)	C(44)–Os(3)–Os(1)	151(1)	Os(3)–C(43)–O(1)	170(2)
C(2)–Os(1)–Os(2)	121(1)	C(30)–Os(1)–Os(2)	51(1)	C(30)–Os(2)–Os(3)	68(1)	Os(3)–C(44)–O(2)	177(1)
C(2)–Os(1)–C(3)	38(1)	C(30)–Os(1)–C(48)	92(1)	C(30)–Os(2)–Os(1)	49(1)	Os(2)–C(45)–O(3)	175(2)
C(2)–Os(1)–C(4)	63(1)	C(30)–Os(1)–C(49)	108(1)	C(30)–Os(2)–C(45)	152(1)	Os(2)–C(46)–O(4)	177(1)
C(2)–Os(1)–C(30)	141(1)	C(48)–Os(1)–Os(3)	148(1)	C(30)–Os(2)–C(46)	116(1)	Os(2)–C(47)–O(5)	165(3)
C(2)–Os(1)–C(48)	111(1)	C(48)–Os(1)–Os(2)	128(1)	C(30)–Os(2)–C(47)	95(1)	Os(1)–C(48)–O(6)	176(3)
C(2)–Os(1)–C(49)	104(1)	C(48)–Os(1)–C(49)	89(1)	C(45)–Os(2)–Os(3)	102(1)	Os(1)–C(49)–O(7)	168(3)
C(3)–Os(1)–Os(3)	77(1)	C(49)–Os(1)–Os(3)	121(1)	C(45)–Os(2)–Os(1)	103(1)		
C(3)–Os(1)–Os(2)	137(1)	C(49)–Os(1)–Os(2)	74(1)	C(45)–Os(2)–C(46)	92(1)		
C(4)–Os(3)–Os(2)	112(1)	C(29)–Os(2)–Os(3)	48(1)	C(45)–Os(2)–C(47)	89(1)		

TABLE 3

Equations of weighted planes, in the form $AX + BY + CZ = D$, in fractional co-ordinates referred to the cell axes. Distances (Å × 10^2) of relevant atoms from the planes are given in square brackets; σ values for these are *ca.* 0·05 for C and 0·003 Å for Os

	A	B	C	D	χ^2 *
Plane (1): Os(1), Os(2), Os(3)	7·88	−16·91	3·46	−2·25	
Plane (2): C(1)—(4) [C(1) 1, C(2) −3, C(3) 2, C(4) −1]	4·58	5·12	6·35	4·81	0·8
Plane (3): C(1)—(4), Os(3) [C(1) 9, C(2) −8, C(3) −3, C(4) 8, Os(3) −0·4]	3·17	5·65	6·91	4·74	13·6
Plane (4): C(37), C(29)—(31) [C(37) −3, C(29) 5, C(30) −5, C(31) 3]	5·70	12·72	−1·08	3·49	4·1
Plane (5): Phenyl (I) [C(1) 6, C(23) −9, C(24) 1, C(25) −3, C(26) 7, C(27) 1, C(28) 2]	13·54	−1·34	−2·90	1·79	7·1
Plane (6): Phenyl (II) [C(2) −1, C(17) 0·2, C(18) 1, C(19) −1, C(20) 1, C(21) −1, C(22) 1]	−3·81	−12·74	5·86	−2·66	0·1
Plane (7): Phenyl (III) [C(3) 1, C(11) −4, C(12) 2, C(13) 2, C(14) −3, C(15) 2, C(16) 2]	9·08	−12·24	5·10	0·11	1·1
Plane (8): Phenyl (IV) [C(4) 5, C(5) −2, C(6) −10, C(7) 5, C(8) 6, C(9) −2, C(10) −3]	13·66	−2·06	−1·60	2·01	3·8
Plane (9): Phenyl (V) [C(30) 2, C(31) −5, C(32) −1, C(33) 2, C(34) −1, C(35) 1, C(36) 1]	13·13	−0·46	−3·97	−0·19	1·6
Plane (10): Phenyl (VI) [C(29) −3, C(37) 5, C(38) 0, C(39) −2, C(40) 2 C(41) −4, C(42) 2]	−3·12	−8·57	3·86	−0·57	2·7

