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1,1,1,2,2,2,3,3,3-Nonacarbonyl-2-ethylene-1,3-μ-hydrido-1,3-μ-(methylthiolato)-*triangulo*-triosmium

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Abstract. $[Os_3(C_2H_4)(CH_3S)(CO)_9H]$, $C_{12}H_8O_9Os_3S$, monoclinic, $P2_1/n$, $a = 10{\cdot}333$ (4), $b = 15{\cdot}735$ (5), $c = 11{\cdot}792$ (4) Å, $\beta = 98{\cdot}07$ (2)°, $U = 1898{\cdot}3$ Å^3, $Z = 4$, $D_c = 3{\cdot}144$ Mg m^{-3}, μ(Mo $K\alpha$) = $20{\cdot}17$ mm^{-1}. Final $R = 0{\cdot}055$ for 2014 unique observed diffractometer data. The Os atoms lie at the vertices of an approximately equilateral triangle. The ethylene ligand π-bonds to an equatorial site on one Os atom and is coplanar with the Os_3 plane. The thiol group and the hydride bridge the other two Os atoms. The hydride position is inferred from the arrangement of the carbonyl ligands, three of which are terminally bound to each metal.

Introduction. $[Os_3(CH_3S)(CO)_9H]$ has a high chemical reactivity and forms a wide range of adducts with small molecules. The reactivity is associated with the variable coordination of the S ligand which may change from face-capping to edge-bridging. An X-ray analysis of the title compound was undertaken to establish the coordination modes of the ethylene and thiol ligands in the solid state. A preliminary report has appeared (Johnson, Lewis, Pippard & Raithby, 1978).

Reaction of $[Os_3(CH_3S)(CO)_9H]$ with ethylene at room temperature yielded a yellow solid. Upon recrystallization from pentane, yellow crystals, in the form of approximately equidimensional blocks, were deposited. Intensities were measured on a Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a crystal $0{\cdot}200 \times 0{\cdot}125 \times 0{\cdot}075$ mm. Lp and semi-empirical absorption corrections (based on a pseudo-ellipsoid model and 241 azimuthal scan data from nine independent reflections) were applied; transmission factors ranged from 0·416 to 0·994 for the full data set. The 3795 reflections recorded in the range $1{\cdot}5 < \theta < 25{\cdot}0°$ were averaged to give 2014 unique observed $[F > 5\sigma(F)]$ intensities. Cell

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

	x	y	z
Os(1)	5429 (1)	4154 (1)	2681 (1)
Os(2)	3330 (1)	3123 (1)	1622 (1)
Os(3)	5960 (1)	2556 (1)	1722 (1)
S(1)	6235 (6)	3927 (4)	892 (6)
C(1)	8030 (32)	4169 (20)	1065 (30)
C(11)	6993 (25)	4710 (17)	3307 (23)
O(11)	7862 (21)	5046 (15)	3808 (20)
C(12)	4478 (27)	5149 (19)	2247 (25)
O(12)	3934 (20)	5784 (13)	2013 (19)
C(13)	4731 (33)	4095 (22)	4079 (31)
O(13)	4285 (22)	4066 (14)	4889 (21)
C(21)	3468 (25)	3603 (18)	167 (25)
O(21)	3456 (20)	3855 (15)	−783 (20)
C(22)	3271 (25)	2640 (16)	3077 (25)
O(22)	3273 (23)	2273 (16)	3955 (22)
C(31)	7719 (29)	2306 (19)	1927 (26)
O(31)	8813 (22)	2119 (15)	2040 (21)
C(32)	5556 (27)	2004 (19)	325 (27)
O(32)	5373 (26)	1655 (18)	−586 (24)
C(33)	5502 (25)	1625 (17)	2576 (24)
O(33)	5261 (22)	1074 (15)	3130 (22)
C(2*a*)	2673 (29)	1910 (29)	753 (62)
C(2*b*)	2644 (109)	2101 (42)	935 (124)
C(3)	1556 (34)	2414 (32)	861 (49)
O(2)	2462 (71)	1368 (40)	713 (65)
C(2′*a*)	1878 (63)	4066 (47)	2068 (100)
C(2′*b*)	2132 (69)	3960 (48)	1832 (76)
C(3′)	1195 (35)	3383 (50)	1464 (77)
O(2′)	1434 (36)	4502 (22)	2105 (42)

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Table 2. *Bond lengths* (Å)

