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**Preliminary communication**

# Halogenation behaviour of bidentate ligand-bridged derivatives of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$

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## Abstract

Reaction of the ligand-bridged derivatives $[M_3(CO)_{10}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]$ and $[M_3(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Ru or Os; R = Me or $Pr^i$) with halogens leads to the formation of cationic products $[M_3(\mu\text{-}X)(CO)_{10}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]^+$ and $[M_3(\mu\text{-}X)(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = Cl, Br or I) in which the halogen bridges an opened edge of the metal atom framework; the crystal structure of $[Ru_3(\mu\text{-}I)(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ is reported.

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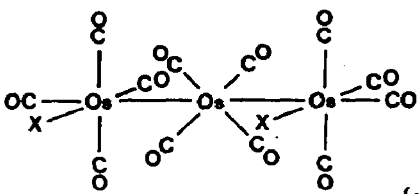
The reaction of $[Os_3(CO)_{12}]$ with halogens has long been known to afford products of the type $[Os_3X_2(CO)_{12}]$ (X = Cl, Br or I) [1,2] in which, as established by X-ray crystallography for the di-iodo derivative [3], the three osmium atoms are collinear while the two halogens are co-ordinated equatorially to the two terminal osmium atoms and in *cis* positions with respect to the triosmium chain (**1**). It has very recently been communicated that intermediates in the formation of *eq,eq*-$[Os_3X_2(CO)_{12}]$ can be detected and/or isolated and in particular that the chlorination or bromination of $[Os_3(CO)_{12}]$ affords *ax,eq*-$[Os_3X_2(CO)_{12}]$ (X = Cl or Br) (**2**) as the first detectable product whereas the corresponding iodination affords an ionic product $[Os_3(\mu\text{-}I)(CO)_{12}]I_3$ (**3**), proposed to contain a bridging iodo group, which rearranges to *ax,eq*-$[Os_3I_2(CO)_{12}]$ and subsequently to *eq,eq*-$[Os_3I_2(CO)_{12}]$ in solution [4]. This communication prompts us to report our results on the halogenation behaviour of substituted derivatives of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ and in particular of the diphosphazane-bridged derivatives $[M_3(CO)_{10}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]$ (**4**) and $[M_3(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**5**) (M = Ru or Os; R = Me or $Pr^i$).

Treatment of the tetrasubstituted derivative $[Ru_3(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**5**; M = Ru, R = Me) [5] with iodine in methanol in the presence of $NH_4PF_6$ was found to lead to the separation of an ionic compound from solution,



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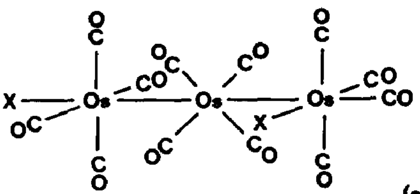

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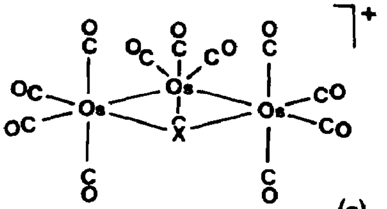

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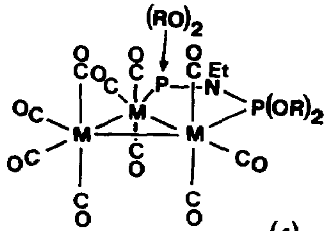


(4)

characterized as the iodo-bridged derivative $[Ru_3(\mu\text{-I})(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ ($\mathbf{6},PF_6$; M = Ru, R = Me, X = I). The structure of this species has been established unequivocally by means of a single crystal X-ray diffraction study on the hexafluorophosphate salt and the stereochemistry of the cation is illustrated in Fig. 1 *. The three ruthenium atoms define an open isosceles triangle {Ru(3)–Ru(1)–Ru(2) 89.0(0)°} with the longest edge {Ru(2) ··· Ru(3) 4.128(1) Å) being bridged by an iodine atom which lies essentially in the plane of the ruthenium atoms. The two diphosphazane ligands bridge the other two ruthenium–ruthenium edges which, significantly, are appreciably longer {2.940(1) and 2.951(1) Å} than the

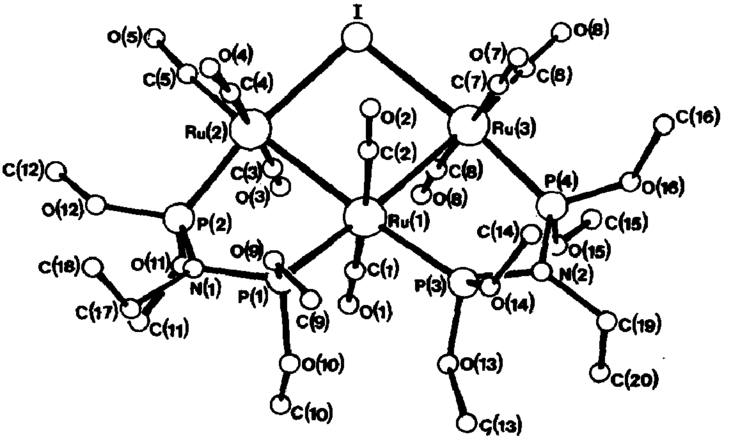
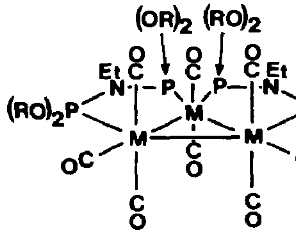


