

2). The C—N bonds also have double-bond character. The mean values 1.69 and 1.74 Å for the S—C bonds and 1.35 Å for the C—N bonds compare well with the values found in the other dithiocarbamates mentioned above.

The terminal propyl groups of each ligand adopt their more usual conformation, lying on alternate sides of the ligand plane.*

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* See deposition footnote.

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1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3- μ -hydrido-2,3- μ -(α - β - η : α - σ -styryl)-triangulo-triosmium

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Abstract. $C_{18}H_8O_{10}Os_3$, $M_r = 954.84$, monoclinic, $C2/c$, $a = 18.717(6)$, $b = 7.636(2)$, $c = 30.211(10)$ Å, $\beta = 91.88(3)^\circ$, $U = 4315.5$ Å³, $Z = 8$, $D_c = 2.94$ Mg m⁻³, $\mu(Mo K\alpha) = 17.7$ mm⁻¹. The structure was refined to an R of 0.064 for 2502 unique observed diffractometer data. The three Os atoms lie at the vertices of a triangle; two of these atoms are each coordinated to three terminal carbonyls and the other is coordinated to four. The styryl ligand σ -coordinates to one Os atom and π -coordinates to another, asymmetrically bridging the shortest Os—Os bond. The distribution of the carbonyl ligands indicates that the hydride bridges the same short edge.

Introduction. The complex $Os_3(CO)_{10}(NCCH_3)_2$ has been shown to be an important, reactive starting material in many reactions of small organic molecules with trinuclear Os clusters (Tachikawa & Shapley, 1977; Johnson, Lewis & Pippard, 1981). The aceto-

nitrile ligands are easily displaced by other groups. A recent publication has reported the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with amides and aldehydes (Johnson, Lewis, Odiaka & Raithby, 1981). In a continuation of this series of reactions of $Os_3(CO)_{10}(NCCH_3)_2$, the complex has been treated with styrene. Here we report the structure of a product from this reaction.

The title compound was prepared by reacting excess styrene with $Os_3(CO)_{10}(NCCH_3)_2$ in refluxing cyclohexane for 30 min (Goudsmit, 1981). The product was purified by thin-layer chromatography. The molecular geometry could not be unambiguously determined by spectroscopic techniques and a single-crystal X-ray analysis was undertaken. Recrystallization from cyclohexane yielded orange, rectangular blocks. 4471 intensities were recorded ($7 < 2\theta < 50^\circ$) on a Stoe four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, using ω scans, and a

crystal 0.31 × 0.11 × 0.08 mm. The data were profile-fitted (Clegg, 1981); Lp corrections, and semi-empirical absorption corrections based on a pseudo-ellipsoid model and 351 azimuthal scan data from 12 independent reflections were applied; transmission factors ranged from 0.056 to 0.177 for the full data set. Equivalent reflections were averaged to give 2502 unique observed intensities [$F > 3\sigma(F)$]. Cell dimensions were derived from the angular measurements of 31 strong reflections ($2\theta < 25^\circ$).

The three Os-atom positions were derived from a Patterson synthesis. Automatic direct methods yielded an Os₃ triangle with approximately correct orientation, but wrongly positioned relative to the cell origin. The other non-hydrogen atoms were determined from subsequent difference syntheses. The structure was refined by blocked-cascade least squares with complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) and weights $w = [\sigma^2(F) + 0.00087|F_o|^2]^{-1}$. The refined parameters included anisotropic thermal parameters for the Os, C, and O atoms. The hydride atom and ethylenic H atoms bonded to C(1) and C(2) were not located; the ring H atoms were placed in idealized positions and constrained to ride on the relevant C atom at a distance of

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$, for Os $\times 10^4$)

