

### Preliminary communication

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## REACTIONS OF $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ WITH AMIDES AND ALDEHYDES; X-RAY CRYSTAL STRUCTURE OF $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CCCH}_2\text{Ph})]$

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### Summary

Reaction of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  with amides and aldehydes has provided a high-yield route to clusters of the type  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{NHCOR})]$  ( $\text{R} = \text{H, Me, Ph, Et, Pr}$ ) and  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{COR})]$  ( $\text{R} = \text{Me, Ph, CH}_2\text{Ph, C}_6\text{H}_{13}$ ), respectively; the molecular structure of  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{COCH}_2\text{Ph})]$  has been established by a single-crystal X-ray analysis.

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The importance of  $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ , because of the easy replacement of the NCMe group, in reactions of trinuclear osmium clusters with many small molecules is well established [1]. The disubstituted complex  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  should prove equally useful in synthesis but has, so far, not been exploited to any great extent. We now report that  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  reacts smoothly with a variety of amides in refluxing cyclohexane (3–4 h) to give the new triosmium derivatives  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{NHCOR})]$  ( $\text{R} = \text{H, Me, Ph, Et, Pr}$ ) in yields ranging from 50–70%. The products are all yellow crystalline solids, and exhibit a singlet resonance at ca. 22  $\tau$  in their  $^1\text{H}$  NMR spectra which is characteristic of a bridging hydride ligand. IR and mass spectroscopic data are given in Table 1\*. The decrease in  $\nu(\text{CO})(\text{amide})$  by 60–90  $\text{cm}^{-1}$  observed in these complexes compared to that in the free ligands is consistent with the coordination of the carbonyl fragment to the  $\text{Os}_3$  triangle (Fig. 1a).

Thermolysis of  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{NHCOH})]$  in refluxing nonane for 40 h gave a yellow product with  $m/e$  873 ( $^{192}\text{Os}$ ) which indicates the loss of a CO fragment from the parent cluster. IR and  $^1\text{H}$  NMR studies of this decarbonylated product indicates that it may have the structure shown in Fig. 1b. The  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum exhibits a doublet metal-hydride resonance at 25.4  $\tau$  which indicates that there is through-space coupling between the hydride and

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\*All compounds gave satisfactory elemental analyses.

TABLE 1

IR AND MASS SPECTROSCOPIC DATA OF  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{NHCOR})]$  DERIVATIVES

R	IR $\nu(\text{CO})^a$	$m/e^b$
H	2110mw, 2070s, 2059s 2024s, 2013s, 2001m, 1988sh, 1985mw, 1979mw 1597 (amide)	901
CH <sub>3</sub>	2109mw, 2069s, 2057s, 2023s, 2009s, 1999m, 1986sh, 1983mw, 1977mw 1576 (amide)	915
Ph	2110mw, 2070s, 2059s, 2023s, 2012s, 1999m, 1987sh, 1984mw, 1977mw 1590 (amide)	977
Et	2109mw, 2069s, 2058s, 2023s, 2011s, 1999m, 1987sh, 1984mw, 1977mw 1570 (amide)	929
Pr	2108mw, 2068s, 2056s, 2022s, 2010s, 1998m, 1985sh 1982mw, 1976mw 1570 (amide)	943

<sup>a</sup> In cyclohexane. <sup>b</sup> Based on  $^{192}\text{Os}$ .

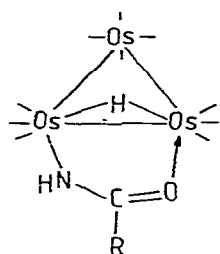
the NH proton. Similar couplings have been observed in  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{NHSO}_2\text{C}_6\text{H}_4\text{Me})]$  [2] and  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{NHN}=\text{CR}^1\text{R}^2)]$  ( $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Ph}$  and  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$ ) [3].

