Table 7. *Position of the* Ag^+ *ions with respect to the* C=C *bonds, and angles between the planes*

M(1) and *M*(2) denote the mid-points of the double bonds C(1)–C(10) and C(4)–C(5) respectively. $\pi(1)$ and $\pi(2)$ are the best planes of C(2)–C(1)–C(10)–C(9) and C(3)–C(4)–C(5)–C(6) respectively.

Distances (Å)

Ag(1)–C(2)	3·130 (8)	Ag(2)–C(3)	3·349 (7)
–C(1)	2·319 (7)	–C(4)	2·669 (6)
–*M*(1)	2·273 (7)	–*M*(2)	2·452 (7)
–C(10)	2·425 (8)	–C(5)	2·416 (7)
–C(9)	3·134 (7)	–C(6)	3·243 (6)

Angles (°)

Ag(1)–C(1)–C(10)	77·6 (4)	Ag(2)–C(5)–C(4)	84·8 (3)
–*M*(1)–C(1)	85·3 (4)	–*M*(2)–C(5)	79·0 (4)
–C(10)–C(1)	69·0 (4)	–C(4)–C(5)	64·4 (4)

Angles of planes (°)

$\pi(1)$–[C(1)–C(10)–Ag(1)]	92·5 (7)
$\pi(2)$–[C(4)–C(5)–Ag(2)]	84·8 (6)

Distances from planes (Å)

Ag(1)–$\pi(1)$	2·359 (8)	Ag(2)–$\pi(2)$	2·539 (7)

that all other geometric parameters (bond lengths, bond and torsion angles) of the double C=C bonds do not exhibit significant differences. The positions of the Ag^+ ions with respect to the C=C bonds are characterized as shown in Table 7. The intraannular distance C(1)–C(4) is 2·857 (10) Å and suggests the presence of some slight electron interaction between these two atoms.

References

Bovill, M. J., Cox, P. J., Cradwick, P. D., Guy, M. H. P., Sim, G. A. & White, D. N. J. (1976). *Acta Cryst.* B**32**, 3203–3209.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Novák, C. (1973). *Czech. J. Phys.* A**23**, 402–411.

Šorm, F., Suchý, M., Holub, M., Línek, A., Hadinec, I. & Novák, C. (1970). *Tetrahedron Lett.* pp. 1893–1896.

Acta Cryst. (1978). B**34**, 3372–3374

Octacarbonyl-1,1-dinitrosyl-1-(trimethyl phosphite)-*triangulo*-triosmium

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Abstract. $C_{11}H_9N_2O_{13}Os_3P$, monoclinic, $P2_1/c$, a = 15·653 (5), b = 8·255 (7), c = 17·263 (5) Å, β = 105·15 (5)°, Z = 4, U = 2153 Å^3, D_x = 3·019 g cm^{-3}, μ(Mo $K\alpha$) = 171·4 cm^{-1}. The structure was refined to an R of 0·061 for 1369 unique diffractometer data. The structure is related to that of $Os_3(CO)_{12}$ by substitution of the four carbonyls on one Os atom by an equatorial trimethyl phosphite and two terminal nitrosyls.

Introduction. $Os_3(CO)_8(NO)_2P(OCH_3)_3$ was obtained from the reaction of trimethyl phosphite with $Os_3(CO)_9(NO)_2$, and crystallized as red elongated plates from hexane (Bhaduri, Johnson, Lewis, Watson & Zuccaro, 1977). The crystal structure has been determined to complement chemical and NMR studies of $Os_3(CO)_9(NO)_2$ and its reactions with a variety of ligands (Bhaduri, Johnson, Lewis, Watson & Zuccaro, 1978).

Layers h,0–9,l were collected on a Stoe two-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. After application of Lp and empirical absorption corrections, equivalent reflexions were averaged to give 1369 reflexions with $F > 6\sigma(F)$ based on counting statistics. a, c and β were determined by a least-squares fit to median ω values for the zero-layer reflexions, and b from the μ angles of the 0k0 reflexions. The Os atoms were located by multisolution $\sum_2$ sign expansion, and the remaining atoms (except H) from difference syntheses. The structure was refined by the full-matrix least-squares method with complex neutral-atom scattering-factors and weights $w = [\sigma^2(F) + 0{\cdot}00136F_o^2]^{-1}$ to $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}0620$ and a corresponding unweighted R index of 0·0614. Interlayer scale factors were refined, so to avoid a nearly singular least-squares matrix the constraint $U_{22} = \frac{1}{2}(U_{11} + U_{33})$ was applied to the anisotropic Os atoms. The remaining atoms were isotropic; methyl H atoms were not included. Final positional and thermal