Fig. 1. The stereochemistry of $[Ru_3(\mu\text{-I})(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ showing the atom labelling scheme. Relevant interatomic distances and angles: Ru(1)–Ru(2), 2.940(1); Ru(1)–Ru(3), 2.951(1); Ru(2) ··· Ru(3), 4.128(1); Ru(2)–I, 2.745(1); Ru(3)–I, 2.754(1); Ru(1)–P(1), 2.254(3); Ru(1)–P(3), 2.266(3); Ru(2)–P(2), 2.237(3); Ru(3)–P(4), 2.246(4) Å; Ru(2)–Ru(1)–Ru(3), 89.0(0); Ru(1)–Ru(2)–I, 84.5(0); Ru(2)–I–Ru(3), 97.3(0); Ru(1)–Ru(3)–I, 84.2(0)°.

corresponding edges of the parent derivative $[Ru_3(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ {2.814(1) and 2.823(1) Å} [5]. The phosphorus atoms are co-ordinated equatorially and lie approximately in the $Ru_3I$ plane but with slight puckering. The axial carbonyl groups are staggered with respect to each other as found previously for $[Ru_3\{\mu\text{-}Ag(OC(O)CF_3)\}(CO)_8(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ [7] and for half of the molecules in the unit cell of $[Ru_3(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ [5]. The $^{31}P\{^1H\}$ NMR spectrum of $[Ru_3(\mu\text{-}I)(CO)_8(\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ exhibited an AA′BB′ pattern of peaks centred at 139.1 ppm ($\delta$ scale, relative to $H_3PO_4$) consistent with the solid-state structure being retained in solution. Significantly, reaction of $[Ru_3(CO)_8(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ with iodine in benzene under reflux conditions has been shown to lead to the fragmentation of the metal atom framework and the formation of $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)]$ and $[RuI_2(CO)_2Ph_2PCH_2PPh_2]$ [8].

Bromination of $[Ru_3(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ in the presence of $NH_4PF_6$ or $NaBPh_4$ was likewise found to afford an ionic product, viz. $[Ru_3(\mu\text{-}Br)(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$Anion (Anion = $PF_6$ or $BPh_4$) (**6**, Anion; M = Ru, R = Me, X = Br) while ionic products identified and characterised as $[Os_3(\mu\text{-}X)(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ (X = Br or I) (**6**, X; M = Os) were observed to be formed on treatment of the osmium-substituted derivatives $[Os_3(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or $Pr^i$) (**5**; M = Os) with bromine or iodine in a suitable non-polar solvent. Chloro-bridged derivatives of the type $[M_3(\mu\text{-}Cl)(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$ (M = Ru or Os; R = Me or $Pr^i$) (**6**, Cl; X = Cl) were found to be produced similarly under related chlorinating conditions and significantly even the irradiation of $[Ru_3(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ in carbon tetrachloride with ultraviolet light was observed to lead to the formation of $[Ru_3(\mu\text{-}Cl)(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]Cl$ (**6**, Cl; M = Ru, R = Me, X = Cl).



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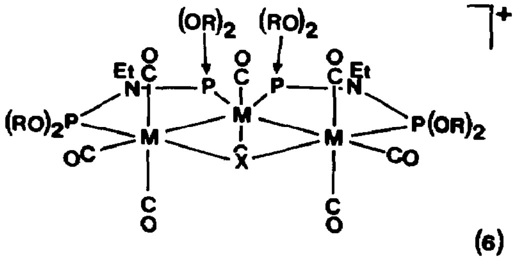

(6)

The halogenation behaviour of the bis-substituted derivatives $[M_3(CO)_{10}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]$ (M = Ru or Os; R = Me or $Pr^i$) (**4**) has also been investi-

