Reaction of $[Os_4(CO)_{12}H_3]^-$ with $[NO][PF_6]$ in the Presence of Trace Amounts of Water; *X*-Ray Determination of the Molecular Structures of $[Os_4(CO)_{12}H_3(\mu\text{-}OPO_3H_2)]$ and $[Os_4(CO)_{12}H_3(\mu\text{-}OH)]$ (2:1 ratio) in the one Crystal †

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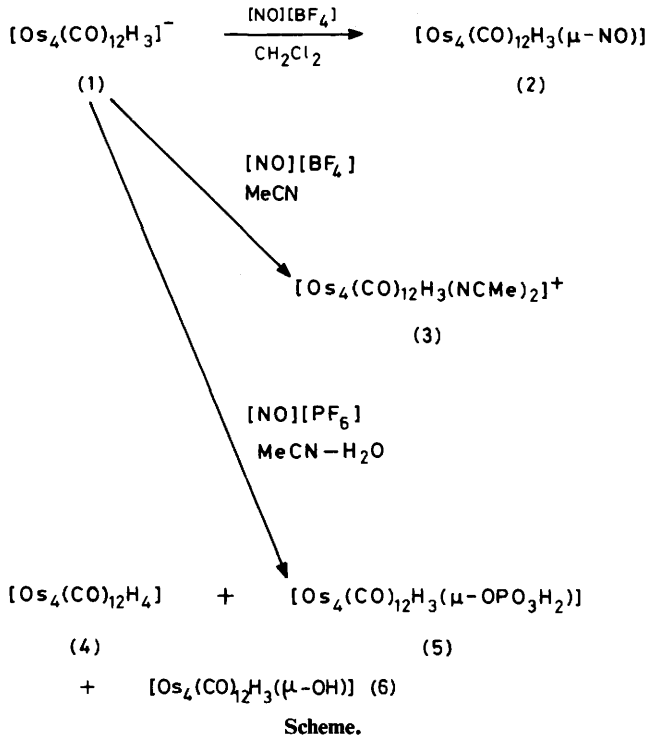
The cluster anion $[Os_4(CO)_{12}H_3]^-$ reacts with commercial $[NO][PF_6]$ in acetonitrile *via* the *in situ* formation of orthophosphoric acid to give the neutral cluster species, $[Os_4(CO)_{12}H_4]$, $[Os_4(CO)_{12}H_3(\mu\text{-}OPO_3H_2)]$, and $[Os_4(CO)_{12}H_3(\mu\text{-}OH)]$. The latter two products crystallise together in a 2:1 ratio in the monoclinic space group $P2_1/c$ with unit-cell dimensions a = 14.315(3), b = 30.732(4), c = 15.314(3) Å, β = 101.48(2)°, and Z = 4. The structure was solved by a combination of direct methods and Fourier-difference techniques and refined by blocked full-matrix least squares to R = 0.051 for 5 091 observed reflections. In each of the $\mu\text{-}OPO_3H_2$ and μ-OH compounds the four osmium atoms define a 'butterfly' configuration with two triangles sharing a common edge but which are not coplanar, supported by the bridging oxygen linkage. The three hydrido-ligands were not located but the Os–Os bond lengths suggest that they bridge in the same arrangement as that found previously in $[Os_4(CO)_{12}H_3I]$ by neutron diffraction.

Some reactions of the anionic carbonyl cluster $[Os_4(CO)_{12}H_3]^-$ (1) with $[NO]^+$ have previously been described. The work established that, depending on the reaction conditions, either the nitrosyl derivative $[Os_4(CO)_{12}H_3(\mu\text{-}NO)]$ (2) [1] or the oxidation product $[Os_4(CO)_{12}H_3(NCMe)_2]^+$ (3) [2] can be obtained. In both cases the importance of using freshly sublimed nitrosonium salts and dried solvents was emphasised. We report here the reaction of (1) with $[NO]^+$ when a trace amount of water is present in the reaction system.

