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Reaction of pentafluoronitrosobenzene with $[Os_3H(\mu\text{-}H)(CO)_{10}(MPh_3)]$ ($M = P$, As, Sb): synthesis and X-ray structure of $[Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)(ONC_6F_4O)]$

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Abstract

The pentafluoronitrosobenzene C_6F_5NO has been shown from infrared spectral, ^{19}F NMR spectral and single-crystal X-ray diffraction studies to undergo oxidation at the *para*-position upon reaction with $[Os_3H(\mu\text{-}H)(CO)_{10}(PPh_3)]$ to afford $[Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)(ONC_6F_4O)]$(I). The arsenic- and stibine- analogues of I ($[Os_3(\mu\text{-}H)(CO)_{10}(MPh_3)(ONC_6F_4O)]$ (M = As, Sb)) were also isolated.

Key words: Osmium; Synthesis

1. Introduction

Reactions of pentafluoronitrosobenzene C_6F_5NO with $[Os_3(CO)_{12}]$ and $[Os_3(CO)_{11}(CH_3CN)]$ have been shown [1,2] to yield $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$ (**1**) and $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ (**2**) respectively. X-ray structural analysis studies have shown that the molecular structure of **1** comprises three osmium atoms capped by pentafluorophenylimido ligands above and below the Os_3 plane; two of the Os atoms are at a non-bonded distance of 3.367 Å. In the case of **2**, the pentafluorophenylnitroso ligand has been shown to adopt an unusual bonding mode, with its nitrogen bridging two non-bonded Os atoms and an oxygen atom bonded to one of the Os atoms.

We now report the reactions of C_6F_5NO with substituted triosmium cluster derivatives $[Os_3H(\mu\text{-}H)(CO)_{10}(MPh_3)]$($M = P$, As, Sb) which afforded novel clusters namely $[Os_3(\mu\text{-}H)(CO)_{10}(MPh_3)(ONC_6F_4O)]$, in each of which the *para*-carbon in the phenyl ring of C_6F_5NO has been oxidized to give the quinone-type structure. The molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)(ONC_6F_4O)]$ (I) has been determined by a single crystal X-ray diffraction study.

2. Results and discussion

Each of the yellow clusters $[Os_3H(\mu\text{-}H)(CO)_{10}MPh_3]$ ($M = P$, As, Sb) in dichloromethane reacts with pentafluoronitrosobenzene to give an orange brown solution. Thin layer chromatography (tlc) using 1:1 dichloromethane/hexane yielded an orange band as the major product. The compound obtained from the orange band resulting from the reaction of C_6F_5NO and $[Os_3H(\mu\text{-}H)(CO)_{10}PPh_3]$ was characterized as $\{Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)(ONC_6F_4O)\}$ (I) by X-ray crystallography (see structure of $[Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)(ONC_6F_4O)]$), indicating that the C_6F_5NO is oxidised at the *para*-position to afford the quinone-type structure. The clusters $[Os_3H(\mu\text{-}H)(CO)_{10}AsPh_3]$ and $[Os_3H(\mu\text{-}H)(CO)_{10}SbPh_3]$ have also been found to oxidise C_6F_5NO to afford the respective cluster derivatives $[Os_3(\mu\text{-}H)(CO)_{10}(AsPh_3)(ONC_6F_4O)]$ (II) and $[Os_3(\mu\text{-}H)(CO)_{10}(SbPh_3)(ONC_6F_4O)]$ (III).

The infrared absorptions of clusters I, II and III display carbonyl stretchings between 2116 and 1978 cm^{-1} (see Experimental section). However, no absorptions are observed at round 1500 cm^{-1}, suggesting unambiguously the absence of pentafluorophenyl ring. The band at 1657 cm^{-1} is assigned to the carbonyl stretching [3] of the ONC_6F_4O moiety. The band of medium intensity at 1327 cm^{-1} is assigned to C–F

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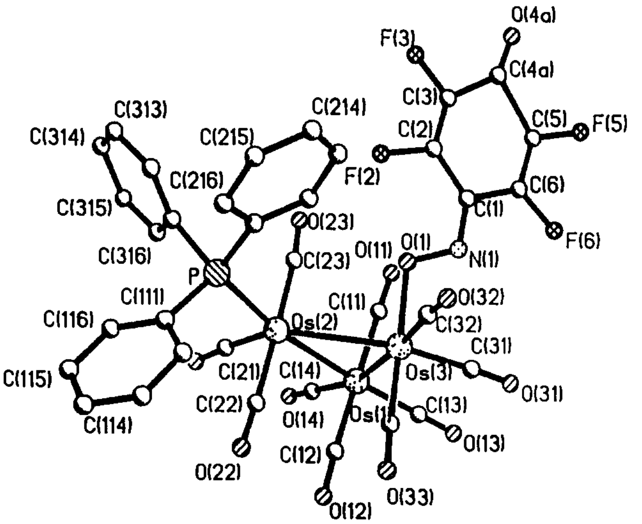

