Metal–Metal Bond Fission in a Trinuclear Osmium Cluster by Triethylphosphine: the *X*-Ray Crystal Structure of $[HOs_3(CO)_{10}(PEt_3)(CF_3CCHCF_3)]$

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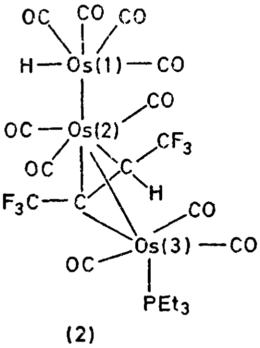
Summary The reaction of $[HOs_3(CO)_{10}(CF_3CCHCF_3)]$ with PEt_3 in hexane at room temperature leads to the formation of $[HOs_3(CO)_{10}(PEt_3)(CF_3CCHCF_3)]$ as the major product; a single crystal *X*-ray analysis reveals the presence of a chain of Os atoms, a terminal hydride ligand, and a vinylic group bridging two of the metal atoms.

The triangular array of metal atoms present in $Os_3(CO)_{12}$ is one of the most stable cluster units known, and usually remains intact in reactions of $Os_3(CO)_{12}$ and related trinuclear osmium complexes with other molecules. In particular, reactions with two-electron donor ligands such as PR_3 and CNR generally result initially in substitution of one or more CO groups,[1,2] although further reaction leading to modification of the ligands and/or the generation of higher nuclearity clusters may take place at elevated temperatures.[2,3] Certain derivatives of $Os_3(CO)_{12}$ such as $[H_2Os_3(CO)_{10}]$ and $[HOs_3(CO)_{10}(CHCH_2)]$ can react with two-electron donor ligands without loss of CO groups.[4] The former does so by virtue of its formal unsaturation whereas in the latter complex the vinyl ligand provides an electrophilic site and becomes attached to the incoming ligand. In all these reactions, however, the triangular array of metal atoms is preserved in the products obtained.

We now report a different mode of reaction of a two-electron donor ligand with a trinuclear osmium complex in which a metal–metal bond is broken at room temperature to give a complex containing a chain of osmium atoms. Thus, when a suspension of the complex $[HOs_3(CO)_{10}(CF_3CCHCF_3)]$ (**1**)[5] in hexane is treated with an equimolar quantity of PEt_3, dissolution takes place within a few minutes at room temperature to give a bright yellow solution. The several products present were separated by t.l.c. and the major component, (**2**), obtained in *ca.* 30% yield, was recrystallised from warm hexane. The stoicheiometry of (**2**) was shown by mass spectrometry to correspond to the formula $[HOs_3(CO)_{10}(PEt_3)(CF_3CCHCF_3)]$ with the parent ion being observed at *m/e* 1138 for ^{192}Os. The ^1H n.m.r. spectrum of (**2**) at -50 °C (CD_2Cl_2) shows a singlet resonance at $\delta -9{\cdot}72$, indicative of a terminal rather than a bridging Os–H ligand, in addition to resonances at δ 2·20 (m, 6H, CH_2P) 1·18 (m, 9H, $MeCH_2P$), and 4·42 [q, 1H, ^3J(HCCF) 11 Hz, CF_3CCHCF_3]. The ^{19}F n.m.r. spectrum (30 °C, CD_2Cl_2) shows two equal intensity resonances at δ 56·87 (s) and 48·29 p.p.m. [d, ^3J(HCCF) 11 Hz], due, respectively, to CCF_3 and $CHCF_3$. The i.r. spectrum of (**2**) in hexane solution shows ν(CO) absorptions at 2119m, 2088m, 2079w, 2057m, 2041sh, 2034sh, 2027s, 2018s, 2013s, and 1992m cm^{-1}.



(**2**)

A complex of analogous stoicheiometry to (**2**) is obtained by treating the vinyl complex $[HOs_3(CO)_{10}(CHCH_2)]$ with PMe_2Ph.[6] The 1 : 1 adduct which is formed has been structurally characterised and shown to have the phosphine ligand bonded to the vinyl group.[7] The spectroscopic properties of (**2**), however, are not in accord with such a formulation, and a single crystal *X*-ray analysis was therefore undertaken to determine its structure. Pale yellow, block-shaped crystals of $[HOs_3(CO)_{10}(PEt_3)(CF_3CCHCF_3)]$ suitable for such an analysis were deposited from hexane.