Results and Discussion

During the early stages of our investigation of the reaction of $[N(PPh_3)_2][Os_4(CO)_{12}H_3]$ [3] with the nitrosonium ion, the reaction was carried out using $[NO][PF_6]$ as purchased, in non-dried AnalaR grade acetonitrile. This reaction gave an off-white precipitate as the major product which was shown to be $[Os_4(CO)_{12}H_4]$ (4) [4] by i.r. and mass spectrometry. A second yellow product was extracted from the filtrate in 1% yield. The i.r. spectrum of this material showed a more complicated pattern of CO bands than that expected for a tetraosmium cluster. The mass spectrum was also complex, with a high mass peak at m/z 1 204 (^{192}Os). Yellow air-stable crystals were obtained from dichloromethane and a single-crystal structure analysis showed the material to be $[Os_4(CO)_{12}H_3(\mu\text{-}OPO_3H_2)]$ (5) and $[Os_4(CO)_{12}H_3(\mu\text{-}OH)]$ (6) which had crystallised together in a 2 : 1 ratio. In addition there was a second independent molecule of the phosphate derivative (5). The overall reaction is depicted in the Scheme. The ν(CO) i.r. spectrum of the yellow complex [of (5) and (6)] was interpreted with the bands at 2 090s, 2 068vs, 2 018s(sh) cm^{-1} being attributed to (5) and bands at 2 080s, 2 061vs, 2 011s, br cm^{-1} attributed to (6) by comparison with the spectrum of (6) obtained by an alternative route.[5]



Scheme.

The molecular structure of the phosphate derivative (5) is shown in Figure 1 and that of the hydroxy complex (6) in Figure 2. Both (5) and (6) have the 'butterfly' Os_4 metal arrangement similar to that found in the structures of (2),[1] (3),[2] $[Os_4(CO)_{12}H_3I]$ (7),[6,7] and $[Os_4(CO)_{12}H_4(OH)]^+$ (8),[5] as predicted for a 62-electron system.[8] A comparison of selected bond distances is shown in Table 1. The molecular

† 1,4-μ-Dihydrogenphosphato-tri-μ-hydrido- and tri-μ-hydrido-1,4-μ-hydroxo-*cyclo*-tetrakis[tricarbonylosmium(I)](5 *Os–Os*).

Supplementary data available (No. SUP 23572, 43 pp.): structure factors, thermal parameters, bond lengths, bond angles for both complexes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Selected interatomic distances (Å) for (5) and (6), together with a comparison of the corresponding Os_4Y geometry for compounds (2), (3), (7), and (8)

	(5; Y = OPO_3H_2)							
	Molecule 1 $x = 1$	Molecule 2 $x = 2$	(6; Y = OH) $x = 3$	(2; Y = NO)	(3) (unsupported Os_4)	(7; Y = I) X-Ray	Neutron	(8; Y = OH)
Os(1x)–Os(2x)	2.972(2)	2.995(2)	2.969(2)	3.010(5)	3.130(1)	3.052(1)	3.055(1)	3.045(2)
Os(1x)–Os(3x)	2.830(2)	2.831(2)	2.826(2)	2.856(5)	2.828(1)	2.876(1)	2.877(1)	3.025(2)
Os(1x) · · · Os(4x)	3.483(2)	3.491(2)	3.475(2)	3.497(4)		3.817(1)		3.537(2)
Os(2x)–Os(3x)	2.940(2)	2.955(2)	2.952(2)	2.960(5)	2.937(1)	2.927(4)	2.927(2)	2.831(2)
Os(2x)–Os(4x)	2.839(2)	2.831(2)	2.841(2)	2.849(5)	2.847(1)	2.876(1)	2.877(1)	3.033(2)
Os(3x)–Os(4x)	3.002(2)	2.992(2)	2.997(2)	3.019(5)	3.145(1)	3.052(1)	3.055(1)	3.048(2)
Os(1x)–Y(x1)	2.136(20)	2.219(24)	2.151(20)	2.100(15)		2.749(4)	2.751(2)	2.080(7)
Os(4x)–Y(x1)	2.156(20)	2.153(24)	2.193(18)	2.100(20)		2.749(4)	2.751(2)	2.102(6)