Reaction of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  with 2-hydroxy-pyridine in refluxing cyclohexane gives the new cluster  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{NC}_5\text{H}_4\text{O})]$  (1 h) in ca. 75% yield. The spectroscopic data (IR ( $\nu(\text{CO})$ )[cyclohexane]: 2110mw, 2069s, 2059s, 2023s, 2016s, 2000m, 1990mw, 1983(sh), 1979mw;  $^1\text{H}$  NMR [ $\text{CD}_2\text{Cl}_2$ ]  $\tau$  1.85 (1H, d), 2.84 (1H, m), 3.65 (2H, m), 20.64 (OsH, s).  $m/e = 951$ ) suggests the structure shown in Fig. 1c, although that illustrated in Fig. 1d cannot be excluded.

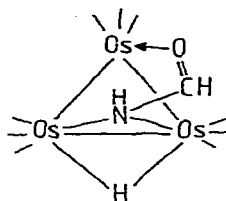
Reaction of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  with aldehydes in refluxing cyclohexane (3 h) under  $\text{N}_2$  leads to the formation of the known [4] clusters  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{COR})]$  ( $\text{R} = \text{Me}$ , Ph,  $\text{CH}_2\text{Ph}$ ,  $\text{C}_6\text{H}_{13}$ ) in significantly improved yields (ca. 50%). These products (Fig. 1e) are air-stable, yellow crystalline solids and the spectroscopic and analytical data obtained for them are in agreement with those reported by Deeming et al. [4]. In order to establish the nature of the bonding of the COR group in these complexes the molecular structure of the  $\text{COCH}_2\text{Ph}$  derivative was determined. Suitable crystals were deposited from pentane as yellow multifaced blocks.

#### Crystal data

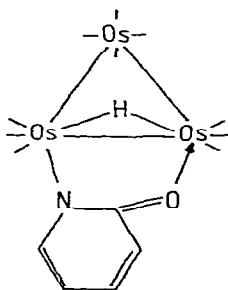
$\text{C}_{18}\text{H}_8\text{O}_{11}\text{Os}_3$ ,  $M$  970.84, monoclinic, space group  $P2_1/c$ ,  $a$  12.908(5),  $b$  9.062(4),  $c$  19.479(7) Å,  $\beta$  102.99(2)°,  $U$  2220.2 Å<sup>3</sup>.  $Z = 4$ ,  $D_c = 2.90$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K_\alpha) = 171.71$  cm<sup>-1</sup>. 4763 Intensities ( $2\theta_{\text{max}} = 60.0^\circ$ ) were recorded on a Stoe four-circle diffractometer using graphite-monochromated Mo  $K_\alpha$  radiation and an  $w/\theta$  scan technique. The data were corrected for absorption and for Lp factors and averaged to give 3495 unique observed reflections



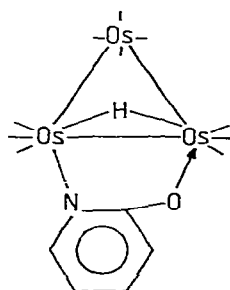
(a)



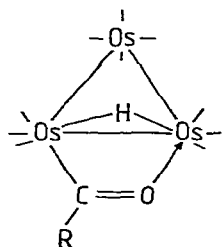
(b)



(c)



(d)



(e)

Fig. 1. Proposed structures for the triosmium derivatives.

[ $F > 3\sigma(F)$ ]. The structure was solved by a combination of direct methods (Os atom location) and Fourier difference techniques, and refined by blocked-cascade least-squares (Os, O and carbonyl C anisotropic) to  $R = 0.060$  and  $R' [\Sigma w^{1/2} \Delta / \Sigma w^{1/2} |F_o|] = 0.057$ . The phenyl ring was refined as a rigid body with the H atoms placed in idealised positions (C—H, 1.08 Å; C—C—H, 120.0°) and assigned a common isotropic temperature factor. The methylene H atoms were also constrained to ride 1.08 Å from the relevant carbon. Final atomic coordinates and bond parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

