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# Nonacarbonyl-$\mu_2$-hydrido-$\mu_2$-(*N*-methylcarboxamido)-*C*:*O*-(*N*-trimethylamine)triosmium(3 *Os*—*Os*)

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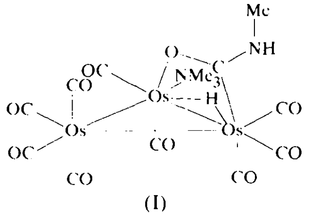
## Abstract

In the title compound, nonacarbonyl-$1\kappa^2C,2\kappa^3C,3\kappa^4C$-$\mu$-hydrido-$1{:}2\kappa^2H$-$\mu$-(*N*-methylcarboxamido)-$1{:}2\kappa^2O{:}C$-(*N*-trimethylamine-$1\kappa N$)triosmium(3 *Os*—*Os*), [$Os_3H(C_2H_4NO)(C_3H_9N)(CO)_9$], the MeHNCO ligand forms a $\mu_2$-C:O bridge between two metal centers, which are also linked by a $\mu$-hydride ligand. These two groups are at opposite sides of the plane defined by the Os atoms. Bond lengths between Os atoms are 2.8149 (8), 2.8777 (8) and 2.9278 (8) Å. The structure shows two metal centers which are heptacoordinated and one which is hexacoordinated.

## Comment

The labile triosmium carbonyl clusters can be prepared by the reaction of $Os_3(CO)_{12}$ with $Me_3NO$ (trimethylamine oxide) in the presence of a coordinating solvent such as $CH_3CN$ (acetonitrile) affording the mono- and disubstituted metal clusters [$Os_3(CO)_{11}(MeCN)$] and [$Os_3(CO)_{10}(MeCN)_2$], respectively (Johnson *et al.*, 1981). However, if the above-mentioned reaction is performed in a less strongly coordinating solvent, *e.g.* THF (tetrahydrofuran), the amine derivative is obtained (Dawson *et al.*, 1982).

Under our reaction conditions, a novel disubstituted carbonyl cluster, (I), is obtained. In this new compound, one carbonyl group has been replaced by a trimethylamine ligand. Also, a nucleophilic attack occurred at one of the axial carbonyls producing a $\mu$-O—C group that bridges two Os atoms as shown in Fig. 1.



(I)

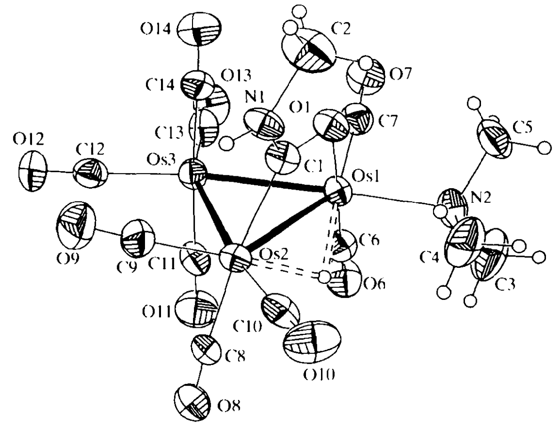


Fig. 1. The molecular structure of the title compound showing 30% probability displacement ellipsoids and the atomic numbering scheme.

The title compound, [$Os_3H(C_3H_9N)(C_2H_4NO)(CO)_9$], has a triosmium triangular core. Two osmium centers (Os1 and Os2) are heptacoordinated and the other one (Os3) is hexacoordinated. The hexacoordinated Os atom shows a distorted octahedral coordination geometry and the heptacoordinated ones have distorted face-capped octahedral coordination environments. The face-capping ligand is a hydride ligand that bridges Os1 and Os2. In all cases, the 'equatorial' octahedral plane corresponds approximately to the plane defined by the triosmium core.

The apical positions (at the same face of the triosmium core) at Os1 and Os2 are occupied by O and C atoms (O1 and C1), respectively, defining a $\mu$-carboxamide bridge between them. Coordination is completed by a trimethylamino group at Os1 and carbonyl groups at the other positions. The least-squares plane defined by Os1, Os2, O1 and C1 forms a dihedral angle of 79.6 (2)° with the planar triosmium core. The $\mu$-carboxamido ligand is highly planar [torsion angle O1—C1—N1—C2 is −2.4 (17)°].

