

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 [Os₃(*s-cis*-C₄H₆)(CO)₁₀]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 [Os₃(CO)₁₂] (Churchill & DeBoer, 1977), and the bridged edge slightly shorter than the 2.863 (2) Å in [Os₃(C₂H₅S)(CO)₁₀H] (Allen, Mason & Hitchcock, 1977). In the latter compound the thiolato bridge is also symmetric. The Os—S lengths in [Os₃(C₂H₄)(CH₃S)H] are not significantly different from the mean length of 2.390 (3) Å in [Os₃(CO)₉H₂S] (Johnson, Lewis, Pippard, Raithby, Sheldrick & Rouse, 1979) where the S atom caps the Os₃ 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 [Os₃(C₂H₅S)(CO)₁₀H] (Allen, Mason & Hitchcock, 1977).

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

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Abstract. [Os₃(C₃H₉O₃P)(CO)₉(NO)₂], C₁₂H₉N₂O₁₄Os₃P, monoclinic, *P*2₁/*c*, *a* = 13.014 (4), *b* = 9.448 (3), *c* = 18.826 (6) Å, β = 101.06 (2)°, *U* = 2271.8 Å³, *Z* = 4, *D*_c = 2.94 Mg m⁻³, μ (Mo *K* α) = 16.86 mm⁻¹. Final *R* = 0.049 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

structural analysis was undertaken to investigate the nature of the nitrosyl bonding and establish the effect of the bulky phosphite on the cluster geometry.

[Os₃{(CH₃O)₃P}(CO)₉(NO)₂] was prepared by refluxing [Os₃{(CH₃O)₃P}(CO)₈(NO)₂] in *n*-heptane under a CO atmosphere for *ca* 30 min (Bhaduri, Johnson, Lewis, Watson & Zuccaro, 1979). Green, rectangular blocks were obtained by recrystallization from chloroform/hexane. 4428 reflections were measured for $3.0 < 2\theta \leq 60.0^\circ$ on a Stoe AED four-circle diffractometer with graphite-monochromated Mo *K* α radiation, an ω - θ scan technique, and a crystal $0.305 \times 0.262 \times 0.120$ mm. Lp corrections and a semi-empirical absorption correction based on a pseudo-ellipsoid model with 396 azimuthal scan data from eight independent reflections were applied; transmission factors ranged from 0.378 to 0.972. The data were averaged to give 3462 unique observed reflections [$F > 3\sigma(F)$]. Cell dimensions were derived from the angular measurements of 20 strong reflections in the range $20 < 2\theta < 30^\circ$.

The three Os atoms were located by multiresolution Σ_2 sign expansion, and the C, N, O, and P atoms from a difference synthesis. The structure was refined by full-matrix least squares with anisotropic temperature factors for Os and P, and individual isotropic tem-

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

	<i>x</i>	<i>y</i>	<i>z</i>
Os(1)	8705 (1)	1227 (1)	835 (1)
Os(2)	8678 (1)	4106 (1)	1345 (1)
Os(3)	6937 (1)	2459 (1)	1647 (1)
C(11)	8485 (14)	-704 (20)	592 (9)
O(11)	8351 (13)	-1848 (19)	429 (8)
C(12)	8943 (15)	1681 (19)	-104 (9)
O(12)	9084 (12)	2077 (16)	-662 (7)
C(13)	10180 (14)	1076 (18)	1199 (8)
O(13)	11036 (12)	1034 (16)	1415 (8)
C(21)	9926 (14)	4505 (18)	1033 (9)
O(21)	10727 (13)	4786 (17)	853 (8)
C(22)	8234 (14)	5772 (19)	1741 (9)
O(22)	7950 (12)	6781 (17)	1977 (8)
C(23)	7819 (14)	4542 (18)	432 (9)
O(23)	7250 (13)	4865 (17)	-119 (8)
C(24)	9409 (12)	3419 (16)	2284 (8)
O(24)	9811 (11)	3073 (15)	2839 (7)
C(31)	7046 (15)	3181 (21)	2610 (10)
O(31)	7145 (12)	3593 (16)	3195 (8)
C(32)	5922 (15)	3866 (20)	1273 (9)
O(32)	5317 (12)	4701 (16)	1000 (7)
N(1)	7141 (11)	1805 (15)	656 (7)
O(10)	6542 (10)	1860 (14)	68 (6)
N(2)	8209 (10)	1136 (13)	1819 (6)
O(20)	8682 (9)	528 (13)	2377 (6)
P(1)	5763 (4)	734 (5)	1782 (2)
O(1)	4520 (11)	1049 (14)	1546 (7)
C(1)	4061 (20)	1314 (27)	778 (13)
O(2)	5699 (11)	149 (15)	2570 (7)
C(2)	6586 (20)	-390 (27)	3047 (12)
O(3)	5993 (10)	-629 (13)	1352 (6)
C(3)	5432 (19)	-1929 (26)	1380 (12)

Table 2. *Bond lengths* (Å)

