

### Preliminary communication

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## REACTIONS OF TRIOSMIUM CLUSTERS WITH ORGANIC AZIDES; X-RAY CRYSTAL STRUCTURES OF $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})(\text{N}_3\text{COPh})]$ , $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{HN}_3\text{Ph})]$ , AND $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-NPh})]$

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### Summary

Organic azides  $[\text{N}_3\text{R}]$  react with  $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$  and with  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  to form  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})(\text{N}_3\text{COR})]$  ( $\text{R} = \text{Ph}$ ) and  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{HN}_3\text{R})]$  ( $\text{R} = \text{Ph}, n\text{-Bu}, \text{CH}_2\text{Ph}, \text{cyclo-C}_6\text{H}_{11}$ ), respectively; the latter may be converted to  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-NR})]$  by thermolysis; the molecular structure of the phenyl derivative of each class of compound has been confirmed by X-ray analysis.

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It has been shown that the cluster  $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$  readily loses the NCMe group to provide a vacant coordination site [1] while  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  behaves as if it contains an Os—Os multiple bond [2]. Both these complexes are susceptible to attack by molecules capable of donating electrons to the cluster and occupying the vacant coordination site. Diazo compounds  $\text{N}_2\text{CHR}$  ( $\text{R} = \text{H}, \text{Me}, \text{CO}_2\text{Et}$ ) and 4-methylsulphonyl azide evolve dinitrogen with  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  to give the bridged species  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-CH}_2\text{R})]$  [3–5] and  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-NHSO}_2\text{C}_6\text{H}_4\text{Me})]$  respectively [6]. The nature of these reactions is sensitive to the diazo compounds employed, thus with diazo compounds  $\text{N}_2\text{CR}^1\text{R}^2$  ( $\text{R}^1 = \text{R}^2 = \text{Ph}$ ;  $\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Me}$ ;  $\text{R}^1 = \text{Ph}, \text{R}^2 = \text{H}$ ;  $\text{R}^1 = \text{R}^2 = \text{Me}$ ) and with  $[(p\text{-tol})\text{N}_2]^+$  dinitrogen is retained and bridged species of the type  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-NHNCR}^1\text{R}^2)]$  [7] and  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-NN})(p\text{-tol})]$  [8], are obtained. Here we report a comparative study with a series of azide species, the reactions of  $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$  and  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  with organic azides, are considered.

The room temperature reaction between  $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$  and  $[\text{N}_3\text{Ph}]$  in  $\text{CH}_2\text{Cl}_2$  gave a yellow product (I) which was purified by TLC (yield 40%). The complex exhibited IR active bands at 2102w, 2070s, 2039m, 2021s, 2008m, 2001m, 1995m, 1977w, 1727w(br), 1663w(br) and a  $m/e$  of 1044