* $\chi^2 = \Sigma(d/\sigma)^2$ and gives the statistical significance of the planarity.[7]

[plane (4), Table 3] moderately inclined (66°) on the osmium plane in the direction of Os(2). Some short ($\leqslant$3 Å) intramolecular contacts (Table 5) obtain between the two organic ligands. None of the phenyl groups, including the bonded extranuclear carbon atoms, deviate significantly from planarity (Table 3); they approach closely (Table 5) some carbonyl groups.

TABLE 4

Interatomic distances (Å) and angles (°), with standard deviations in parentheses, in the organic ligand Ph_2C_2

(*a*) Distances			
C(29)–C(30)	1·33(3)	Os(2)–C(30)–Os(1)	80(1)
C(30)–C(31)	1·52(4)	Os(2)–C(30)–C(29)	75(2)
C(31)–C(32)	1·40(4)	Os(2)–C(30)–C(31)	127(2)
C(32)–C(33)	1·43(5)	Os(1)–C(30)–C(29)	108(2)
C(33)–C(34)	1·32(6)	Os(1)–C(30)–C(31)	124(2)
C(34)–C(35)	1·35(3)	C(29)–C(30)–C(31)	125(2)
C(35)–C(36)	1·47(6)	C(30)–C(31)–C(32)	119(2)
C(36)–C(31)	1·42(5)	C(30)–C(31)–C(36)	119(3)
C(29)–C(37)	1·57(4)	C(32)–C(31)–C(36)	121(3)
C(37)–C(38)	1·41(4)	C(31)–C(32)–C(33)	119(3)
C(38)–C(39)	1·37(4)	C(32)–C(33)–C(34)	118(4)
C(39)–C(40)	1·41(4)	C(33)–C(34)–C(35)	128(4)
C(40)–C(41)	1·42(4)	C(34)–C(35)–C(36)	117(4)
C(41)–C(42)	1·37(4)	C(35)–C(36)–C(31)	117(3)
C(42)–C(37)	1·40(4)	C(29)–C(37)–C(38)	122(3)
		C(29)–C(37)–C(42)	118(3)
(*b*) Angles		C(38)–C(37)–C(42)	120(3)
Os(3)–C(29)–Os(2)	78(1)	C(37)–C(38)–C(39)	120(3)
Os(3)–C(29)–C(30)	109(2)	C(38)–C(39)–C(40)	119(3)
Os(3)–C(29)–C(37)	130(2)	C(39)–C(40)–C(41)	124(3)
Os(2)–C(29)–C(30)	70(2)	C(40)–C(41)–C(42)	115(3)
Os(2)–C(29)–C(37)	118(2)	C(41)–C(42)–C(37)	123(3)
C(30)–C(29)–C(27)	122(2)		

The fact that the C(1)–C(2), C(2)–C(3), and C(3)–C(4) bond lengths are not significantly different, and the values of the angles and distances involving the four chelate carbons and Os(1) and Os(3) (Table 6), both suggest that the bonding between Ph_4C_4 and the cluster is attained *via* σ bonds of Os(3) with C(1) and C(4) and a donation of the four π electrons of the osmacyclopentadiene ring to Os(1). According to the geometry of the complex the diphenylacetylene is a four-electron donor to the whole cluster, in agreement with the requirements of the noble-gas rule. It seems reasonable to suppose that C(29) and C(30) are σ-bonded to Os(3) and Os(1) respectively and that the C(29)—C(30) bond is a π-donor to Os(2).