Table 1. *Atom coordinates* (×10⁴) *and isotropic temperature factors* (Å² ×10³)

	x	y	z	U
Os(1)	6971 (1)	4421 (3)	3110 (1)	
Os(2)	8580 (1)	4806 (3)	2721 (1)	
Os(3)	8413 (1)	2521 (2)	3918 (1)	
P	6180 (8)	3240 (18)	3932 (7)	46 (3)
O(1)	5220 (20)	3869 (43)	3780 (18)	60 (9)
C(1)	4614 (37)	3879 (78)	2946 (32)	80 (17)
O(2)	1646 (19)	1325 (39)	3859 (16)	47 (8)
C(2)	5670 (41)	383 (87)	4345 (37)	95 (20)
O(3)	6512 (18)	3481 (44)	4869 (16)	52 (8)
C(3)	6523 (31)	5053 (67)	5239 (27)	56 (13)
N(11)	6429 (23)	3390 (53)	2221 (21)	52 (10)
O(11)	6028 (25)	2904 (54)	1606 (23)	89 (12)
N(12)	6990 (23)	6230 (55)	3519 (20)	46 (10)
O(12)	6843 (28)	7620 (64)	3677 (25)	105 (14)
C(21)	8288 (34)	3162 (78)	1945 (31)	69 (15)
O(21)	8036 (24)	2294 (54)	1445 (22)	83 (11)
C(22)	8843 (29)	6366 (65)	3499 (26)	50 (12)
O(22)	9029 (28)	7490 (59)	3953 (25)	103 (14)
C(23)	8185 (31)	6411 (67)	1928 (27)	53 (13)
O(23)	7825 (24)	7372 (51)	1398 (22)	78 (11)
C(24)	9731 (32)	4650 (64)	2676 (27)	53 (12)
O(24)	10497 (28)	4402 (55)	2688 (23)	95 (13)
C(31)	7931 (30)	1024 (67)	3100 (27)	55 (13)
O(31)	7529 (20)	99 (44)	2615 (18)	57 (8)
C(32)	8705 (27)	4147 (62)	4689 (25)	45 (11)
O(32)	8884 (26)	5154 (54)	5221 (23)	87 (12)
C(33)	8103 (28)	1016 (62)	4643 (26)	46 (11)
O(33)	7878 (21)	396 (43)	5117 (19)	63 (9)
C(34)	9549 (31)	1678 (71)	4053 (26)	55 (12)
O(34)	10269 (25)	1116 (51)	4130 (21)	79 (11)

Table 2. *Bond lengths* (Å)

Os(2)–Os(1)	2·790 (5)	Os(3)–Os(1)	2·802 (5)
Os(3)–Os(2)	2·860 (6)	P–Os(1)	2·327 (14)
N(11)–Os(1)	1·77 (4)	N(12)–Os(1)	1·65 (4)
C(21)–Os(2)	1·88 (6)	C(22)–Os(2)	1·83 (5)
C(23)–Os(2)	1·89 (5)	C(24)–Os(2)	1·83 (5)
C(31)–Os(3)	1·88 (5)	C(32)–Os(3)	1·86 (5)
C(33)–Os(3)	1·91 (5)	C(34)–Os(3)	1·87 (5)
O(1)–P	1·55 (3)	O(2)–P	1·59 (4)
O(3)–P	1·58 (3)		
C(1)–O(1)	1·50 (6)	C(2)–O(2)	1·48 (7)
C(3)–O(3)	1·45 (6)		
O(11)–N(11)	1·16 (5)	O(12)–N(12)	1·21 (5)
O(21)–C(21)	1·11 (6)	O(22)–C(22)	1·20 (6)
O(23)–C(23)	1·23 (6)	O(24)–C(24)	1·21 (5)
O(31)–C(31)	1·18 (5)	O(32)–C(32)	1·21 (5)
O(33)–C(33)	1·10 (5)	O(34)–C(34)	1·19 (5)

parameters are given in Table 1, with bond lengths and angles in Tables 2 and 3.*

Discussion. The triangular cluster (Fig. 1) consists of two $Os(CO)_4$ groups and an $Os(NO)_2P(OCH_3)_3$ group linked by Os—Os bonds; each Os atom obeys the 18-electron rule. Although in the presence of very heavy elements it is difficult to distinguish between C and N on the basis of X-ray data alone, the assignment is supported by the reasonable U values obtained for N,

Table 3. *Bond angles* (°)