	x	y	z	U_{eq}
Os(1)	4217 (1)	3755 (1)	6676 (1)	427 (3)
Os(2)	3259 (1)	6678 (1)	6673 (1)	451 (3)
Os(3)	3023 (1)	3735 (1)	6075 (1)	425 (3)
C(11)	4956 (16)	5345 (37)	6835 (9)	70 (11)
O(11)	5411 (11)	6256 (22)	6929 (6)	74 (8)
C(12)	4041 (13)	3140 (28)	7290 (7)	50 (8)
O(12)	3951 (11)	2705 (26)	7633 (5)	80 (8)
C(13)	4780 (17)	1710 (42)	6584 (8)	73 (12)
O(13)	5207 (14)	613 (29)	6516 (7)	103 (11)
C(21)	2406 (19)	8090 (29)	6555 (8)	63 (11)
O(21)	1899 (13)	8914 (29)	6501 (7)	100 (10)
C(22)	3769 (14)	8038 (33)	7109 (7)	58 (9)
O(22)	4092 (11)	8934 (22)	7338 (5)	79 (8)
C(23)	3745 (13)	7850 (35)	6185 (8)	60 (10)
O(23)	4027 (11)	8535 (21)	5921 (6)	73 (7)
C(24)	2820 (16)	5442 (40)	7158 (8)	74 (11)
O(24)	2563 (12)	4814 (29)	7438 (5)	88 (9)
C(31)	2598 (15)	5307 (36)	5653 (8)	65 (11)
O(31)	2338 (11)	6263 (24)	5409 (6)	83 (8)
C(32)	2184 (13)	3724 (31)	6409 (8)	56 (9)
O(32)	1650 (11)	3622 (30)	6583 (6)	100 (10)
C(33)	2765 (15)	1627 (39)	5742 (9)	64 (11)
O(33)	2626 (12)	472 (29)	5543 (7)	92 (10)
C(1)	4226 (11)	4344 (33)	5979 (6)	46 (8)
C(2)	4076 (12)	2997 (29)	5669 (7)	44 (8)
C(3)	4085 (13)	3299 (31)	5184 (7)	50 (8)
C(4)	4156 (13)	1822 (36)	4905 (8)	64 (10)
C(5)	4202 (16)	1817 (55)	4474 (8)	105 (16)
C(6)	4197 (15)	3471 (55)	4274 (8)	129 (20)
C(7)	4105 (18)	4944 (61)	4517 (10)	126 (19)
C(8)	4054 (14)	4882 (40)	4984 (8)	66 (11)

$U_{eq} = \frac{1}{3}$ trace of the orthogonalized U matrix.

Table 2. Bond lengths (\AA)

Os(1)—Os(2)	2.863 (2)	Os(1)—Os(3)	2.834 (2)
Os(1)—C(11)	1.890 (28)	Os(1)—C(12)	1.951 (22)
Os(1)—C(13)	1.909 (32)	Os(1)—C(1)	2.154 (20)
Os(2)—Os(3)	2.909 (2)	Os(2)—C(21)	1.951 (31)
Os(2)—C(22)	1.907 (24)	Os(2)—C(23)	1.971 (25)
Os(2)—C(24)	1.947 (27)	Os(3)—C(31)	1.906 (26)
Os(3)—C(32)	1.894 (25)	Os(3)—C(33)	1.951 (29)
Os(3)—C(1)	2.326 (21)	Os(3)—C(2)	2.421 (22)
C(11)—O(11)	1.128 (34)	C(12)—O(12)	1.106 (27)
C(13)—O(13)	1.181 (40)	C(21)—O(21)	1.145 (39)
C(22)—O(22)	1.133 (30)	C(23)—O(23)	1.104 (31)
C(24)—O(24)	1.098 (33)	C(31)—O(31)	1.136 (32)
C(32)—O(32)	1.149 (32)	C(33)—O(33)	1.093 (36)
C(1)—C(2)	1.415 (31)	C(2)—C(3)	1.481 (29)
C(3)—C(4)	1.417 (35)	C(3)—C(8)	1.353 (37)
C(4)—C(5)	1.310 (35)	C(5)—C(6)	1.400 (56)
C(6)—C(7)	1.357 (57)	C(7)—C(8)	1.418 (40)

Table 3. Bond angles ($^\circ$)