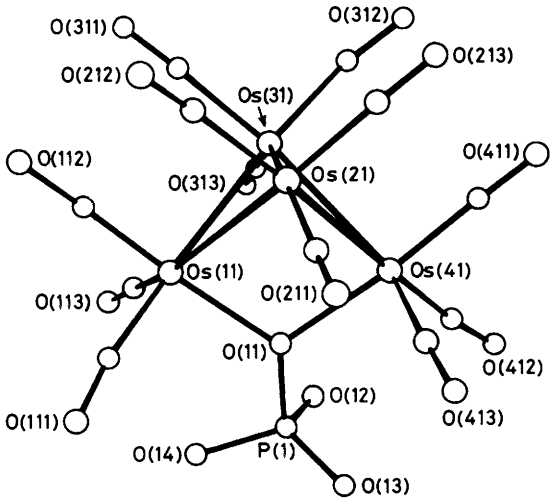


Figure 1. Molecular structure of $[Os_4(CO)_{12}H_3(\mu\text{-}OPO_3H_2)]$ (5), molecule 1. Average Os–C bond lengths are 1.86(3) [1.88(4)] Å (values for molecule 2 are given in square brackets), average C–O 1.18(4) [1.17(5)] Å, and average Os–C–O 172(2) [172(2)]°. The P–O bond lengths are O(x1) 1.60(2) [1.54(2)], O(x2) 1.52(2) [1.57(3)], O(x3) 1.45(2) [1.46(2)], and O(x4) 1.55(2) [1.46(2)] Å

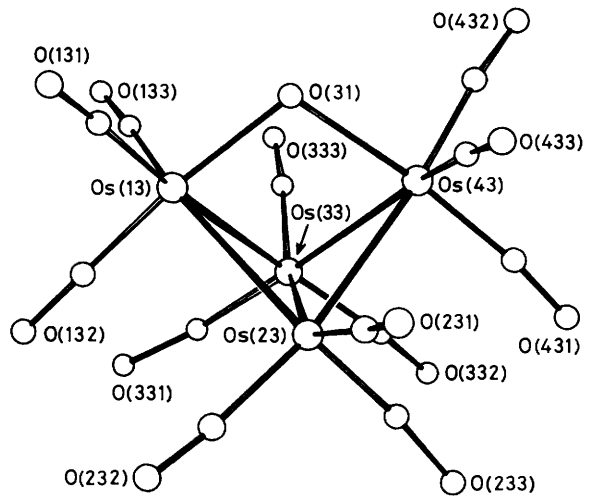


Figure 2. Molecular structure of $[Os_4(CO)_{12}H_3(\mu\text{-}OH)]$ (6). Average Os–C bond length is 1.87(3) Å and average C–O 1.18(5) Å, average Os–C–O, 173(2)°

geometries of (5) and (6) are essentially the same as that reported for other Os_4 butterfly complexes and detailed tables of bond lengths and angles are contained in the supplementary material.

In the phosphate (5) and the hydroxy compound (6) the two Os triangles are joined by the Os(2)–Os(3) ' hinge ' bond and the dihedral angle between the Os(1)Os(2)Os(3) and Os(2)Os(3)Os(4) planes is 92.5[92.2]° [for molecules 1 and 2 of (5) respectively] and 92.5° for (6). These angles are the same as that found (93°) for $[Os_4(CO)_{12}H_3(\mu\text{-}NO)]$ (2).[1] In the phosphate complex the two wing-tip Os atoms Os(1) and Os(4) are bonded to an oxygen atom of the phosphate ligand and to one axial and two equatorial carbonyl groups. The hinge Os atoms each have three terminal carbonyls associated with them. The Os(1x)–O(x1)–Os(4x) bridging angles are 109(1), 105(1), and 106(1)° for molecules 1 and 2 of (5), and for (6) respectively (see Figures for the numbering scheme used).