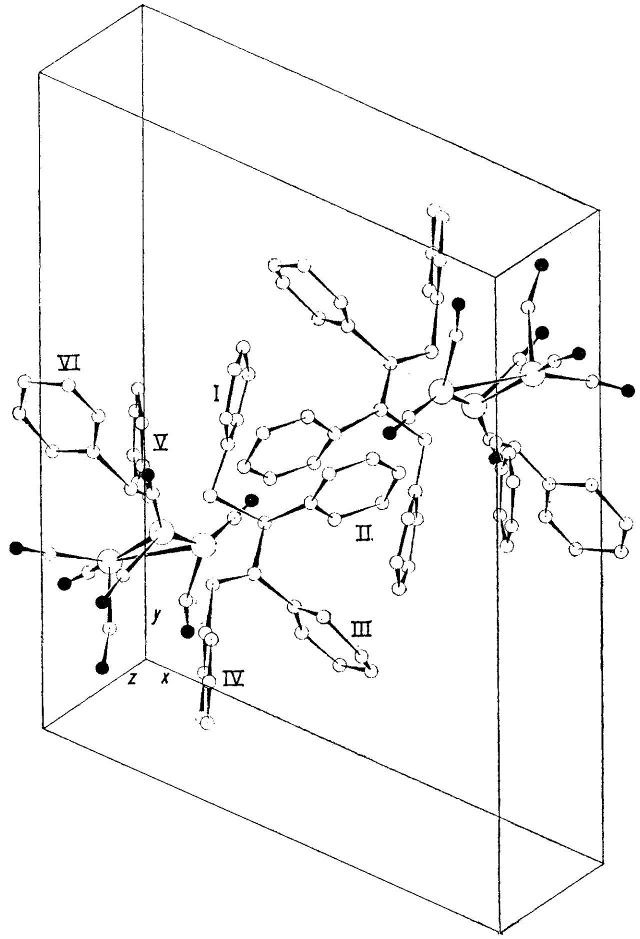

FIGURE 2 Clinographic projection, along the z axis, of the contents of one unit cell

TABLE 5

Principal intramolecular contacts ($\leqslant$3·0 Å)

Contact	Distance	Contact	Distance
Os(3) · · · C(30)	2·81(2)	C(4) · · · C(44)	3·04(4)
Os(2) · · · O(1)	2·92(3)	C(23) · · · C(43)	2·98(4)
Os(1) · · · C(29)	2·87(2)	C(29) · · · C(44)	3·00(3)
C(1) · · · C(43)	2·89(4)	C(29) · · · C(46)	3·00(4)
C(3) · · · C(48)	2·92(4)	C(30) · · · C(48)	2·94(4)
C(4) · · · C(29)	2·81(4)	C(38) · · · C(46)	3·03(4)
C(4) · · · C(30)	2·92(4)		

Figure 2 shows a clinographic projection, down the z axis, of the contents of one unit cell. The molecules are coupled, through the centre of symmetry at the origin, so as to establish short intermolecular contacts (Table 7) between carbonyl groups; other close contacts, along [001], enable the formation of infinite chains in the z direction.

TABLE 6

Interatomic distances (Å) and angles (°), with standard deviations in parentheses in the organic ligand C_4Ph_4

(*a*) Distances

C(1)–C(2)	1·37(4)
C(2)–C(3)	1·47(4)
C(3)–C(4)	1·44(4)
C(4)–C(5)	1·50(4)
C(5)–C(6)	1·37(5)
C(6)–C(7)	1·41(6)
C(7)–C(8)	1·41(6)
C(8)–C(9)	1·38(6)
C(9)–C(10)	1·41(6)
C(10)–C(5)	1·42(6)
C(3)–C(11)	1·51(4)
C(11)–C(12)	1·40(6)
C(12)–C(13)	1·33(7)
C(13)–C(14)	1·38(6)
C(14)–C(15)	1·40(7)
C(15)–C(16)	1·43(7)
C(16)–C(17)	1·40(7)
C(2)–C(17)	1·52(5)
C(17)–C(18)	1·40(5)
C(18)–C(19)	1·41(6)
C(19)–C(20)	1·41(5)
C(20)–C(21)	1·35(5)
C(21)–C(22)	1·44(5)
C(22)–C(17)	1·41(5)
C(1)–C(23)	1·45(4)
C(23)–C(24)	1·44(4)
C(24)–C(25)	1·45(5)
C(25)–C(26)	1·36(5)
C(26)–C(27)	1·41(6)
C(27)–C(28)	1·40(5)
C(28)–C(23)	1·39(4)