Os(2)—Os(1)—Os(3)	61.4 (1)	Os(2)—Os(1)—C(11)	87.3 (9)
Os(3)—Os(1)—C(11)	136.2 (9)	Os(2)—Os(1)—C(12)	93.7 (7)
Os(3)—Os(1)—C(12)	116.9 (7)	C(11)—Os(1)—C(12)	93.4 (11)
Os(2)—Os(1)—C(13)	170.3 (8)	Os(3)—Os(1)—C(13)	109.2 (8)
C(11)—Os(1)—C(13)	99.2 (13)	C(12)—Os(1)—C(13)	93.0 (10)
Os(2)—Os(1)—C(1)	81.9 (6)	Os(3)—Os(1)—C(1)	53.5 (6)
C(11)—Os(1)—C(1)	94.9 (11)	C(12)—Os(1)—C(1)	170.4 (9)
C(13)—Os(1)—C(1)	90.4 (10)	Os(1)—Os(2)—Os(3)	58.8 (1)
Os(1)—Os(2)—C(21)	160.1 (7)	Os(3)—Os(2)—C(21)	101.9 (7)
Os(1)—Os(2)—C(22)	97.1 (8)	Os(3)—Os(2)—C(22)	155.7 (8)
C(21)—Os(2)—C(22)	102.4 (11)	Os(1)—Os(2)—C(23)	93.0 (7)
Os(3)—Os(2)—C(23)	87.2 (8)	C(21)—Os(2)—C(23)	90.4 (11)
C(22)—Os(2)—C(23)	92.1 (10)	Os(1)—Os(2)—C(24)	84.2 (9)
Os(3)—Os(2)—C(24)	91.9 (8)	C(21)—Os(2)—C(24)	92.4 (12)
C(22)—Os(2)—C(24)	87.6 (11)	C(23)—Os(2)—C(24)	177.1 (12)
Os(1)—Os(3)—Os(2)	59.8 (1)	Os(1)—Os(3)—C(31)	136.8 (8)
Os(2)—Os(3)—C(31)	88.9 (8)	Os(1)—Os(3)—C(32)	108.0 (7)
Os(2)—Os(3)—C(32)	77.5 (7)	C(31)—Os(3)—C(32)	91.4 (11)
Os(1)—Os(3)—C(33)	120.8 (8)	Os(2)—Os(3)—C(33)	171.2 (8)
C(31)—Os(3)—C(33)	94.8 (11)	C(32)—Os(3)—C(33)	94.3 (11)
Os(1)—Os(3)—C(1)	48.1 (5)	Os(2)—Os(3)—C(1)	78.2 (6)
C(31)—Os(3)—C(1)	100.1 (10)	C(32)—Os(3)—C(1)	152.9 (9)
C(33)—Os(3)—C(1)	109.0 (10)	Os(1)—Os(3)—C(2)	71.9 (5)
Os(2)—Os(3)—C(2)	112.7 (5)	C(31)—Os(3)—C(2)	97.8 (9)
C(32)—Os(3)—C(2)	166.3 (9)	C(33)—Os(3)—C(2)	74.8 (10)
C(1)—Os(3)—C(2)	34.6 (8)	Os(1)—C(11)—O(11)	178.1 (24)
Os(1)—C(12)—O(12)	176.3 (21)	Os(1)—C(13)—O(13)	170.3 (28)
Os(2)—C(21)—O(21)	177.5 (22)	Os(2)—C(22)—O(22)	173.9 (22)
Os(2)—C(23)—O(23)	178.0 (25)	Os(2)—C(24)—O(24)	176.9 (26)
Os(3)—C(31)—O(31)	178.4 (22)	Os(3)—C(32)—O(32)	174.1 (20)
Os(3)—C(33)—O(33)	177.8 (28)	Os(1)—C(1)—Os(3)	78.4 (7)
Os(1)—C(1)—C(2)	119.3 (17)	Os(3)—C(1)—C(2)	76.4 (13)
Os(3)—C(2)—C(1)	69.0 (12)	Os(3)—C(2)—C(3)	120.0 (15)
C(1)—C(2)—C(3)	122.2 (20)	C(2)—C(3)—C(4)	117.9 (21)
C(2)—C(3)—C(8)	125.4 (21)	C(4)—C(3)—C(8)	116.7 (21)
C(3)—C(4)—C(5)	127.3 (29)	C(4)—C(5)—C(6)	115.3 (32)
C(5)—C(6)—C(7)	120.9 (26)	C(6)—C(7)—C(8)	121.7 (36)
C(3)—C(8)—C(7)	118.1 (29)		

0.96 (1) \AA with isotropic thermal parameters fixed at 1.2 times U_{eq} for the C atom. The refinement converged to $R = 0.064$ and $R' = (\sum w^{1/2} \Delta / \sum w^{1/2} |F_o|) = 0.060$. The final atomic coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms are listed in Table 1,* and bond lengths and angles in Tables 2 and 3, respectively.