The Os–Os bond lengths in compounds (5) and (6) show the same pattern of Os(1)–Os(3), Os(2)–Os(4) short (2.826—2.841 Å, see Table 1) and Os(1)–Os(2), Os(2)–Os(3), Os(3)–Os(4) long (2.940—3.002 Å) distances as found for the structures of (2), (3), and (7). This suggests that all five complexes [(2), (3), and (5)—(7)] have the same hydride distribution, bridging the three longer Os–Os edges as confirmed by a neutron diffraction study for (7).[7] The tetrahydride (8) adopts a different hydride distribution in which the hinge bond is unbridged.[5]

The presence of the phosphate ligand may be attributed to the hydrolysis of hexafluorophosphoric acid (present as an impurity in the $[NO][PF_6]$) due to the presence of water; fluorophosphoric acid interconverts with relative ease to orthophosphoric acid in the presence of water.[9] The formation of (5) may involve the intermediate formation of the cation (3) which could then react with either H_2O or H_3PO_4 to yield the hydroxide (6) or the phosphate (5) respectively. Previously[5] the hydroxy-bridged complex (6) has been reported to be formed by treatment of N_2O_4 with $[Os_4(CO)_{12}H_4]$ (4) where the source of water was thought to arise from the reduction of CO. However we now believe that the water is present in trace amounts in all commercial sources of ' NO ' in these types of reactions and only the rigorous exclusion of water can be expected to give the desired N-containing products.

Experimental

The reaction was carried out under an atmosphere of nitrogen, however the products were stable in air in the solid state. Acetonitrile (AnalaR grade) and $[NO][PF_6]$ were used as purchased.

The salt $[N(PPh_3)_2][Os_4(CO)_{12}H_3]$ (250 mg, 0.15 mmol) was dissolved in acetonitrile and a solution of $[NO][PF_6]$ (53 mg,