Fig. 1. An ORTEP drawing of [$Os_3(CO)_{10}(PPh_3)(ONC_6F_4O)$].

stretching as this falls within the range 1350–1150 cm^{-1} reported for C–F stretching of the C=C–F group [4] while the band at 976 cm^{-1} is attributed to N–O stretching.

Four sets of ^{19}F NMR resonance signals between δ 68–85 (see Experimental section) corresponding to the presence of four fluorines, are observed in each of the fluorine NMR spectra of I, II and III. A singlet was observed for ^{31}P NMR at δ −2.15 for I. The ^1H NMR spectrum of cluster I shows a doublet at δ −13.67 indicating the presence of a bridging hydride (J(P–H) = 11.76 Hz). The bridging hydride signals for clusters II and III are located at δ −13.81 and −14.20 respectively. The presence of a phenyl group is indicated in each case by the multiplet at δ *ca.* 7.5. No terminal hydride signal is observed.

TABLE 1. Atomic Coordinates ($\times 10^4$) and equivalent isotropic coefficients ($Å \times 10^3$) for **I**

	x	y	z	U_{eq}
Os(1)	1778(1)	303(1)	1652(1)	42(1)
Os(2)	1672(1)	2157(1)	2669(1)	38(1)
Os(3)	1653(1)	3210(1)	1298(1)	42(1)
P	1510(1)	3822(4)	3365(2)	42(1)
O(1)	1141(2)	2822(11)	1059(5)	57(4)
N(1)	993(3)	2736(16)	413(6)	67(5)
C(11)	1309(4)	0(16)	1255(7)	62(6)
C(12)	2236(3)	780(16)	2031(7)	54(6)
C(13)	1860(4)	−427(16)	866(8)	58(6)
C(14)	1828(4)	−1469(18)	2128(8)	64(7)
C(21)	1773(3)	602(17)	3261(7)	52(6)
C(22)	2131(3)	2723(14)	3008(7)	44(5)
C(23)	1209(4)	1556(15)	2350(6)	47(5)
C(31)	1662(4)	2691(17)	423(7)	56(6)
C(32)	1546(5)	5187(20)	1097(9)	72(7)
C(33)	2108(4)	3629(17)	1538(7)	55(6)
O(11)	1038(3)	−283(13)	1024(5)	75(5)
O(12)	2511(3)	1005(12)	2236(5)	68(5)
O(13)	1913(3)	−857(14)	401(6)	93(6)
O(14)	1849(3)	−2512(14)	2390(6)	86(6)
O(21)	1854(3)	−328(13)	3629(5)	76(5)
O(22)	2398(3)	3013(12)	3235(5)	68(5)
O(23)	946(3)	1217(12)	2224(5)	66(4)
O(31)	1679(3)	2351(14)	−78(5)	84(6)
O(32)	1496(3)	6302(14)	957(6)	92(6)
O(33)	2372(3)	3935(13)	1656(5)	72(5)
C(111)	1861(3)	4508(16)	4014(6)	48(5)
C(112)	2062(3)	5552(16)	3873(7)	53(6)
C(113)	2334(4)	5992(18)	4339(8)	68(7)
C(114)	2425(4)	5355(21)	4963(8)	75(7)
C(115)	2231(4)	4331(19)	5103(7)	69(7)
C(116)	1953(4)	3924(17)	4633(7)	60(6)
C(211)	1287(3)	5360(15)	2948(6)	48(5)
C(212)	1074(3)	5237(16)	2308(7)	54(6)
C(213)	880(4)	6371(20)	2003(8)	75(7)
C(214)	886(4)	7647(20)	2336(10)	74(8)
C(215)	1096(4)	7763(16)	2967(9)	65(7)
C(216)	1294(4)	6668(15)	3281(8)	63(7)
C(311)	1232(3)	3128(15)	3828(7)	47(5)
C(312)	1027(5)	4029(23)	4028(11)	111(11)
C(313)	842(6)	3495(28)	4430(12)	134(15)
C(314)	842(5)	2091(27)	4600(11)	106(11)
C(315)	1046(5)	1237(22)	4383(10)	95(19)
C(316)	1233(5)	1773(19)	4011(9)	82(9)
C(1)	680(4)	2728(22)	228(8)	85(8)
C(2)	446(5)	2913(36)	592(11)	146(16)
C(3)	127(7)	2767(65)	326(14)	281(33)
C(5)	198(6)	2376(42)	−747(11)	174(17)
F(2)	566(3)	3092(20)	1261(6)	164(9)
F(3)	−79(4)	3025(49)	691(11)	439(35)
F(5)	74(4)	2229(36)	−1380(8)	318(20)
F(6)	725(3)	2349(20)	−868(6)	153(8)
C(4A)	−165(33)	3732(143)	−257(71)	332(63)
C(4B)	−21(15)	2346(64)	−384(29)	121(17)
O(4A)	−326(9)	2871(42)	−581(18)	129(11)
O(4B)	−296(13)	1481(60)	−584(26)	218(20)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.1. *Structure of [$Os_3(\mu$-$H)(CO)_{10}(PPh_3)(ONC_6F_4O)$] (I)*