Os(2)–Os(1)	2·852 (1)	S(1)–Os(1)	2·402 (7)
Os(3)–Os(1)	2·842 (1)	S(1)–Os(3)	2·402 (6)
Os(3)–Os(2)	2·847 (1)	C(1)–S(1)	1·876 (33)
C(11)–Os(1)	1·894 (25)	C(21)–Os(2)	1·989 (29)
C(12)–Os(1)	1·882 (29)	C(22)–Os(2)	1·885 (29)
C(13)–Os(1)	1·892 (38)	C(2*a*)–Os(2)	2·225 (35)
C(31)–Os(3)	1·842 (30)	C(2*b*)–Os(2)	1·892 (8)
C(32)–Os(3)	1·856 (31)	C(3)–Os(2)	2·225 (35)
C(33)–Os(3)	1·876 (29)	C(2′*a*)–Os(2)	2·224 (36)
O(11)–C(11)	1·134 (30)	C(2′*b*)–Os(2)	1·848 (61)
O(12)–C(12)	1·160 (31)	C(3′)–Os(2)	2·225 (36)
O(13)–C(13)	1·118 (38)	O(21)–C(21)	1·187 (31)
O(31)–C(31)	1·157 (32)	O(22)–C(22)	1·186 (33)
O(32)–C(32)	1·198 (35)	C(3)–C(2*a*)	1·420 (5)
O(33)–C(33)	1·133 (33)	O(2)–C(2*b*)	1·192 (61)
C(3′)–C(2′*a*)	1·420 (5)	O(2′)–C(2′*b*)	1·190 (59)

Table 3. *Bond angles* (°)

Os(3)–Os(1)–Os(2)	60·0 (1)	S(1)–Os(1)–Os(2)	82·3 (1)
Os(3)–Os(2)–Os(1)	59·8 (1)	S(1)–Os(1)–Os(3)	53·7 (2)
Os(2)–Os(3)–Os(1)	60·2 (1)	S(1)–Os(3)–Os(1)	53·7 (2)
C(11)–Os(1)–Os(2)	171·2 (8)	S(1)–Os(3)–Os(2)	82·5 (2)
C(11)–Os(1)–Os(3)	111·2 (8)	Os(3)–S(1)–Os(1)	72·5 (2)
C(11)–Os(1)–S(1)	91·7 (8)	C(1)–S(1)–Os(1)	109·5 (11)
C(12)–Os(1)–Os(2)	91·0 (8)	C(1)–S(1)–Os(3)	108·0 (10)
C(12)–Os(1)–Os(3)	138·7 (9)	C(21)–Os(2)–Os(1)	91·2 (8)
C(12)–Os(1)–S(1)	96·7 (9)	C(21)–Os(2)–Os(3)	88·3 (8)
C(12)–Os(1)–C(11)	96·0 (11)	C(22)–Os(2)–Os(1)	87·1 (8)
C(13)–Os(1)–Os(2)	89·7 (10)	C(22)–Os(2)–Os(3)	89·3 (8)
C(13)–Os(1)–Os(3)	115·0 (10)	C(22)–Os(2)–C(21)	177·5 (11)
C(13)–Os(1)–S(1)	168·5 (10)	C(2*a*)–Os(2)–Os(1)	148·5 (12)
C(13)–Os(1)–C(11)	95·3 (13)	C(2*a*)–Os(2)–Os(3)	88·7 (12)
C(13)–Os(1)–C(12)	91·7 (12)	C(2*a*)–Os(2)–C(21)	89·0 (22)
C(31)–Os(3)–Os(1)	112·2 (9)	C(2*a*)–Os(2)–C(22)	91·6 (22)
C(31)–Os(3)–Os(2)	172·2 (9)	C(2*b*)–Os(2)–Os(1)	152·4 (36)
C(31)–Os(3)–S(1)	94·2 (9)	C(2*b*)–Os(2)–Os(3)	92·8 (36)
C(32)–Os(3)–Os(1)	137·3 (9)	C(2*b*)–Os(2)–C(21)	91·3 (48)
C(32)–Os(3)–Os(2)	90·9 (9)	C(2*b*)–Os(2)–C(22)	89·4 (48)
C(32)–Os(3)–S(1)	94·8 (9)	C(3)–Os(2)–Os(1)	174·2 (13)
C(32)–Os(3)–C(31)	96·4 (13)	C(3)–Os(2)–Os(3)	126·0 (12)
C(33)–Os(3)–Os(1)	113·5 (8)	C(3)–Os(2)–C(21)	89·9 (17)
C(33)–Os(3)–Os(2)	87·4 (8)	C(3)–Os(2)–C(22)	92·0 (17)
C(33)–Os(3)–S(1)	166·7 (8)	C(3)–Os(2)–C(2*a*)	37·2 (6)
C(33)–Os(3)–C(31)	94·7 (12)	C(3)–Os(2)–C(2*b*)	33·2 (41)
C(33)–Os(3)–C(32)	94·0 (12)	C(2′*a*)–Os(2)–Os(1)	90·8 (20)
O(11)–C(11)–Os(1)	171·3 (26)	C(2′*a*)–Os(2)–Os(3)	150·5 (20)
O(12)–C(12)–Os(1)	176·8 (24)	C(2′*a*)–Os(2)–C(21)	95·0 (34)
O(13)–C(13)–Os(1)	178·1 (31)	C(2′*a*)–Os(2)–C(22)	86·8 (34)
Os(21)–C(21)–Os(2)	173·6 (24)	C(2′*a*)–Os(2)–C(3)	83·4 (22)
O(22)–C(22)–Os(2)	174·2 (25)	C(2′*b*)–Os(2)–Os(1)	91·0 (24)
O(31)–C(31)–Os(3)	177·4 (27)	C(2′*b*)–Os(2)–Os(3)	150·6 (24)
O(32)–C(32)–Os(3)	176·0 (27)	C(2′*b*)–Os(2)–C(21)	88·5 (31)
O(33)–C(33)–Os(3)	177·1 (25)	C(2′*b*)–Os(2)–C(22)	93·3 (30)
C(3)–C(2*a*)–Os(2)	71·4 (4)	C(2′*b*)–Os(2)–C(3)	83·3 (2·7)
C(3)–C(2*b*)–Os(2)	88·6 (41)	C(3′)–Os(2)–Os(3)	172·0 (20)
O(2)–C(2*b*)–Os(2)	162·6 (104)	C(3′)–Os(2)–C(21)	92·9 (25)
C(2a)–C(3)–Os(2)	71·4 (4)	C(3′)–Os(2)–C(22)	89·5 (25)
C(3′)–C(2′*a*)–Os(2)	71·4 (4)	C(3′)–Os(2)–C(2′*a*)	37·2 (6)
O(2′)–C(2′*b*)–Os(2)	171·9 (73)	C(3′)–Os(2)–C(2′*b*)	37·4 (37)
C(2′*a*)–C(3′)–Os(2)	71·4 (4)		