(*b*) Angles

Os(3)–C(1)–Os(1)	71(1)
Os(3)–C(1)–C(2)	116(2)
Os(3)–C(1)–C(23)	120(2)
Os(1)–C(1)–C(2)	65(2)
Os(1)–C(1)–C(23)	135(2)
C(2)–C(1)–C(23)	123(2)
Os(1)–C(2)–C(1)	82(2)
Os(1)–C(2)–C(3)	70(2)
Os(1)–C(2)–C(17)	129(2)
C(1)–C(2)–C(3)	118(2)
C(1)–C(2)–C(17)	120(3)
C(3)–C(2)–C(17)	121(3)
Os(1)–C(3)–C(2)	72(1)
Os(1)–C(3)–C(4)	74(1)
Os(1)–C(3)–C(11)	135(2)
C(2)–C(3)–C(4)	111(2)
C(2)–C(3)–C(11)	123(2)
C(4)–C(3)–C(11)	124(2)
Os(3)–C(4)–Os(1)	74(1)
Os(3)–C(4)–C(5)	126(2)
Os(1)–C(4)–C(3)	69(1)
Os(1)–C(4)–C(5)	127(2)
C(3)–C(4)–C(5)	116(2)
C(4)–C(5)–C(6)	124(3)
C(4)–C(5)–C(10)	116(3)
C(6)–C(5)–C(10)	120(3)
C(5)–C(6)–C(7)	118(4)
C(6)–C(7)–C(8)	117(4)
C(7)–C(8)–C(9)	129(4)
C(8)–C(9)–C(10)	110(4)
C(9)–C(10)–C(5)	125(4)
C(3)–C(11)–C(12)	120(3)
C(3)–C(11)–C(16)	118(3)
C(12)–C(11)–C(16)	121(4)
C(11)–C(12)–C(13)	118(4)
C(12)–C(13)–C(14)	125(4)
C(13)–C(14)–C(15)	118(4)
C(14)–C(15)–C(16)	119(5)
C(15)–C(16)–C(11)	118(4)
C(2)–C(17)–C(18)	118(3)
C(2)–C(17)–C(22)	122(3)
C(18)–C(17)–C(22)	120(3)
C(17)–C(18)–C(19)	120(3)
C(18)–C(19)–C(20)	120(3)
C(19)–C(20)–C(21)	121(4)
C(20)–C(21)–C(22)	121(3)
C(21)–C(22)–C(17)	119(3)
C(1)–C(23)–C(24)	122(2)
C(1)–C(23)–C(28)	117(3)
C(24)–C(23)–C(28)	120(3)
C(23)–C(24)–C(25)	116(3)
C(24)–C(25)–C(26)	122(4)
C(25)–C(26)–C(27)	121(4)
C(26)–C(27)–C(28)	118(3)
C(27)–C(28)–C(23)	122(3)

TABLE 7

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

Contact	Distance	Contact	Distance
C(35) · · · O(1$^{\mathrm{I}}$)	3·33(5)	O(1) · · · O(6$^{\mathrm{II}}$)	3·10(3)
C(36) · · · O(1$^{\mathrm{I}}$)	3·34(4)	O(1) · · · O(3$^{\mathrm{IV}}$)	3·28(3)
C(43) · · · O(6$^{\mathrm{II}}$)	3·30(3)	O(2) · · · O(6$^{\mathrm{II}}$)	3·15(3)
C(44) · · · O(6$^{\mathrm{II}}$)	3·27(3)	O(3) · · · O(7$^{\mathrm{III}}$)	3·12(3)
C(45) · · · O(7$^{\mathrm{III}}$)	3·24(3)	O(5) · · · O(7$^{\mathrm{III}}$)	3·10(4)
C(47) · · · O(7$^{\mathrm{III}}$)	3·33(4)	O(7) · · · O(7$^{\mathrm{III}}$)	3·11(3)

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

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

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