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36925 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structure of the title compound closely resembles that of the μ -1-butenyl, HO₃(CO)₁₀(CHCHCH₂CH₃) (Guy, Reichert & Sheldrick, 1976), and μ -vinyl, HO₃(CO)₁₀(C₂H₃) (Orpen, Pippard, Sheldrick & Rouse, 1978), analogues. A similar mode of coordination of the organic ligand has been observed in the structures of H₃Os₄(CO)₁₁(C₆H₉) (Bhaduri *et al.*, 1979) and H₃Os₄(CO)₁₁(CHCHPh) (Johnson, Lewis, Orpen, Raithby & Rouse, 1981). The molecular geometry is shown in Fig. 1. The three Os atoms lie at the vertices of a triangle, the shortest edge of which is bridged by the organic group. C(1) forms a σ bond to Os(1), and C(1) and C(2) form a π bond to Os(3). The distribution of the carbonyls indicates that the hydride also bridges the short Os(1)–Os(3) edge. The *cis* Os–Os–C(carbonyl) angles for Os(1)–Os(3) average 114 (2)° compared to 89 (2)° for the other edges, the steric influence of the hydride causing the adjacent carbonyls to bend away from the Os(1)–Os(3) edge. Three terminal carbonyls are coordinated to Os(1) and Os(3), while there are two axial and two equatorial carbonyls bonded to Os(2).

The bridged Os(1)–Os(3) distance in the title complex is the same as that [2.834 (1) Å] in HO₃(CO)₁₀(CHCHCH₂CH₃) (Guy *et al.*, 1976). The two unbridged Os–Os bonds are also similar in length to those [2.858 (1) and 2.923 (1) Å] for the unbridged bonds in the butenyl analogue. Again the longest Os–Os bond is associated with the metal atom that is π -bonded to the organic ligand. Similar trends are observed in the structure of HO₃(CO)₁₀(C₂H₃) (Orpen *et al.*, 1978). The Os(1)–C(1) σ bond and the Os(3)–C(1) and Os(3)–C(2) distances which make up the π bond are not significantly different from the equivalent bond lengths in HO₃(CO)₁₀(CHCHCH₂CH₃). The C(1)–C(2) bond length is similar to the value of 1.40 (3) Å for the equivalent bond in the butenyl complex, and this distance is consistent with a formal C–C double bond donating electron density to a metal atom. The bond parameters in the CH=C(H)Ph ligand in the title compound are generally similar to those reported for this ligand in H₃Os₄(CO)₁₁(CHCHPh) (Johnson, Lewis, Orpen, Raithby & Rouse, 1981). However, the neutron structure of the Os₄ cluster indicates a more symmetrical coordination of C(1) to the two Os atoms which it bridges [Os–C 2.15 (1) Å for the σ bond, Os–C 2.15 (1) and 2.30 (1) Å for the π bond] and the Os–C distances making up the π bond are also slightly shorter.

The ten carbonyl groups are all terminal and Os–C–O angles deviate from linearity by less than 10°. The Os–C and C–O bond lengths average 1.93 (5) and 1.13 (5) Å, respectively. These values are

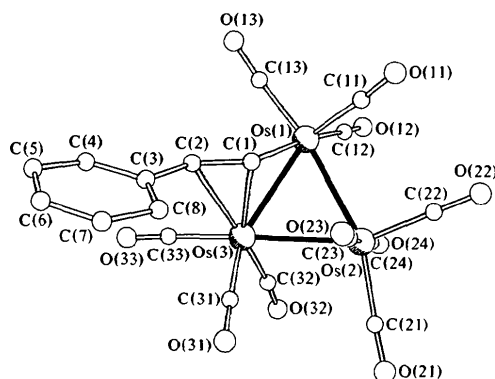


Fig. 1. The molecular structure of HO₃(CO)₁₀(CHCHPh).

similar to those reported in other trinuclear Os clusters. Although the e.s.d.'s in the Os–C(carbonyl) bonds are rather high to make any assessment of the bonding, the trends indicate that the Os–C axial bonds on Os(2) are longer than the equatorial. This is consistent with the *trans* influence of the carbonyl groups, where the competition of two *trans* carbonyls for electrons from the same metal orbital results in bond lengthening.

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