The molecular structure of I was determined by a single-crystal X-ray diffraction study and is shown in Fig. 1. The atomic coordinates and selected bond distances and angles are given in Tables 1 and 2 respectively. The osmium atoms form a triangular array with ten terminally bound carbon monoxide ligands with typical C–O bond lengths of 1.094–1.152 Å. The triphenylphosphine ligand assumes an equatorial site on Os(2) with the Os(2)–P bond distance found to be 2.375(4) Å, comparable to the Os–P bond length of 2.370(5) Å found in the parent cluster [$Os_3H(\mu$-$H)(CO)_{10}PPh_3$] [5]. The bridging hydride was not located crystallographically and was incorporated on the basis of electron count and NMR data. The hydride-

TABLE 2. Selected bond lengths (Å) and bond angles (°) for I

Os(1)–Os(2)	2.892(1)	Os(1)–C(11)	1.945(17)
Os(1)–Os(3)	2.844(1)	O(1)–N(1)	1.320(14)
Os(2)–Os(3)	3.021(1)	O(1)–C(1)	2.211(17)
Os(2)–P	2.375(4)	N(1)–C(1)	1.271(21)
Os(3)–O(1)	2.117(9)		
Os(2)–Os(1)–Os(3)	63.6(1)	Os(1)–Os(3)–O(1)	89.9(3)
Os(1)–Os(3)–Os(2)	59.0(1)	Os(2)–Os(3)–O(1)	85.0(3)
Os(1)–Os(2)–Os(3)	57.4(1)	Os(3)–O(1)–N(1)	113.8(9)
Os(1)–Os(2)–P	170.6(1)	O(1)–N(1)–C(1)	117.1(14)
Os(3)–Os(2)–P	115.9(1)		

bridged Os(2)–Os(3) distance (3.021(1) Å) is significantly longer than the non bridged Os(1)–Os(2) (2.891(1) Å) and Os(1)–Os(3) (2.844(1) Å) bonds.

In agreement with the ^{19}F NMR spectral data as well as the IR spectral data, the X-ray structural analysis shows the presence of four fluorine atoms. The fluorine at the *para*-position of the parent pentafluorophenyl ring has been replaced by an oxygen atom and the ring is no longer aromatic [6*]. The C(1)–N(1) bond of 1.27(2) Å is comparable with the CN double bond described in $[Os_3(\mu\text{-}H)(\mu\text{-}N{=}CHCF_3)(CO)_{10}]$ (1.271(8) Å) [7] and $[Os_3(\mu\text{-}H)(\mu\text{-}C{=}NH^tBu)(CO)_{10}]$ (1.298(10) Å) [8]. The O(1)–N(1) bond length of 1.320(14) Å is significantly longer than average N–O bond distances [9] in metal clusters containing nitrosyl ligand where the ligand is terminally bound [1.17(2) Å], doubly bridging [1.22(2) Å] and triply bridging [1.247(5) Å]. The C(2)–C(3) (1.31(4) Å) and C(5)–C(6) (1.35(3) Å) are shorter than the C–C single bond and typical of a C=C double bond (1.34 Å) [10].

3. Experimental section

C_6F_5NO was prepared as previously described [11] and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ as reported in the literature [12,13]. The infrared spectrum was recorded on a Perkin-Elmer 983G infrared spectrometer. ^{19}F NMR data were obtained on a Jeol FX90Q Fourier Transformation (90 MHz) NMR spectrometer. $CDCl_3$ was employed as the solvent and CF_3COOH as the internal standard. Elemental analyses for C and F were conducted by the Microanalytical Laboratory of the National University of Singapore.