Os(3)–Os(1)–Os(2)	61·5 (2)	Os(3)–Os(2)–Os(1)	59·4 (2)
Os(2)–Os(2)–Os(1)	59·0 (2)		
P–Os(1)–Os(2)	148·5 (3)	P–Os(1)–Os(3)	87·1 (4)
N(11)–Os(1)–Os(2)	96 (1)	N(11)–Os(1)–Os(3)	107 (1)
N(12)–Os(1)–Os(2)	94 (1)	N(12)–Os(1)–Os(3)	111 (1)
C(21)–Os(2)–Os(1)	91 (2)	C(21)–Os(2)–Os(3)	89 (2)
C(22)–Os(2)–Os(1)	87 (1)	C(22)–Os(2)–Os(3)	88 (1)
C(23)–Os(2)–Os(1)	96 (1)	C(23)–Os(2)–Os(3)	155 (1)
C(24)–Os(2)–Os(1)	164 (2)	C(24)–Os(2)–Os(3)	105 (2)
C(31)–Os(3)–Os(1)	83 (2)	C(31)–Os(3)–Os(2)	89 (2)
C(32)–Os(3)–Os(1)	88 (1)	C(32)–Os(3)–Os(2)	89 (1)
C(33)–Os(3)–Os(1)	112 (1)	C(33)–Os(3)–Os(2)	170 (1)
C(34)–Os(3)–Os(1)	152 (1)	C(34)–Os(3)–Os(2)	94 (2)
N(11)–Os(1)–P	96 (1)	N(12)–Os(1)–P	94 (1)
N(12)–Os(1)–N(11)	139 (2)	C(23)–Os(2)–C(21)	91 (2)
C(23)–Os(2)–C(22)	90 (2)	C(24)–Os(2)–C(21)	88 (2)
C(24)–Os(2)–C(22)	92 (2)	C(24)–Os(2)–C(23)	99 (2)
C(22)–Os(2)–C(21)	177 (2)	C(34)–Os(3)–C(31)	91 (2)
C(33)–Os(3)–C(31)	86 (2)	C(34)–Os(3)–C(33)	94 (2)
C(32)–Os(3)–C(33)	93 (2)	C(34)–Os(3)–C(32)	97 (2)
C(32)–Os(3)–C(31)	170 (2)	O(1)–P–Os(1)	113 (1)
O(2)–P–Os(1)	112 (1)	O(2)–P–O(1)	108 (2)
O(3)–P–Os(1)	119 (1)	O(3)–P–O(1)	100 (2)
O(3)–P–O(2)	101 (2)	C(1)–O(1)–P	120 (3)
C(2)–O(2)–P	119 (3)	C(3)–O(3)–P	122 (3)
O(11)–N(11)–Os(1)	171 (4)	O(12)–N(12)–Os(1)	165 (4)
O(21)–C(21)–Os(2)	172 (5)	O(22)–C(22)–Os(2)	173 (4)
O(23)–C(23)–Os(2)	172 (4)	O(24)–C(24)–Os(2)	173 (5)
O(31)–C(31)–Os(3)	171 (4)	O(33)–C(33)–Os(3)	167 (4)
O(32)–C(32)–Os(3)	176 (4)	O(34)–C(34)–Os(3)	178 (5)

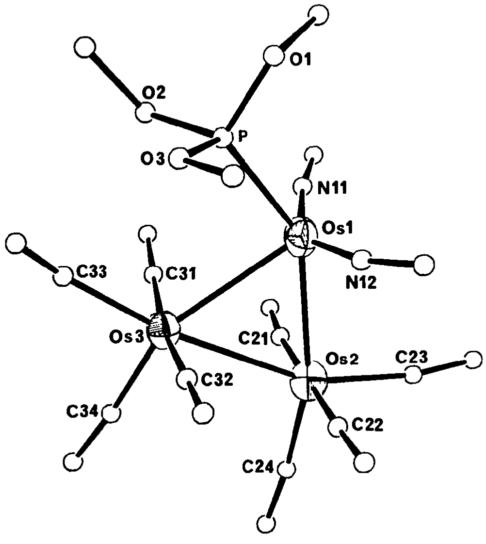

Fig. 1. The molecule of $Os_3(CO)_8(NO)_2P(OCH_3)_3$, showing the labelling scheme and 50% probability thermal ellipsoids for the Os atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33703 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the significantly shorter Os—N than Os—C bond lengths, the low-temperature ^{13}C NMR spectrum, and the electron count required for neutral Os atoms under the 18-electron rule. Ignoring the phosphite and nitrosyl substituents, the molecule possesses approximate *mm* symmetry; the P atom lies 0·14 Å from the Os_3 plane and the nitrosyls are approximately equidistant on opposite sides of it. The $(OC)_4Os—Os(CO)_4$ distance [2·860 (6) Å] is close to the mean value in $Os_3(CO)_{12}$ [2·877 (3) Å; Churchill & De Boer, 1977] but the other two Os—Os bonds are appreciably shorter. Although the molecular symmetry does not require the Os—N bonds to be equal, the apparent discrepancy is probably simply a reflexion of the relatively large uncertainties, since almost identical *R* indices (*R* 0·0615, *R′* 0·0620) were obtained in a separate refinement in which both Os—N, and both N—O, distances were constrained to be equal.