dimensions were derived from the angular measurements of 15 strong reflections ($10\cdot0 < \theta < 15\cdot0°$).

The Os atoms were located by multisolution $\sum_2$ sign expansion, and all the other non-hydrogen atoms from a subsequent difference synthesis. The ethylene ligand and the equatorial carbonyl bonded to the same Os atom were positionally disordered. In the refinement of the disordered fragment the four Os–C(ethylene) distances were constrained to be equal, as were the two C–O carbonyl distances. These Os–C and C–O distances refined to 2·23 (4) and 1·19 (6) Å, respectively. The ethylene C–C distances were fixed at 1·42 Å, and the Os–C(carbonyl) lengths at 1·89 Å. The structure was refined by full-matrix least squares with complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) and the weighting scheme $w = 0\cdot4733/[\sigma^2(F) + 0\cdot004|F_o|^2]$. The refined parameters included anisotropic thermal parameters for the Os and S atoms, and common isotropic temperature factors for the related disordered atoms. The two sets of disordered atoms were refined with site-occupation factors of k and $1 - k$ respectively; k refined to 0·614 (30). The H atoms were not located. The converged residuals were $R = 0\cdot055$ and $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0\cdot057$. Final atomic coordinates are given in Table 1, bond lengths and angles in Tables 2 and 3.*

Discussion. The structure of the title compound (Fig. 1) confirms that the S donor ligand is no longer capping the metal triangle as in $[Fe_3(C_3H_7S)(CO)_9H]$ (Bau, Don, Greatrex, Haines, Love & Wilson, 1975) but bridges an Os–Os edge. The Os_2S plane makes an angle of 103·5 (2)° with the Os_3 triangle. This change in coordination of the S donor ligand permits the ethylene group to π-bond to the third Os atom. The C atoms of the ethylene ligand are coplanar with the Os_3

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34905 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

