Table 3. *Bond distances* (Å) *and angles* (°) *involving* H *atoms*

The e.s.d.'s are in the ranges 0·03–0·04 Å and 1–2°.

H(4)–N(4)	0·90	H(51)–C(5)	1·06	C(7)–C(8)–H(81)	111	N(9)–C(8)–H(82)	111
H(52)–C(5)	0·97	H(71)–C(7)	1·03	H(81)–C(8)–H(82)	109	N(9)–C(10)–H(101)	112
H(72)–C(7)	1·02	H(81)–C(8)	1·01	C(11)–C(10)–H(102)	113	H(101)–C(10)–H(102)	102
H(82)–C(8)	1·01	H(101)–C(10)	1·00	C(10)–C(11)–H(111)	109	H(111)–C(11)–H(112)	108
H(102)–C(10)	1·00	H(111)–C(11)	1·04	C(12)–C(13)–H(13)	116	C(14)–C(13)–H(13)	121
H(112)–C(11)	0·98	H(13)–C(13)	1·03	C(13)–C(14)–H(14)	121	C(15)–C(14)–H(14)	118
H(14)–C(14)	1·04	H(15)–C(15)	0·99	C(14)–C(15)–H(15)	119	C(16)–C(15)–H(15)	121
H(16)–C(16)	1·03	H(17)–C(17)	0·99	C(15)–C(16)–H(16)	121	C(17)–C(16)–H(16)	117
H(181)–C(18)	1·05	H(182)–C(18)	1·08	C(12)–C(17)–H(17)	116	C(16)–C(17)–H(17)	122
H(191)–C(19)	1·06	H(192)–C(19)	1·00	N(9)–C(18)–H(181)	110	C(19)–C(18)–H(181)	107
H(201)–C(20)	1·00	H(202)–C(20)	0·98	H(181)–C(18)–H(182)	109	C(18)–C(19)–H(191)	109
H(24)–C(24)	1·00	H(25)–C(25)	1·01	C(20)–C(19)–H(192)	103	H(191)–C(19)–H(192)	114
H(27)–C(27)	1·10	H(28)–C(28)	1·00	C(19)–C(20)–H(201)	108	C(21)–C(20)–H(202)	108
				H(201)–C(20)–H(202)	105	C(23)–C(24)–H(24)	119
C(3)–N(4)–H(4)	114	C(5)–N(4)–H(4)	121	C(25)–C(24)–H(24)	120	C(24)–C(25)–H(25)	119
N(4)–C(5)–H(51)	106	C(6)–C(6)–H(52)	111	C(26)–C(25)–H(25	121	C(26)–C(27)–H(27)	123
H(51)–C(5)–H(52)	110	C(6)–C(7)–H(71)	110	C(28)–C(27)–H(27)	119	C(23)–C(28)–H(28)	115
C(8)–C(7)–H(72)	114	H(71)–C(7)–H(72)	101	C(27)–C(28)–H(28)	124		

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972. Tech. Rep. TR 192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1968). *J. Chem. Phys.* **42**, 3175–3187.

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Hexadecacarbonylpentaosmium

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Abstract. $Os_5(CO)_{16}$, trigonal, $P3_121$, $a = b = 9{\cdot}204$ (2), $c = 24{\cdot}818$ (4) Å, $U = 1820{\cdot}8$ Å^3, $Z = 3$, $D_x = 3{\cdot}83$ g cm^{-3}, μ(Mo $K\alpha$) = 252·05 cm^{-1}. The structure was refined to an R of 0·033 for 809 unique diffractometer data. The $Os(CO)_4$ and four $Os(CO)_3$ groups form a distorted trigonal bipyramidal Os_5 cluster, with all carbonyls terminal. A crystallographic twofold axis bisects the $Os(CO)_4$ group, which is equatorial.

Introduction. $Os_5(CO)_{16}$, one of the few known pentanuclear carbonyls, was isolated from the pyrolysis products of $Os_3(CO)_{12}$ by Eady, Johnson & Lewis (1972, 1975). The crystal structure has been determined to confirm the predicted trigonal bipyramidal structure and locate the carbonyl groups; a preliminary communication has appeared (Eady, Johnson, Lewis, Reichert & Sheldrick, 1976).