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References

Bhaduri, S., Johnson, B. F. G., Lewis, J., Watson, D. J. & Zuccaro, C. (1977). *J. Chem. Soc. Chem. Commun.* pp. 477–478.

Bhaduri, S., Johnson, B. F. G., Lewis, J., Watson, D. J. & Zuccaro, C. (1978). *J. Chem. Soc. Dalton Trans.* In the press.

Churchill, M. R. & De Boer, B. G. (1977). *Inorg. Chem.* **16**, 878–884.

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Tricarbonyl{3-4:6-7-η-(2-isopropylthio-8-benzoylbicyclo[3.2.1]octadiene)}iron

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Abstract. $C_{21}H_{20}FeO_4S$, triclinic, $P\bar{1}$, $a = 9{\cdot}437\ (6)$, $b = 10{\cdot}249\ (5)$, $c = 11{\cdot}545\ (6)$ Å, $\alpha = 84{\cdot}67\ (5)$, $\beta = 71{\cdot}44\ (4)$, $\gamma = 67{\cdot}54\ (5)^\circ$, $U = 977{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}441$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 8{\cdot}39$ cm^{-1}. The structure was solved by direct methods and refined to an *R* of 0·030 for 2045 diffractometer data. The bicyclo[3.2.1]octadiene ligand has *M-exo* stereochemistry at C(2), and coordinates the Fe atom *via* two π-alkene bonds.

Introduction. Yellow crystals of the title compound were obtained from the reaction of the {2–4:6-7-η-(8-benzoylbicyclo[3.2.1]octadienylium)}tricarbonyliron cation with the nucleophile 2-propanethiol by Charles (1977). The crystal structure has been determined in order to establish the orientation of the substituents on the bicyclic diene.

2539 intensities were measured on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. After application of Lp but not absorption corrections, equivalent reflexions were averaged to give 2045 unique reflexions with $F > 4\sigma(F)$ based on counting statistics. Unit-cell dimensions were determined from the diffractometer angles of 15 reflexions. The Fe and S atoms were located by multi-

Table 1. *Atom coordinates* ($\times 10^4$)

	x	*y*	*z*
Fe	7948 (1)	3545 (1)	3441 (1)
S	11501 (1)	−1181 (1)	2754 (1)
O(9)	12279 (3)	2965 (2)	−562 (2)
C(1)	10218 (3)	1253 (3)	1456 (2)
C(2)	9950 (3)	561 (3)	2698 (2)
C(3)	9857 (3)	1579 (3)	3620 (2)
C(4)	10507 (3)	2603 (3)	3278 (2)
C(5)	11078 (3)	2935 (3)	1945 (2)
C(6)	9491 (3)	3737 (3)	1720 (2)
C(7)	8891 (3)	2725 (3)	1589 (2)
C(8)	11768 (3)	1591 (2)	1172 (2)
C(9)	12496 (3)	1797 (3)	−171 (3)
C(10)	13486 (3)	515 (3)	−1005 (2)
C(11)	14213 (4)	709 (3)	−2230 (3)
C(12)	15119 (4)	−442 (4)	−3028 (3)
C(13)	15324 (4)	−1779 (4)	−2627 (3)
C(14)	14644 (4)	−1976 (3)	−1424 (3)
C(15)	13720 (3)	−839 (3)	−603 (3)
C(16)	10764 (5)	−2286 (3)	2116 (3)
C(17)	9425 (6)	−2587 (4)	3070 (5)
C(18)	12167 (6)	−3625 (4)	1564 (4)
C(19)	6725 (4)	2607 (3)	4330 (3)
O(19)	5914 (3)	2054 (3)	4929 (2)
C(20)	7842 (4)	4688 (3)	4563 (3)
O(20)	7764 (3)	5415 (3)	5293 (2)
C(21)	6344 (4)	4874 (4)	3031 (3)
O(21)	5318 (3)	5696 (3)	2746 (3)