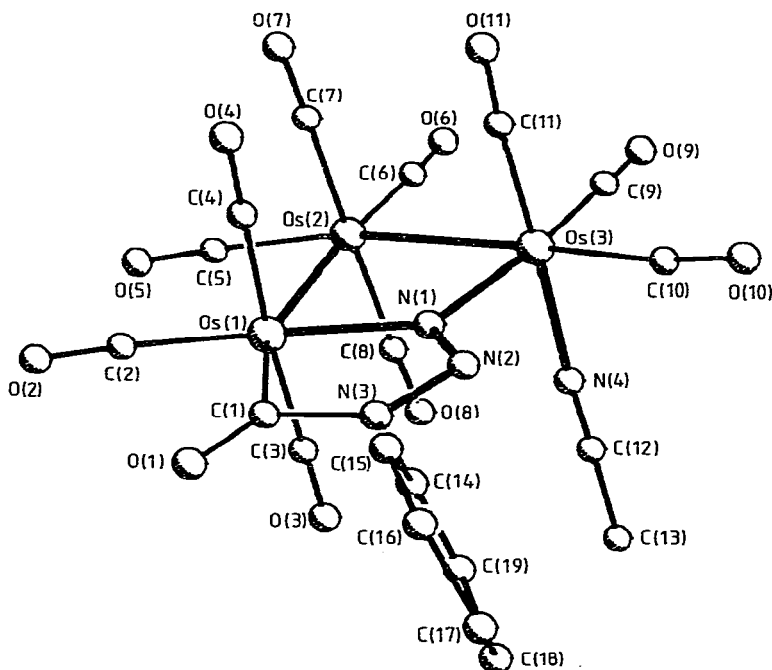


Fig. 1. The molecular structure of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})(\text{N}_3\text{COPh})]$  (I). Bond lengths: Os(1)—Os(2), 2.943(1); Os(2)—Os(3), 2.937(1); Os(1)—N(1), 2.084(10); Os(3)—N(1), 2.128(12); Os(1)—C(1), 2.048(17); N(1)—N(2), 1.24(2); N(2)—N(3), 1.38(2); N(3)—C(1), 1.42(2); C(1)—O(1), 1.22(2); Os(3)—N(4), 2.083(15) Å. Bond angles: Os(1)—Os(2)—Os(3), 75.8(1); Os(1)—N(1)—Os(3), 121.3(10); N(1)—N(2)—N(3), 110.6(11); N(2)—N(3)—C(1), 122.1(13); Os(1)—C(1)—N(3), 109.0(11); Os(1)—C(1)—O(1), 132.5(1.1)°.

(based on  $^{192}\text{Os}$ ). The  $^1\text{H}$  NMR spectrum showed resonances at  $\delta$  7.34m and 2.64s ppm ( $\text{CD}_2\text{Cl}_2$ ) indicating the presence of a phenyl ring and suggesting that the NCMe group had been retained. In order to elucidate the structure a single crystal X-ray analysis was undertaken\*.

The molecular structure of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})(\text{N}_3\text{COPh})]$  (I) is shown in Fig. 1 together with some important bond parameters. One edge of the  $\text{Os}_3$  triangular arrangement observed in  $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$  [9] has been lengthened so as to be non-bonding [ $\text{Os}(1)\cdots\text{Os}(3)$  3.612(2) Å], and is symmetrically bridged by one of the terminal N atoms, N(1), of the azide. The N atom of the azide bound to the phenyl ring, N(3), has coordinated to C(1), the carbon atom of an equatorial carbonyl ligand on Os(1). The Os(1), Os(3), N(1), N(2), N(3), C(1), O(1) unit is essentially planar. The N(1)—N(2) bond length is significantly shorter than the N(2)—N(3) distance which may indicate that the bonding within the ligand in this complex is not very different from a resonance hybrid of the type  $\text{N}\equiv\text{N}^+-\text{NR}^-$  in the free ligand. If this is the case the formation of the N—C bond with C(1) may be explained in terms of an nucleophilic attack on the carbonyl group by the azide N atom carrying

\*Crystal data:  $\text{C}_{19}\text{H}_8\text{N}_4\text{O}_{11}\text{Os}_3$ ,  $M = 1038.89$ , triclinic  $P\bar{1}$ ,  $a$  9.029(3),  $b$  12.720(5),  $c$  13.433(5) Å,  $\alpha$  102.69(2),  $\beta$  102.52(2),  $\gamma$  104.75(2)°,  $U$  1393.4 Å<sup>3</sup>,  $Z = 2$ ,  $D_c$  2.48 g cm<sup>-3</sup>,  $F(000) = 932$ , Mo- $K_\alpha$  radiation ( $\lambda$  0.710 69 Å),  $\mu(\text{Mo-}K_\alpha)$  136.89 cm<sup>-1</sup>. 3739 unique observed diffractometer data [ $F > 3\sigma(F)$ ],  $R = 0.057$ ,  $R_w = 0.058$ . Unresolved disordered solvent molecule also present.