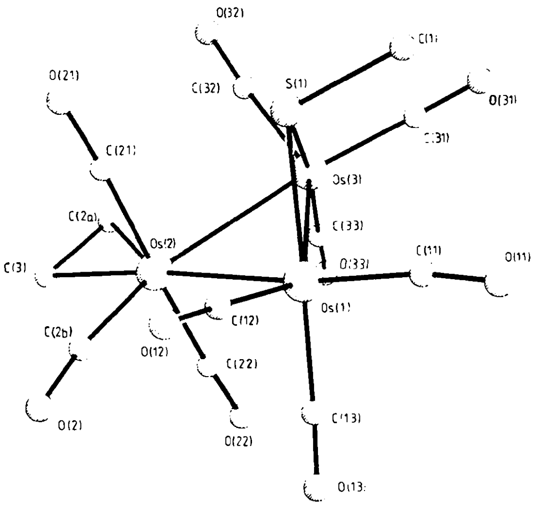

Fig. 1. A molecule of $[Os_3(C_2H_4)(CH_3S)(CO)_9H]$. Only one orientation of the disordered fragment is shown for clarity.

plane [maximum atomic deviation 0·01 (1) Å]. This mode of bonding by ethylene to a cluster has not previously been characterized crystallographically, but a similar bonding configuration has been observed for the two halves of the diene fragment in $[Os_3(s\text{-}cis\text{-}C_4H_6)(CO)_{10}]$(Pierpont, 1978).

The shortest edge, Os(1)—Os(3), is bridged by the thiol ligand and, from the distribution of the carbonyl groups, the hydride. The average *cis* Os(1)—Os(3)—C(carbonyl) angle is 113 (1)° compared to an angle of 89 (2)° for the carbonyl ligands associated with the other edges. Similar trends have been observed in a number of hydrido clusters (Churchill, DeBoer & Rotella, 1976) and these have been evidenced for the location of hydrides along the metal—metal edges. In the absence of another bridging ligand a hydride causes a lengthening of the metal—metal bond, but in this case, the bridging thiol has an equal and opposite shortening effect such that the bridged Os—Os bond is 0·008 Å shorter than the average of the unbridged metal–metal distances. All three Os—Os bonds are shorter than the 2·877 (3) Å in $[Os_3(CO)_{12}]$ (Churchill & DeBoer, 1977), and the bridged edge slightly shorter than the 2·863 (2) Å in $[Os_3(C_2H_5S)(CO)_{10}H]$ (Allen, Mason & Hitchcock, 1977). In the latter compound the thiolato bridge is also symmetric. The Os—S lengths in $[Os_3(C_2H_4)(CH_3S)H]$ are not significantly different from the mean length of 2·390 (3) Å in $[Os_3(CO)_9H_2S]$ (Johnson, Lewis, Pippard, Raithby, Sheldrick & Rouse, 1979) where the S atom caps the Os_3 triangle.

The carbonyl ligands are all essentially linear with an average Os—C—O angle of 176 (2)°. The mean Os—C and C—O distances of 1·88 (2) and 1·16 (3) Å, respectively, are similar to those reported for $[Os_3(C_2H_5S)(CO)_{10}H]$ (Allen, Mason & Hitchcock, 1977).

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1,1,1,2,2,2,2,3,3-Nonacarbonyl-1,3;1,3-di-μ-nitrosyl-3-(trimethyl phosphite)-*triangulo*-triosmium

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Abstract. $[Os_3(C_3H_9O_3P)(CO)_9(NO)_2]$, $C_{12}H_9N_2O_{14}Os_3P$, monoclinic, $P2_1/c$, $a = 13{\cdot}014$ (4), $b = 9{\cdot}448$ (3), $c = 18{\cdot}826$ (6) Å, $\beta = 101{\cdot}06$ (2)°, $U = 2271{\cdot}8$ Å^3, $Z = 4$, $D_c = 2{\cdot}94$ Mg m^{-3}, μ(Mo $K\alpha$) = 16·86 mm^{-1}. Final $R = 0{\cdot}049$ for 3462 unique diffractometer data. The Os atoms define an isosceles triangle with one long edge which is bridged by the two nitrosyl groups. The phosphite ligand occupies an equatorial coordination site on one of the metal atoms bound to the bridging nitrosyls. The carbonyl ligands are all terminal.

Introduction. The structural chemistry of transition-metal carbonyl clusters is well established. There are, however, few examples of clusters containing nitrosyl ligands. This group, which is introduced to the reaction as nitrogen monoxide gas, seems to have little tendency to either displace a carbonyl or form an addition compound with transition-metal carbonyl clusters under mild conditions. Although the nitrosyl and carbonyl ligands have similar steric requirements, the nitrosyl is formally a three-electron donor and is more readily able to modify its mode of bonding. This

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