Black crystals were grown by slow evaporation of the red–pink solution in toluene containing a little ethyl acetate. Intensities were determined with an automated Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and a crystal in the form of a hexagonal prism 0·07 × 0·07 × 0·03 mm (layers 0–8kl). Empirical absorption corrections were applied, and interlayer scale factors obtained by a linear least-squares analysis of common reflexions. Equivalent reflexions were then averaged to yield 809 unique observed data. Unit-cell dimensions were obtained by a least-squares fit to diffractometer zero-layer ω angle measurements.

The Os atoms were located by multisolution tangent refinement, and the remaining atoms by difference syntheses. The structure was refined by full-matrix least squares with anisotropic Os and isotropic light atoms, complex neutral-atom scattering factors and the

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2 $\times 10^3$)

	x	y	z	U
Os(1)	1295 (2)	0	3333	
Os(2)	4750 (2)	1442 (2)	3637 (1)	
Os(3)	4032 (2)	1588 (2)	2574 (1)	
C(1)	−578 (43)	−1062 (46)	3833 (14)	34 (9)
O(1)	−1618 (34)	−1586 (31)	4127 (10)	57 (7)
C(2)	4868 (45)	1911 (46)	4388 (16)	49 (11)
O(2)	5134 (40)	2243 (38)	4833 (13)	80 (10)
C(3)	6919 (49)	1551 (50)	3651 (17)	45 (11)
O(3)	8118 (38)	1551 (36)	3649 (12)	68 (8)
C(4)	2838 (52)	960 (49)	1927 (17)	58 (12)
O(4)	2136 (37)	527 (36)	1501 (13)	78 (9)
C(5)	4174 (49)	3713 (52)	2462 (17)	54 (12)
O(5)	4447 (36)	5061 (36)	2436 (11)	68 (9)
C(6)	6031 (51)	2034 (53)	2301 (17)	56 (12)
O(6)	7389 (45)	2386 (42)	2132 (14)	93 (11)
C(7)	5758 (54)	3703 (55)	3487 (18)	57 (13)
O(7)	6451 (37)	5191 (41)	3466 (11)	72 (8)
C(8)	2178 (41)	1968 (41)	3769 (14)	25 (9)
O(8)	2423 (34)	3188 (38)	4018 (11)	65 (9)

Table 2. *Anisotropic temperature factors* (Å^2 $\times 10^3$)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	32 (1)	37 (1)	33 (1)	0 (1)	0 (1)	19 (1)
Os(2)	32 (1)	31 (1)	34 (1)	1 (1)	−3 (1)	10 (1)
Os(3)	45 (1)	40 (1)	31 (1)	8 (1)	5 (1)	23(1)

weighting scheme $w = 1/[\sigma^2(F) + 0{\cdot}0005\,|F_o|^2]$. Refinement converged to $R' = \Sigma\, w^{1/2}\Delta/\Sigma\, w^{1/2}|F_o| = 0{\cdot}034$ and $R = 0{\cdot}033$. Positional and thermal parameters are given in Tables 1 and 2, the derived bond lengths and angles in Table 3.*

Refinement with the C—O lengths constrained to be equal gave virtually identical R indices, but refinement of the enantiomorph in $P3_221$ increased them by about 0·009 (and so was rejected).

Discussion. Os(1) lies in a special position on a crystallographic twofold axis; it is attached to four carbonyls and the other four Os atoms, and so is effectively eight-coordinated. The remaining Os atoms are

Table 3. *Bond lengths* (Å) *and angles* (°)

Os(2)—Os(1)	2·867 (3)	C(5)—Os(3)	1·914 (43)
Os(3)—Os(1)	2·889 (3)	C(6)—Os(3)	1·805 (42)
Os(3)—Os(2)	2·738 (3)	O(1)—C(1)	1·103 (36)
Os(2′)—Os(2)	2·748 (4)	O(2)—C(2)	1·138 (42)
Os(3′)—Os(2)	2·764 (3)	O(3)—C(3)	1·103 (41)
C(1)—Os(1)	1·945 (36)	O(4)—C(4)	1·137 (40)
C(8)—Os(1)	1·908 (35)	O(5)—C(5)	1·197 (43)
C(2)—Os(2)	1·905 (39)	O(6)—C(6)	1·200 (46)
C(3)—Os(2)	1·949 (40)	O(7)—C(7)	1·188 (46)
C(7)—Os(2)	1·844 (44)	O(8)—C(8)	1·199 (40)
C(4)—Os(3)	1·868 (42)		