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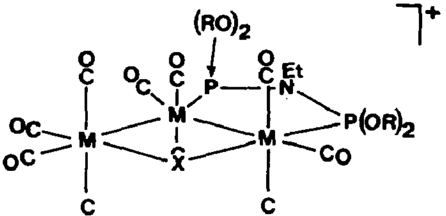
* *Crystal data*: $C_{20}H_{34}F_6IN_2O_{16}P_5Ru_3$, $M = 1257.44$, monoclinic, space group $P2_1/c$, $a$ 10.356(5), $b$ 15.224(7), $c$ 25.927(12) Å, $\beta$ 92.69(5)°, $U$ 4083.2 Å$^3$, $D_c$ 2.045 g cm$^{-3}$, $Z = 4$, Mo-$K_\alpha$ radiation, $\lambda$ 0.71069 Å, $\mu$ 19.51 cm$^{-1}$. 5029 unique reflection intensities were measured on a Nonius CAD-4 diffractometer in the range $2° \leq \theta \leq 23°$, 3908 of which were classed as observed ($I > 3\sigma(I)$). These data were corrected for absorption using the empirical ($\chi$ scan) method and used in the solution and refinement [6] of the structure. Final $R = 0.060$, $R_w = 0.076$ for 288 parameters, maximum shift over e.s.d. in last full-matrix least-squares cycle 0.05, featureless final difference Fourier with maximum peak height 0.9 e Å$^{-3}$. Atomic co-ordinates, interatomic distances and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

gated and again their treatment with bromine or iodine was found to give ionic products, in these cases of formula $[M_3(\mu\text{-}X)(CO)_{10}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]X$ ($X = Br$ or I) (7, X).

It is now well established that the halogenation of dinuclear and metal cluster compounds involves the formal insertion of a halogenium ion $X^+$ across a metal–metal bond leading to the formation of products in which the two metal atoms concerned are linked by the halogen in an open bridge-bonding co-ordination mode. Thus reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$, $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$, $[Fe_2(\mu\text{-}SR)_2(CO)_4L_2]$ ($R = Me$, etc.; $L = CO$, $PPh_3$, etc.), $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$ and $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4L'_2]$ ($L' = CO$ or $P(OMe)_3$) with halogens has been shown to lead to the formation of the cationic species $[Fe_2(\mu\text{-}X)(\eta\text{-}C_5H_5)_2(CO)_4]^+$, $[Ru_2(\mu\text{-}X)(\eta\text{-}C_5H_5)_2(CO)_4]^+$, $[Fe_2(\mu\text{-}X)(\mu\text{-}SR)_2(CO)_4L_2]^+$, $[Mn_2(\mu\text{-}X)(CO)_{10}]^+$, $[Re_2(\mu\text{-}X)(CO)_{10}]^+$ and $[Mo_2(\mu\text{-}X)(\eta\text{-}C_5H_5)_2(CO)_4L'_2]^+$ ($X = Cl$, Br or I) respectively [9–13]. In certain cases these ionic species have been shown to react further with halide ions to afford neutral products, and for $[Fe_2(\mu\text{-}X)(\eta\text{-}C_5H_5)_2(CO)_4]^+$, $[Ru_2(\mu\text{-}X)(\eta\text{-}C_5H_5)_2(CO)_4]^+$ and $[Mo_2(\mu\text{-}X)(\eta\text{-}C_5H_5)_2(CO)_6]^+$ for instance, halide ion attack produces mononuclear $[FeX(\eta\text{-}C_5H_5)(CO)_2]$, $[RuX(\eta\text{-}C_5H_5)(CO)_2]$ and $[MoX(\eta\text{-}C_5H_5)(CO)_3]$, respectively [9,10,13]. It can thus be assumed that the conversion of $[Os_3(\mu\text{-}I)(CO)_{12}]I_3$ to $[Os_3I_2(CO)_{12}]$ involves iodide ion attack on the cation $[Os_3(\mu\text{-}I)(CO)_{12}]^+$ (**3**), and with the object of establishing whether the substituted di-iodide $[Os_3I_2(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**8**) can be synthesised analogously, the reaction of $[Os_3(\mu\text{-}I)(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (**5**; $M = Os$, $X = I$) with iodide ions was investigated. A reaction between $[Os_3(\mu\text{-}I)(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]I$ (**6**, I; $M = Os$, $R = Me$, $X = I$) and excess iodide ions was indeed found to occur but, significantly, the product was shown to be the parent species $[Os_3(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**5**; $M = Os$, $R = Me$) resulting from the iodide ions functioning as a reducing agent. This result parallels those observed previously for $[Mo_2(\mu\text{-}I)(\eta\text{-}C_5H_5)_2(CO)_4\{P(OMe)_3\}_2]BPh_4$ and $[M_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$Anion ($M = Fe$ or Ru; $X = Cl$, Br or I; $R = Me$ or $Pr^i$), which proved to be inert to halide ion attack [13,14].



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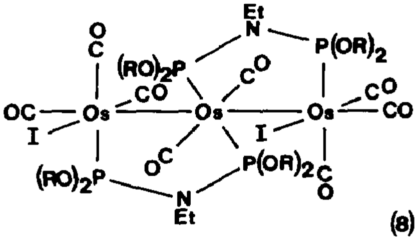

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