Table 2. Fractional atomic co-ordinates for (5) and (6)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Os(11)	0.354 31(10)	0.278 94(5)	0.301 93(11)	O(121)	0.113 0(19)	−0.108 0(10)	0.307 0(19)
Os(21)	0.265 24(9)	0.353 91(4)	0.193 90(8)	C(122)	0.040 7(21)	0.007 6(10)	0.314 6(20)
Os(31)	0.367 35(10)	0.362 86(5)	0.379 57(9)	O(122)	−0.036 2(21)	0.012 0(10)	0.327 9(20)
Os(41)	0.159 03(9)	0.341 17(4)	0.329 84(9)	C(123)	0.202 4(26)	−0.019 3(13)	0.447 1(28)
Os(12)	0.169 91(10)	−0.014 61(5)	0.323 88(10)	O(123)	0.209 9(15)	−0.023 3(8)	0.525 6(16)
Os(22)	0.229 91(11)	−0.020 64(5)	0.147 70(10)	C(221)	0.314 0(31)	−0.028 7(15)	0.075 8(31)
Os(32)	0.359 54(10)	−0.039 10(5)	0.319 32(10)	O(221)	0.367 5(18)	−0.036 4(9)	0.023 8(18)
Os(42)	0.332 04(9)	0.050 01(5)	0.239 60(10)	C(222)	0.156 9(34)	−0.072 5(17)	0.115 2(34)
Os(13)	−0.129 14(9)	0.152 51(5)	0.396 97(9)	O(222)	0.111 6(25)	−0.101 2(13)	0.089 6(26)
Os(23)	−0.234 70(9)	0.118 74(5)	0.223 58(10)	C(223)	0.157 3(29)	0.014 2(14)	0.060 0(29)
Os(33)	−0.224 62(10)	0.212 15(5)	0.269 31(10)	O(223)	0.107 4(19)	0.036 6(9)	0.007 5(19)
Os(43)	−0.078 15(9)	0.167 17(5)	0.186 39(9)	C(321)	0.398 3(28)	−0.038 1(14)	0.443 3(30)
P(1)	0.180 2(5)	0.238 5(2)	0.396 4(6)	O(321)	0.422 6(19)	−0.030 0(9)	0.519 5(20)
P(2)	0.188 1(6)	0.091 8(3)	0.365 6(7)	C(322)	0.484 9(32)	−0.044 6(15)	0.291 8(29)
O(11)	0.220 6(12)	0.276 9(6)	0.343 7(12)	O(322)	0.561 1(20)	−0.046 9(9)	0.284 0(19)
O(12)	0.200 4(13)	0.256 6(7)	0.490 4(13)	C(323)	0.340 7(24)	−0.098 0(13)	0.331 6(25)
O(13)	0.078 8(13)	0.230 3(6)	0.367 9(13)	O(323)	0.326 4(21)	−0.136 6(11)	0.339 1(21)
O(14)	0.250 5(18)	0.199 7(9)	0.401 4(18)	C(421)	0.403 9(28)	0.095 5(15)	0.313 5(28)
C(111)	0.337 7(27)	0.226 8(14)	0.239 6(28)	O(421)	0.455 1(21)	0.119 2(11)	0.352 3(21)
O(111)	0.317 8(22)	0.191 9(12)	0.207 3(23)	C(422)	0.428 9(25)	0.043 6(12)	0.177 7(25)
C(112)	0.464 6(28)	0.284 3(14)	0.270 9(28)	O(422)	0.489 0(20)	0.038 3(10)	0.127 3(21)
O(112)	0.533 7(21)	0.287 6(10)	0.224 3(21)	C(423)	0.266 8(32)	0.088 1(16)	0.143 8(33)
C(113)	0.419 3(26)	0.256 6(13)	0.413 4(28)	O(423)	0.228 2(20)	0.112 2(10)	0.095 2(20)
O(113)	0.458 5(20)	0.240 1(11)	0.476 3(21)	O(31)	−0.013 3(12)	0.161 2(6)	0.328 2(12)
C(211)	0.167 3(20)	0.334 1(10)	0.103 1(21)	C(131)	−0.057 1(24)	0.110 4(13)	0.475 9(25)
O(211)	0.107 3(16)	0.322 8(7)	0.044 0(16)	O(131)	−0.017 3(19)	0.086 5(10)	0.526 1(19)
C(212)	0.362 1(23)	0.359 8(12)	0.118 8(23)	C(132)	−0.231 1(31)	0.139 4(15)	0.444 3(30)
O(212)	0.413 3(18)	0.361 2(9)	0.076 9(18)	O(132)	−0.302 4(19)	0.136 3(9)	0.475 3(19)
C(213)	0.220 5(31)	0.411 2(17)	0.167 8(31)	C(133)	−0.096 9(23)	0.203 3(12)	0.467 2(24)
O(213)	0.193 1(18)	0.446 6(10)	0.160 2(18)	O(133)	−0.078 7(20)	0.230 8(10)	0.511 7(21)
C(311)	0.497 5(26)	0.371 0(12)	0.365 7(24)	C(231)	−0.187 8(27)	0.067 4(14)	0.17 72(27)
O(311)	0.571 2(22)	0.373 8(10)	0.356 2(21)	O(231)	−0.155 8(19)	0.033 6(10)	0.151 7(20)
C(312)	0.359 3(33)	0.422 7(18)	0.423 9(35)	C(232)	−0.327 7(35)	0.084 3(18)	0.271 2(36)
O(312)	0.333 3(28)	0.457 9(15)	0.429 2(29)	O(232)	−0.380 2(22)	0.066 2(11)	0.306 8(22)
C(313)	0.399 1(34)	0.346 1(17)	0.477 8(37)	C(233)	−0.304 4(27)	0.125 6(13)	0.118 0(28)
O(313)	0.430 1(22)	0.333 7(11)	0.566 2(24)	O(233)	−0.364 3(23)	0.130 8(11)	0.045 1(25)
C(411)	0.116 4(23)	0.397 5(12)	0.315 8(23)	C(331)	−0.312 8(31)	0.219 9(15)	0.331 6(31)
O(411)	0.086 9(17)	0.432 8(9)	0.308 5(17)	O(331)	−0.374 6(21)	0.228 9(10)	0.388 5(21)
C(412)	0.098 0(25)	0.334 9(13)	0.430 1(26)	C(332)	−0.285 9(27)	0.237 8(14)	0.161 7(28)
O(412)	0.055 8(15)	0.334 6(8)	0.485 7(16)	O(332)	−0.330 1(20)	0.255 7(11)	0.102 0(21)
C(413)	0.056 2(21)	0.321 7(10)	0.239 9(21)	C(333)	−0.159 6(27)	0.267 7(14)	0.311 9(27)
O(413)	−0.010 6(16)	0.310 1(8)	0.190 8(15)	O(333)	−0.121 8(20)	0.297 0(11)	0.341 7(21)
O(21)	0.220 3(15)	0.053 2(7)	0.315 0(15)	C(431)	−0.144 5(23)	0.173 6(11)	0.071 9(24)
O(22)	0.230 9(22)	0.134 3(11)	0.332 6(22)	O(431)	−0.196 6(18)	0.180 5(9)	0.003 7(19)
O(23)	0.086 0(16)	0.095 0(8)	0.357 6(16)	C(432)	0.024 1(21)	0.202 4(10)	0.173 7(20)
O(24)	0.232 3(17)	0.084 1(9)	0.458 5(19)	O(432)	0.086 7(18)	0.225 2(9)	0.158 3(18)
C(121)	0.130 9(30)	−0.071 1(16)	0.321 0(30)	C(433)	−0.017 5(31)	0.115 8(16)	0.154 3(31)
				O(433)	0.014 9(20)	0.085 3(11)	0.129 8(20)