The Os—Os distances are 2.8149 (8) (Os1—Os3), 2.8777 (8) (Os2—Os3) and 2.9278 (8) Å (Os1—Os2). The latter value is significantly greater than the other two and strongly supports the hypothesis of the existence of a hydride center, suggested by an otherwise unbalanced electron count around each metal center and confirmed by the $^1$H NMR spectrum, where the −12.86 p.p.m. low-field signal is clear evidence of a bridging hydride. Unfortunately, it was impossible to confidently detect the isolated H atom by standard crystallographic methods alone. However, through the theoretical approach proposed in the *XHYDEX* package (Orpen, 1980) which used potential functions to localize hydride ions in clusters, a unique site for the hydrogen was found (attached to both Os1 and Os2 as expected) and is the one finally reported.

## Experimental

A solution of $Os_3(CO)_{12}$ (0.2 g, 0.22 mmol) in dried THF (50 ml) was taken to reflux under nitrogen for 20 min. $Me_3NO$ (0.05 g, 0.66 mmol) dissolved in MeOH (0.5 ml) was then added and the solution kept under reflux. The course of the reaction was monitored by IR; after 1 h, the IR spectrum showed a complete disappearance of the carbonyl bands from $Os_3(CO)_{12}$. Thin-layer chromatography ($SiO_2$) of the yellow-green residue (hexane) gave mainly one yellow-green band, from which $[Os_3H(C_3H_9N)(C_2H_4NO)(CO)_9]$ as amber crystals was obtained. IR spectra were recorded in $C_6H_{12}$ (cyclohexane) and $^1$H NMR spectra in $C_2D_6CO$ (300 MHz, 296 K). IR ($\nu$, cm$^{-1}$): 2098 (*w*), 2057 (*s*), 2023 (*vs*), 2009 (*m*), 1999 (*s*), 1935 (*w*), 1932 (*w*). The hydride position was proposed using *XHYDEX* software (Orpen, 1980).

*Crystal data*

$[Os_3H(C_2H_4NO)(C_3H_9N)-(CO)_9]$
$M_r = 940.87$
Monoclinic
$P2_1/n$
$a = 12.932$ (2) Å
$b = 11.273$ (2) Å
$c = 14.921$ (3) Å
$\beta = 100.160$ (14)°
$V = 2141.2$ (7) Å$^3$
$Z = 4$
$D_x = 2.919$ Mg m$^{-3}$
$D_m$ not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 7.5$–12.5°
$\mu = 17.81$ mm$^{-1}$
$T = 293$ (2) K
Polyhedron
0.18 × 0.16 × 0.10 mm
Amber

*Data collection*

Siemens *R*3*m* diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (*SHELXTL*; Sheldrick, 1993)
$T_{\min} = 0.041$, $T_{\max} = 0.169$
3978 measured reflections
3800 independent reflections
2724 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 25.06°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = -17 \rightarrow 17$
2 standard reflections every 98 reflections intensity decay: <1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.079$
$S = 1.02$
3766 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 3.33P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.80$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.76$ e Å$^{-3}$
Extinction correction: *SHELXTL/PC* (Sheldrick, 1991)
Extinction coefficient: 0.00040 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Os1—O1 | 2.157 (8) | Os2—Os3 | 2.8777 (8) |
| Os1—N2 | 2.264 (10) | O1—C1 | 1.260 (13) |
| Os1—Os3 | 2.8149 (8) | C1—N1 | 1.323 (14) |
| Os1—Os2 | 2.9278 (8) | N1—C2 | 1.45 (2) |
| Os2—C1 | 2.072 (12) | | |
| O1—Os1—Os3 | 88.4 (2) | Os1—Os3—Os2 | 61.89 (2) |
| N2—Os1—Os3 | 167.4 (3) | C1—O1—Os1 | 105.6 (7) |
| O1—Os1—Os2 | 68.4 (2) | O1—C1—N1 | 117.7 (11) |
| N2—Os1—Os2 | 108.3 (3) | O1—C1—Os2 | 121.1 (9) |
| Os3—Os1—Os2 | 60.11 (2) | N1—C1—Os2 | 121.0 (8) |
| Os3—Os2—Os1 | 58.00 (2) | C1—N1—C2 | 118.7 (10) |
| O1—C1—N1—C2 | −2.4 (17) | | |

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1993). Program(s) used to refine structure: *XL* in *SHELXTL*. Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *XCIF* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1418). Services for accessing these data are described at the back of the journal.

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