Os(2)—Os(1)	2.888 (2)	C(11)—Os(1)	1.889 (19)
Os(3)—Os(1)	3.217 (2)	C(12)—Os(1)	1.900 (16)
Os(3)—Os(2)	2.894 (2)	C(13)—Os(1)	1.916 (18)
N(1)—Os(1)	2.072 (14)	C(21)—Os(2)	1.867 (17)
N(2)—Os(1)	2.077 (11)	C(22)—Os(2)	1.880 (18)
N(1)—Os(3)	2.031 (12)	C(23)—Os(2)	1.907 (18)
N(2)—Os(3)	2.050 (13)	C(24)—Os(2)	1.952 (15)
P(1)—Os(3)	2.281 (4)	C(31)—Os(3)	1.915 (18)
O(10)—N(1)	1.227 (18)	C(32)—Os(3)	1.910 (20)
O(20)—N(2)	1.251 (16)	O(11)—C(11)	1.128 (22)
O(1)—P(1)	1.621 (14)	O(12)—C(12)	1.163 (18)
O(2)—P(1)	1.600 (13)	O(13)—C(13)	1.111 (21)
O(3)—P(1)	1.580 (12)	O(21)—C(21)	1.187 (20)
C(1)—O(1)	1.476 (27)	O(22)—C(22)	1.143 (20)
C(2)—O(2)	1.415 (27)	O(23)—C(23)	1.193 (21)
C(3)—O(3)	1.434 (25)	O(24)—C(24)	1.123 (18)
O(31)—C(31)	1.153 (20)	O(32)—C(32)	1.163 (22)

perature factors for the other non-hydrogen atoms. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed, with the weighting scheme $w = 0.8405/\sigma^2(F)$ for the final stages of refinement. The final residuals were $R = 0.049$ and $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.044$. The H atoms were not located. Final atomic coordinates are given in Table 1, bond lengths and angles in Tables 2 and 3.*

Discussion. The structure, Fig. 1, is closely related to those of [Ru₃(CO)₁₀(NO)₂] (Norton, Collman, Dolcetti & Robinson, 1972) and [Os₃{(CH₃)₃N}(CO)₉(NO)₂] (Johnson, Lewis, Raithby & Zuccaro, 1979). In these compounds the metal atoms define an isosceles triangle with one edge lengthened to such an extent that there can be little direct metal—metal bonding; this Os...Os distance in the title compound is 3.217 (1) Å. In all three complexes the long edge is bridged by two nitrosyl ligands which lie on opposite sides of the *M*₃ triangle. The Os—N(nitrosyl) distances found here are similar to the mean value of 2.04 (2) Å in [Os₃{(CH₃)₃N}(CO)₉(NO)₂] (Johnson, Lewis, Raithby & Zuccaro, 1979). As in other cluster compounds the phosphite ligand coordinates to an equatorial site on the cluster. The Os—P bond is single, and the length agrees closely with the 2.285 (5) Å in [Os₃{(CH₃O)₃P}(CO)₁₁] (Benfield, Johnson, Raithby & Sheldrick, 1978). The unbridged Os—Os bond *trans* to the phosphite donor ligand is slightly longer than the other metal—metal bond, but both distances are similar to the Os—Os single-bond value of 2.877 (3) Å in [Os₃(CO)₁₂] (Churchill & DeBoer, 1977).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34958 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond angles (°)