0.46 mmol) dissolved in acetonitrile added. The solution was stirred for 1 h during which time $[Os_4(CO)_{12}H_4]$ (4) separated. The solvent was evaporated to dryness and thin-layer chromatography using a 70 : 30 CH_2Cl_2-tetrahydrofuran mixture as eluant gave a yellow-green band which was extracted with tetrahydrofuran. Yellow crystals of this material were obtained by slow evaporation from a dichloromethane solution.

X-Ray Structural Analysis.—Crystal data. $2(C_{12}H_5O_{16}Os_4P)\cdot(C_{12}H_4O_{13}Os_4)$, $M = 3\,510.83$, Monoclinic, $a = 14.315(3)$, $b = 30.732(4)$, $c = 15.314(3)$ Å, $\beta = 101.48(3)°$, $U = 6\,602.33$ Å^3, $D_c = 3.531$ g cm^{-1}, $Z = 4$, $F(000) = 6\,128$, μ(Mo-K_α) = 222.34 cm^{-1}, Mo-K_α radiation, space group $P2_1/c$. 5 091 Reflections [$I \geqslant 3\sigma(I)$] were collected on a Philips PW1100 diffractomer in the range ($3 \leqslant \theta \leqslant 25°$) and were corrected for absorption using the azimuthal scan method.

The method of data collection was similar to that reported in previous publications [10] from these laboratories. The structure was solved by multi-solution Σ_2 sign expansion and Fourier-difference methods and refined by blocked full-matrix least squares to an R value of 0.051, $R' = 0.049$ with $w = 1/\sigma^2(F)$, using the SHELX system [11] of programs. Complex neutral-atom scattering factors were employed.[12] Table 2 lists the final atomic positional parameters.

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