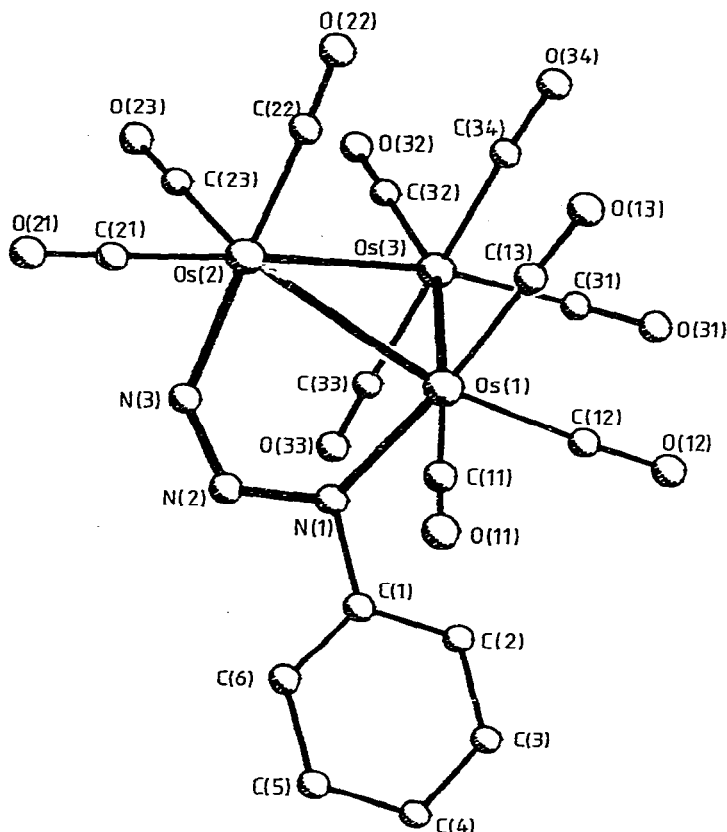


Fig. 2. The molecular structure of  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{HN}_3\text{Ph})]$  (II). Bond lengths: Os(1)—Os(2), 2.900(1); Os(1)—Os(3), 2.888(1); Os(2)—Os(3), 2.900(1); Os(1)—N(1), 2.137(10); Os(2)—N(3), 2.110(10); N(1)—N(2), 1.32(2); N(2)—N(3), 1.29(2); N(1)—C(1), 1.45(1) Å. Bond angles: Os(2)—Os(1)—Os(3), 60.1(1); Os(1)—Os(2)—Os(3), 59.7(1); Os(1)—Os(3)—Os(2), 60.1(1); Os(1)—N(1)—N(2), 128.6(8); N(1)—N(2)—N(3), 117.5(10); Os(2)—N(3)—N(2), 131.3(8)°.

the partial negative charge [10]. The NCMe group has not been displaced in the reaction and occupies an axial site on Os(3).

Reaction of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  with  $[\text{N}_3\text{R}]$  in hexane for 24 h leads to the formation of complexes  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{HN}_3\text{R})]$  (II, R = Ph; III, R = n-Bu; IV, R =  $\text{CH}_2\text{Ph}$ ; V, R = cyclo- $\text{C}_6\text{H}_{11}$ ). The products were purified by TLC (yields 43–81%) and obtained as yellow crystalline solids. They were characterised by analytical and spectroscopic techniques\* and the molecular structure of II was established from an X-ray analysis\*\*.

The structure of II is illustrated in Fig. 2 which includes some bond param-

\*Analysis to within 0.40% of the required values for C, H and N. The appropriate molecular ions was observed in the mass spectra of each of these compounds. PMR spectra for these compounds ( $\delta$  (ppm,  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$ , 20°C)) showed the following signals: N—H, 8.35 ± 0.34; Os—H, -12.68 ± 0.18; and signals appropriate to the function R. The carbonyl IR spectra of compounds II–V were nearly identical; the phenyl compound I in hexane solution, for instance, gave absorptions at 2110w, 2069s, 2061s, 2047w, 2026s, 2015s, 2010(sh), 2001m, 1990w, and 1975w  $\text{cm}^{-1}$ .

\*\*Crystal data:  $\text{C}_{16}\text{H}_7\text{N}_3\text{O}_{10}\text{Os}_3$ ,  $M = 971.85$ , monoclinic,  $P2_1/c$ ,  $a$  9.665(3),  $b$  8.823(4),  $c$  25.571(14) Å;  $\beta$  100.17(4)°,  $U$  2 146.3 Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  3.01  $\text{g cm}^{-3}$ ,  $F(000) = 1727$ , Mo- $K_\alpha$  radiation ( $\lambda$  0.71069 Å),  $\mu(\text{Mo-}K_\alpha)$  177.63  $\text{cm}^{-1}$ . 3 155 unique observed diffractometer data [ $F > 3\sigma(F)$ ],  $R = 0.042$ ,  $R_w = 0.042$ .

eters. The Os atoms define an equilateral triangle, one edge of which is bridged by the azide ligand. The two coordinated N atoms, N(1) and N(3), occupy axial coordination sites on the same side of the Os<sub>3</sub> triangle. The two N—N distances, N(1)—N(2) and N(2)—N(3), are equivalent indicative of some delocalisation of electron density over the whole azide unit. The hydride was not located directly but the equatorial carbonyl groups adjacent to the bridged Os(1)—Os(2) edge bend away from it (average *cis*-Os—Os—C 118°). This indicates that the hydride also bridges this edge and lies in the plane of the metals. Symmetrically bridging triazine ligands have been reported previously in the cluster [Cu<sub>4</sub>(MeN<sub>3</sub>Me)<sub>4</sub>] [11].