3.1. Preparation of $[Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)(ONC_6F_4O)]$ (I)

$[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (58.2 mg, 66 μmol), triphenylphosphine (17.3 mg, 66 μmol) and freshly distilled CH_2Cl_2 (5 ml) were placed in a 100 ml 2-necked flask equipped with a nitrogen inlet and a bubbler. The reaction mixture was stirred in N_2 atmosphere and a yellow solution of $[Os_3H(\mu\text{-}H)(CO)_{10}PPh_3]$ resulted immediately.

Pentafluoronitrosobenzene (13.1 mg, 66.5 μmol) in 15 ml CH_2Cl_2 was added dropwise over 30 min to the yellow solution, whereupon the colour changed to orange. At the end of the addition, the orange brown solution was subjected to rotary evaporation and the residue TLC using 1:1 CH_2Cl_2: hexane as eluant yielding (I) as an orange band (R_f: 0.21; 61 mg). I displays carbonyl stretchings at 2116m, 2078m, 2065m, 2034vs, 2025m, 2017m, 2006w, 1996w, 1985w, 1978w and four ^{19}F NMR signals at 68.00(m), 69.21(m), 83.64(m), 84.47(m). Yield: *ca.* 7%. (Found: C, 31.25; H, 1.30; N, 1.09; F, 5.99; P, 2.36. Calcd. for $[Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)(ONC_6F_4O)]$: C, 31.20; H, 1.22; N, 1.07; F, 5.81; P, 2.37%).

3.2. Preparation of $[Os_3H(\mu\text{-}H)(CO)_{10}(AsPh_3)(ONC_6F_4O)]$ (II)

This is similar to that for the phosphine analogue except for the replacement of triphenylphosphine by triphenylarsine. II displays carbonyl stretchings at 2116m, 2078m, 2067m, 2034vs, 2025s, 2017m, 2005w, 1996w, 1985w, 1978w and four ^{19}F NMR signals at 68.11(m), 69.21(m), 83.75(m), 84.56(m). Yield: *ca.* 8%. (Found: C, 30.61; H, 1.20; N, 0.93; F, 5.43; As, 5.80. Calcd. for $[Os_3H(\mu\text{-}H)(CO)_{10}(AsPh_3)(ONC_6F_4O)]$: C, 30.19; H, 1.18; N, 1.04; F, 5.62; As, 5.55%).

3.3. Preparation of $[Os_3H(\mu\text{-}H)(CO)_{10}(SbPh_3)(ONC_6F_4O)]$ (III)

This preparation is similar to that for the phosphine analogue except for the replacement of triphenylphosphine by triphenylstibine. III displays carbonyl stretchings at 2115m, 2076m, 2067m, 2035vs, 2026s, 2015m, 2005s, 1995w, 1986w, 1978w and four ^{19}F NMR signals at 68.05(m), 68.98(m), 83.69(m), 84.47(m). Yield: *ca.* 6.5%. (Found: C, 29.37; H, 0.99; N, 1.06; F, 4.89. Calcd. for $[Os_3H(\mu\text{-}H)(CO)_{10}(SbPh_3)(ONC_6F_4O)]$: C, 29.18; H, 1.14; N, 1.00; F, 5.43%).

3.4. Crystal structure determination

Crystals suitable for X-ray structural analysis were obtained from hexane/dichloromethane solutions. A yellow crystal of 0.30 × 0.35 × 0.42 mm dimensions was used for data collection. Crystal data for I: $[C_{34}H_{15}NO_{12}F_4POs_3]$, monoclinic, $C2/c$, a = 42.432(14), b = 9.408(4), c = 20.983(7) Å. β = 106.820(2)°, V = 8018(5) Å^3; $Z = 8$; $D_c = 2.165$ cm^{-3}; μ(Mo Kα) = 96.12 cm^{-1}; T = 25°C. Siemens diffractometer R3m/V, Mo Kα radiation. Of the 14705 data points measured ($3.0 \leq 2\theta \leq 50.0°$), 6848 were independent ($R_{int} = 2.31\%$), and 4215 were considered ob-

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* Reference number with an asterisk indicates a note in the list of references.

served $[6\sigma(F_o)]$. The structure was solved by direct methods. An empirical (psi-scan) absorption correction was performed. The ratio of the transmission coefficients was 0.5326/0.7538. Refinement: all atoms anisotropic; $R(F) = 0.037$, $R_w(F) = 0.051$, goodness-of-fit = 0.80, $\Delta/\sigma = 1.745$, $\Delta/\sigma_{max} = 0.052$. SHELXTL software (G.M. Sheldrick, Siemens, Madison, WI) was used for all the computations.

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