Table 3 (*cont.*)

Os(3)—Os(1)—Os(2)	56·8 (1)	C(7)—Os(2)—Os(2′)	135·0 (14)
Os(2′)—Os(1)—Os(2)	57·3 (1)	C(7)—Os(2)—Os(3′)	157·0 (14)
Os(3′)—Os(1)—Os(2)	57·4 (1)	C(4)—Os(3)—Os(1)	100·1 (12)
Os(3′)—Os(1)—Os(3)	103·5 (1)	C(4)—Os(3)—Os(2)	158·8 (12)
Os(3)—Os(2)—Os(1)	62·0 (1)	C(4)—Os(3)—Os(2′)	103·4 (12)
Os(2′)—Os(2)—Os(1)	61·4 (1)	C(5)—Os(3)—Os(1)	102·0 (12)
Os(3′)—Os(2)—Os(1)	61·7 (1)	C(5)—Os(3)—Os(2)	107·2 (13)
Os(2′)—Os(2)—Os(3)	60·5 (1)	C(5)—Os(3)—Os(2′)	161·7 (13)
Os(3′)—Os(2)—Os(2′)	59·6 (1)	C(6)—Os(3)—Os(1)	153·1 (13)
Os(2)—Os(3)—Os(1)	61·2 (1)	C(6)—Os(3)—Os(2)	97·4 (13)
Os(2′)—Os(3)—Os(1)	60·9 (1)	C(6)—Os(3)—Os(2′)	95·0 (13)
Os(2′)—Os(3)—Os(2)	59·9 (1)	C(8)—Os(1)—C(1)	88·0 (14)
C(1)—Os(1)—Os(2)	124·3 (10)	C(1′)—Os(1)—C(1)	101·2 (21)
C(1)—Os(1)—Os(3)	178·8 (10)	C(8′)—Os(1)—C(1)	88·4 (14)
C(1)—Os(1)—Os(2′)	123·4 (10)	C(8′)—Os(1)—C(8)	174·4 (20)
C(1)—Os(1)—Os(3′)	77·7 (10)	C(3)—Os(2)—C(2)	91·7 (17)
C(8)—Os(1)—Os(2)	64·2 (10)	C(7)—Os(2)—C(2)	90·1 (18)
C(8)—Os(1)—Os(3)	92·3 (10)	C(7)—Os(2)—C(3)	91·2 (18)
C(8)—Os(1)—Os(2′)	121·4 (10)	C(5)—Os(3)—C(4)	85·4 (17)
C(8)—Os(1)—Os(3′)	91·2 (10)	C(6)—Os(3)—C(4)	97·0 (18)
C(2)—Os(2)—Os(1)	106·6 (11)	C(6)—Os(3)—C(5)	99·9 (18)
C(2)—Os(2)—Os(3)	156·8 (11)	O(1)—C(1)—Os(1)	176·4 (34)
C(2)—Os(2)—Os(2′)	134·5 (11)	O(2)—C(2)—Os(2)	171·8 (35)
C(8)—Os(2)—Os(3′)	75·9 (11)	O(3)—C(3)—Os(2)	177·1 (40)
C(3)—Os(2)—Os(1)	154·1 (12)	O(4)—C(4)—Os(3)	176·1 (38)
C(3)—Os(2)—Os(3)	106·3 (12)	O(5)—C(5)—Os(3)	170·8 (38)
C(3)—Os(2)—Os(2′)	92·7 (12)	O(6)—C(6)—Os(3)	177·4 (38)
C(3)—Os(2)—Os(3′)	107·2 (12)	O(7)—C(7)—Os(2)	170·8 (40)
C(7)—Os(2)—Os(1)	106·6 (14)	O(8)—C(8)—Os(1)	166·4 (31)
C(7)—Os(2)—Os(3)	75·4 (14)		

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32008 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