The triazine clusters II—V decompose in refluxing DME after 24 h to give the complexes [Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-NR)] (VI, R = Ph; VII, R = n-Bu; VIII, R = CH<sub>2</sub>Ph; IX, R = cyclo-C<sub>6</sub>H<sub>11</sub>) in high yield (62—38%). The phenyl derivative VI [12] and a methyl analogue [13] are known. The spectroscopic data for these clusters is in close agreement with the values reported for the phenyl derivative [12]. The molecular geometry of VI was confirmed by a single

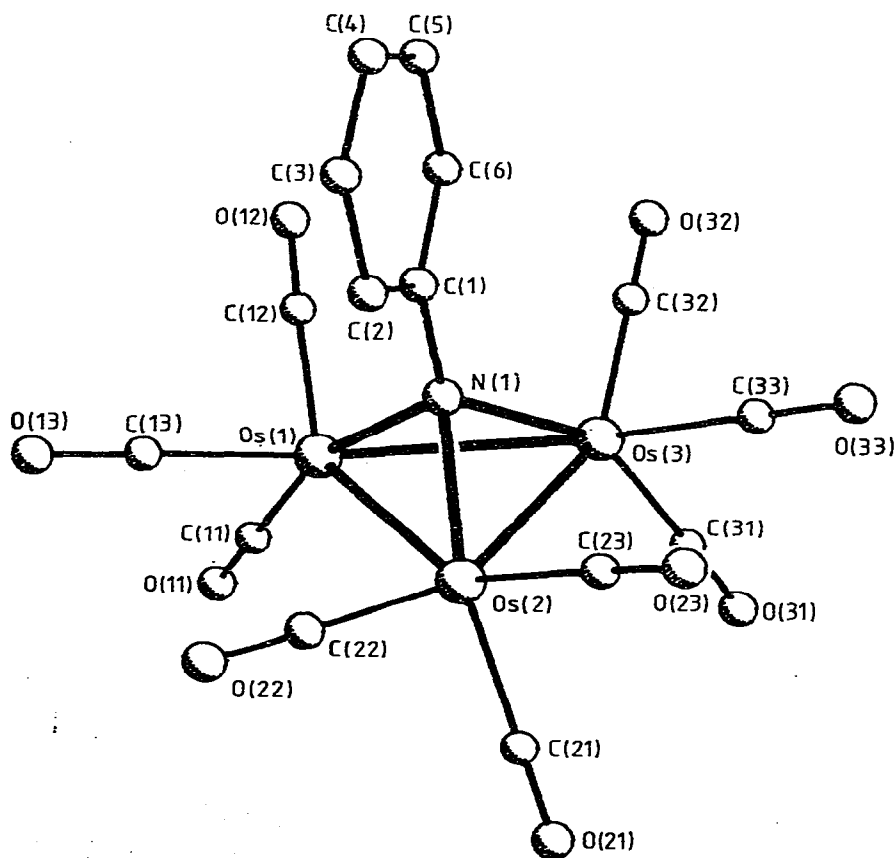


Fig. 3. The molecular structure of [Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-NPh)] (VI). Bond lengths: Os(1)—Os(2), 2.848(1); Os(1)—Os(3), 2.846(1); Os(2)—Os(3), 2.715(1); Os(1)—N(1), 2.099(8); Os(2)—N(1), 2.074(8); Os(3)—N(1), 2.078(9); N(1)—C(1), 1.448(12) Å. Bond angles: Os(2)—Os(1)—Os(3), 57.0(1); Os(1)—Os(2)—Os(3), 61.5(1); Os(1)—Os(3)—Os(2), 61.6(1); Os(1)—N(1)—Os(2), 86.1(3); Os(1)—N(1)—Os(3), 85.9(3); Os(2)—N(1)—Os(3), 81.7(3)°.

crystal X-ray analysis\*. The structure of VI is shown in Fig. 3 together with some bond parameters. The Os atoms lie at the vertices of an isosceles triangle, the two longer edges of which are bridged by the hydride ligands (from the distribution of the carbonyl ligands). The N atom symmetrically caps the metal triangle. The bond parameters are very similar to those recently reported for the methyl analogue [13].

The reactions of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  with primary, secondary, or aryl azides seems to be a general means of synthesizing the corresponding nitrogen-capped clusters in good yield, and is restricted only by the hazards involved in preparing the lower aliphatic azides.

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\*Crystal data:  $\text{C}_{15}\text{H}_7\text{NO}_9\text{Os}_3$ ,  $M = 915.82$ , monoclinic  $P2_1/c$ ,  $a$  11.630(4),  $b$  9.217(4),  $c$  18.527(7) Å,  $\beta$  99.71(2)°,  $U$  1 957.5 Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  3.11 g cm<sup>-3</sup>,  $F(000) = 1$  611, Mo- $K_\alpha$  radiation ( $\lambda$  0.71069 Å),  $\mu(\text{Mo-}K_\alpha) = 194.64$  cm<sup>-1</sup>. 2 861 unique observed diffractometer data [ $F > 4\sigma(F)$ ],  $R = 0.033$ ,  $R_w = 0.034$ .