Os(3)—Os(1)—Os(2)	56.3 (1)	C(11)—Os(1)—Os(2)	168.3 (5)
Os(3)—Os(2)—Os(1)	67.6 (1)	C(11)—Os(1)—Os(3)	112.0 (5)
Os(2)—Os(3)—Os(1)	56.1 (1)	C(12)—Os(1)—Os(2)	96.4 (5)
Os(3)—N(1)—Os(1)	103.2 (6)	C(12)—Os(1)—Os(3)	128.3 (6)
O(10)—N(1)—Os(1)	126.3 (11)	C(13)—Os(1)—Os(2)	91.5 (5)
O(10)—N(1)—Os(3)	130.1 (12)	C(13)—Os(1)—Os(3)	128.0 (4)
Os(3)—N(2)—Os(1)	102.4 (5)	C(21)—Os(2)—Os(3)	158.6 (5)
O(20)—N(2)—Os(1)	125.5 (10)	C(22)—Os(2)—Os(1)	161.0 (5)
O(20)—N(2)—Os(3)	131.6 (9)	C(22)—Os(2)—Os(3)	93.4 (5)
C(12)—Os(1)—C(11)	92.2 (7)	C(23)—Os(2)—Os(1)	86.9 (5)
C(13)—Os(1)—C(11)	96.3 (8)	C(23)—Os(2)—Os(3)	87.0 (5)
C(13)—Os(1)—C(12)	91.1 (7)	C(24)—Os(2)—Os(1)	87.3 (4)
C(21)—Os(2)—Os(1)	91.1 (5)	C(24)—Os(2)—Os(3)	84.6 (4)
C(22)—Os(2)—C(21)	107.9 (7)	C(31)—Os(3)—Os(1)	130.4 (6)
C(23)—Os(2)—C(21)	93.9 (7)	C(31)—Os(3)—Os(2)	94.3 (6)
C(23)—Os(2)—C(22)	90.3 (7)	C(32)—Os(3)—Os(1)	125.7 (5)
C(24)—Os(2)—C(21)	92.9 (7)	C(32)—Os(3)—Os(2)	92.7 (5)
C(24)—Os(2)—C(22)	93.0 (7)	P(1)—Os(3)—Os(1)	110.5 (1)
C(24)—Os(2)—C(23)	171.2 (7)	P(1)—Os(3)—Os(2)	166.5 (1)
C(32)—Os(3)—C(31)	91.3 (7)	O(1)—P(1)—Os(3)	119.5 (5)
N(1)—Os(1)—Os(2)	74.4 (4)	O(2)—P(1)—Os(3)	120.3 (6)
N(1)—Os(1)—Os(3)	37.9 (4)	O(3)—P(1)—Os(3)	109.2 (5)
N(2)—Os(1)—Os(2)	73.5 (3)	O(2)—P(1)—O(1)	95.2 (7)
N(2)—Os(1)—Os(3)	38.5 (4)	O(3)—P(1)—O(1)	106.6 (7)
N(1)—Os(3)—Os(1)	38.8 (4)	O(3)—P(1)—O(2)	104.0 (7)
N(1)—Os(3)—Os(2)	74.8 (4)	C(1)—O(1)—P(1)	119.6 (12)
N(2)—Os(3)—Os(1)	39.1 (3)	C(2)—O(2)—P(1)	122.1 (13)
N(2)—Os(3)—Os(2)	73.7 (3)	C(3)—O(3)—P(1)	122.1 (11)
N(1)—Os(1)—C(11)	96.7 (7)	P(1)—Os(3)—C(31)	94.5 (6)
N(1)—Os(1)—C(12)	96.9 (7)	P(1)—Os(3)—C(32)	96.2 (6)
N(1)—Os(1)—C(13)	164.5 (6)	P(1)—Os(3)—N(1)	95.4 (4)
N(2)—Os(1)—C(11)	96.7 (6)	P(1)—Os(3)—N(2)	94.9 (4)
N(2)—Os(1)—C(12)	166.5 (7)	O(11)—C(11)—Os(1)	178.1 (17)
N(2)—Os(1)—C(13)	98.0 (6)	O(12)—C(12)—Os(1)	174.3 (16)
N(2)—Os(1)—N(1)	72.1 (5)	O(13)—C(13)—Os(1)	177.7 (17)
N(1)—Os(3)—C(31)	168.0 (7)	O(21)—C(21)—Os(2)	178.0 (16)
N(1)—Os(3)—C(32)	94.3 (6)	O(22)—C(22)—Os(2)	179.0 (18)
N(2)—Os(3)—C(31)	99.0 (7)	O(23)—C(23)—Os(2)	176.3 (15)
N(2)—Os(3)—C(32)	164.2 (6)	O(24)—C(24)—Os(2)	176.9 (14)
N(2)—Os(3)—N(1)	73.4 (5)	O(31)—C(31)—Os(3)	177.7 (17)
O(32)—C(32)—Os(3)	175.5 (15)		

The carbonyl groups are all terminal and approximately linear. The Os—C distances for the two axial carbonyls on Os(2) are longer than those for the two equatorial ones on that atom. This reflects the competition between the two axial ligands for electron density from the same set of metal orbitals and results in the individual bonds being weaker. The Os—C—(carbonyl) bonds *trans* to the bridging nitrosyl ligands are also fairly long which suggests that the nitrosyl groups can act as π -acceptor ligands.

The dimensions of the phosphite group show no significant deviations from the expected values.

In the related complex [Os₃{(CH₃O)₃P}(CO)₈(NO)₂] (Rivera & Sheldrick, 1978), the two nitrosyl groups are terminally bound to the same Os atom. In this complex and in the title compound the nitrosyls formally act as three-electron donors, though in the former case all three electrons are donated to the same metal and the terminal Os—N(nitrosyl) lengths are 1.77 (4) and 1.65 (4) Å. [Os₃{(CH₃O)₃P}(CO)₈(NO)₂] is an 'electron precise' 48-electron system while [Os₃{(CH₃O)₃P}(CO)₉(NO)₂] has an additional pair of electrons resulting in the breaking of a metal—metal bond. The bridging nitrosyl configuration may be favoured here since two three-centre Os—N—Os bonds could stabilize the cluster in the absence of a direct metal—metal bond.

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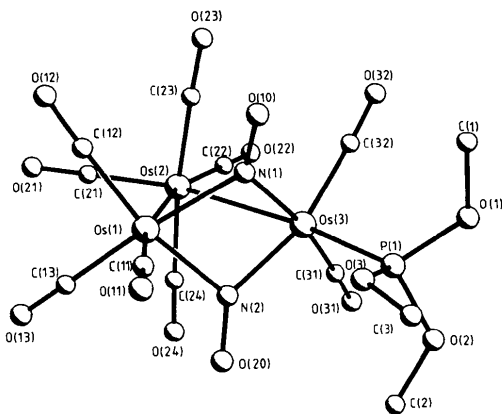


Fig. 1. The molecular structure of [Os₃{(CH₃O)₃P}(CO)₉(NO)₂].