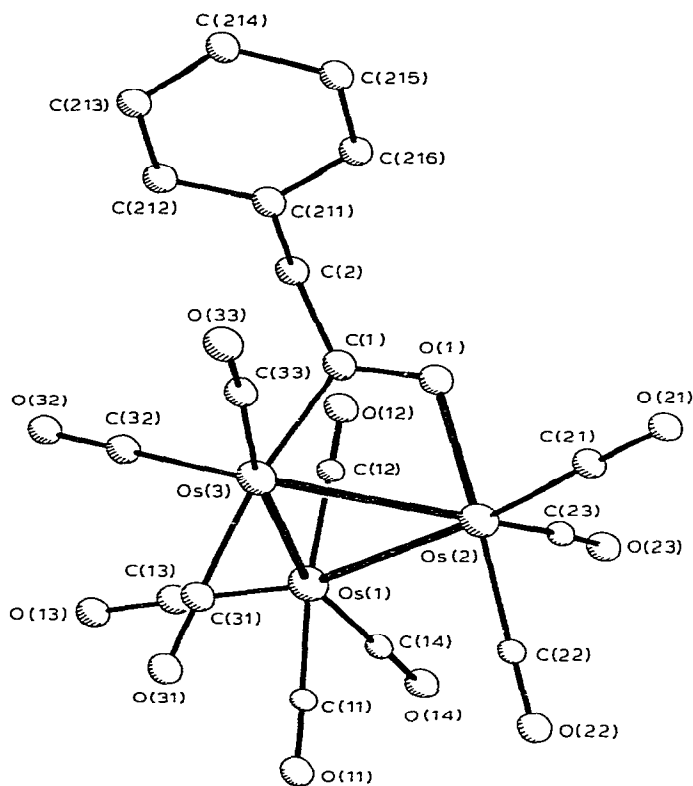


Fig. 2. The molecular structure of  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{COCH}_2\text{Ph})]$ , hydrogen atoms have been omitted for clarity. Bond lengths: Os(1)—Os(2), 2.847(2); Os(1)—Os(3), 2.884(2); Os(2)—Os(3), 2.884(1); Os(2)—O(1), 2.12(1); Os(3)—C(1), 2.10(2) Å. Bond angles: Os(3)—C(1)—O(1), 116(1); Os(3)—C(1)—C(2), 127(1); O(1)—C(1)—C(2), 117(2); Os(2)—O(1)—C(1), 109(1)°.

The molecular structure of  $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{COCH}_2\text{Ph})]$  is shown in Fig. 2 together with some important bond parameters. The three Os atoms define an isosceles triangle, one edge of which is bridged by both the hydride and the  $\text{COCH}_2\text{Ph}$  group. Although the hydride was not located directly, the carbonyl group *cis* to the Os(2)—Os(3) edge bend away from it (mean Os—Os—C 110°) while those *cis* to the Os(1)—Os(2) and Os(1)—Os(3) edges do not (mean Os—Os—C 94°). This bending effect has been shown to be caused by the presence of a bridging hydride in a number of hydrido-carbonyl clusters [5]. The most interesting feature of the structure is the mode of coordination of the CO fragment of the  $\text{COCH}_2\text{Ph}$  ligand. Spectroscopic studies [4] have been unable to distinguish between coordination to the second Os atom via an oxygen lone pair of electrons or through the C—O  $\pi$ -electrons. This structure shows that O(1) bonds to Os(2) via the lone pair on the oxygen and the C—O bond length of 1.26(2) Å is close to the expected double-bond value. A similar mode of coordination of a COR ligand has been observed in the structures of  $[\text{Fe}(\text{CO})_3\text{COPh}]_2$  [6] and  $[(\eta\text{-C}_5\text{H}_5)\text{Ir}-\mu\text{-(COPh)}-\mu\text{-(COMe)}-\mu\text{-(PPh}_2\text{)}\text{Mn}(\text{CO})_3]$  [7]. It is probable that the NHCOR ligands in the analogous amides also coordinate via the oxygen lone pair.

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