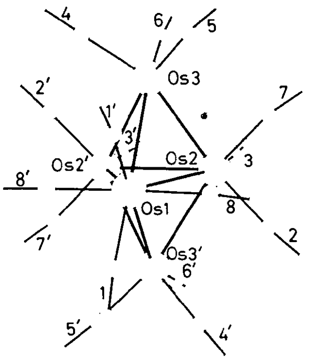

Fig. 1. Molecular structure and numbering scheme.

each bonded to three carbonyls. The significantly longer Os—Os bonds to Os(1) may serve to redress the resulting electron imbalance. The Os—C and C—O bonds are respectively equal within experimental error, with means 1·89 (4) and 1·16 (4) Å; refinement with the C—O distances constrained to be equal yielded 1·16 (1) Å. There are two short non-bonded Os···C interactions, both associated with significant departures from linear Os—C—O units: C(8)···Os(2) 2·66 (4), C(7)···Os(3) 2·89 (4) Å; Os(1)—C(8)—O(8) 166 (3), Os(2)—C(7)—O(7) 171 (4)°. The molecular structure (Fig. 1) is consistent with the Johnson (1976) model in which close-packed carbonyl groups adopt a polyhedral arrangement. The high density [3·83 g cm^{-3}, in contrast to 3·19 g cm^{-3} in $Os_6(CO)_{18}$; Mason, Thomas & Mingos, 1973] implies efficient packing of the molecules, which can be seen in Fig. 2.

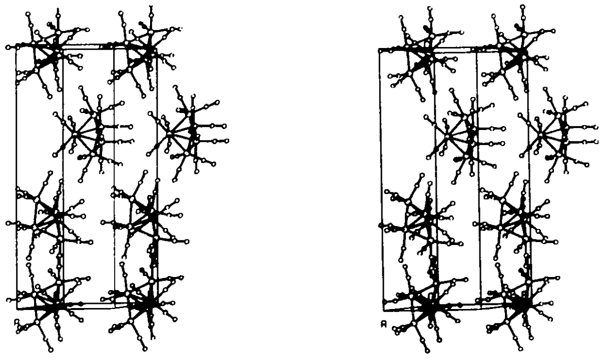

Fig. 2. Stereoscopic view of the crystal packing down **a***.

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References

EADY, C. R., JOHNSON, B. F. G. & LEWIS, J. (1972). *J. Organomet. Chem.* **37**, C39–C40.
EADY, C. R., JOHNSON, B. F. G. & LEWIS, J. (1975). *J. Chem. Soc. Dalton*, pp. 2606–2611.
EADY, C. R., JOHNSON, B. F. G., LEWIS, J., REICHERT, B. E. & SHELDRICK, G. M. (1976). *Chem. Commun.* p. 271.
JOHNSON, B. F. G. (1976). *Chem. Commun.* pp. 211–213.
MASON, R., THOMAS, K. M. & MINGOS, D. M. P. (1973). *J. Amer. Chem. Soc.* **95**, 3802–3804.

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Di-μ-cyclononaallyl-hexacarbonyldiosmium

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Abstract. $C_{24}H_{28}O_6Os_2$, monoclinic, $P2_1/c$, $a = 7{\cdot}174\,(4)$, $b = 8{\cdot}850\,(4)$, $c = 19{\cdot}173\,(10)$ Å, $\beta = 103{\cdot}11\,(4)°$, $U = 1185{\cdot}6$ Å^3, $Z = 2$, $D_x = 2{\cdot}22$ g cm^{-3}. The structure was solved by the heavy-atom method and refined to an R of 0·027 for 1145 independent diffractometer data. The centrosymmetric molecule contains two $Os(CO)_3$ units, with each Os σ-bonded to the central allyl C of a cyclononaallyl group π-bonded to the other Os.

Introduction. When $Fe_2(CO)_9$ reacts with cyclonona-1,2-diene, the latter dimerizes and the product contains a di(cyclononaallyl) group π-bonded to an $Fe_2(CO)_6$ unit which retains an Fe—Fe bond (Howell, Lewis, Matheson & Russell, 1975). The same diene reacts with $H_2Os_3(CO)_{10}$ to yield a product of similar empirical formula (with Fe replaced by Os; Bryan, Johnson & Lewis, 1976), but the single-crystal X-ray determination reported here reveals a quite different structure.