Crystal data: $C_{20}H_{17}F_6O_{10}Os_3P$, $M = 1\,132{\cdot}91$, monoclinic, $a = 10{\cdot}718(3)$, $b = 17{\cdot}101(6)$, $c = 15{\cdot}699(5)$ Å, $\beta = 94{\cdot}83(2)°$, $U = 2\,867{\cdot}2$ Å^3, $Z = 4$, $D_c = 2{\cdot}62$ g cm^{-3}; μ-(Mo-K_α) = 133·81 cm^{-1}, space group $P2_1/c$. 7 081 intensities ($2\theta_{max} = 60{\cdot}0°$) were measured on an AED four-circle diffractometer using graphite-monochromated Mo-K_α radiation and an w/θ scan technique. The data were corrected for absorption and Lorentz polarisation factors, and averaged to give 2 754 unique observed intensities $[F > 5\sigma(F)]$. The Os atoms were located by multi-solution Σ_2 sign expansion, and the other non-hydrogen atoms from a subsequent electron-density difference synthesis. The structure was refined by blocked full-matrix least-squares. The Os, P, and F atoms were assigned anisotropic thermal parameters, and the $>CH_2$ and –Me hydrogen atoms, with common isotropic temperature factors, were placed in geometrically idealised positions, and allowed to ride 1·08 Å from the relevant carbon atom. The weighting scheme $w = 1{\cdot}7956/[\sigma^2(F) + 0{\cdot}0005\,F^2]$ was employed. The current residuals are $R = 0{\cdot}066$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0{\cdot}062$.†

The molecular structure is shown in the Figure which includes some important bond parameters. The Os–Os–Os backbone is bent, and the phosphine is co-ordinated to a terminal Os *trans* to the Os(2)–Os(3) bond. The vinylic ligand σ-bonds to Os(3) and π-bonds to Os(2). The C(8)–C(9) distance suggests that this bond has been reduced below double-bond character, and is slightly longer than the

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† The atomic co-ordinates for this work are available on request from the Director of 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.

value of 1·396(3) Å found for the vinylic C–C bond in $[HOs_3(CO)_{10}(CHCH_2)]$.[8] All the carbonyl groups are terminal, and their arrangement on the terminal Os atoms is slightly staggered with respect to those on the central metal atom. Os(1) has an octahedral co-ordination geometry with the sixth position occupied by a terminal hydride, although this was not located in the *X*-ray analysis. The Os(1)–Os(2) distance is similar to the value of 2·935-(2) Å in $[Os_3(CO)_{12}I_2]$,[9] where the Os–Os–Os arrangement is linear, but the Os(2)–Os(3) bond is shorter, presumably due to the influence of the vinylic ligand.

The reaction of (**1**) with PEt_3 to give (**2**) is clearly very unusual for a trinuclear osmium complex with a two-electron donor ligand, and can be formally regarded as a reduction reaction in the sense that two electrons have been added to the cluster. Such reductions are more common for higher nuclearity clusters, as in the reaction of $[Os_6(CO)_{18}]$ with $2I^-$ to give $[Os_6(CO)_{18}]^{2-}$ (and I_2)[10] or with CNR to give $Os_6(CO)_{18}(CNR)_2$.[11] Both these reactions take place at room temperature, and in the latter case the number of metal-metal bonds present is clearly reduced. The factors which cause this mode of reaction to be favoured for (**1**) are not clear at the present time but are presumably associated with the presence of the CF_3CCHCF_3 ligand. It may be that the presence of this electron-withdrawing group facilitates reduction of the cluster, and further experiments are in progress to test this hypothesis.

We thank the S.R.C. for support (to Z. D.) and Johnson Matthey and Co. Ltd. for the loan of OsO_4.

(*Received*, 30*th May* 1979; *Com.* 561.)

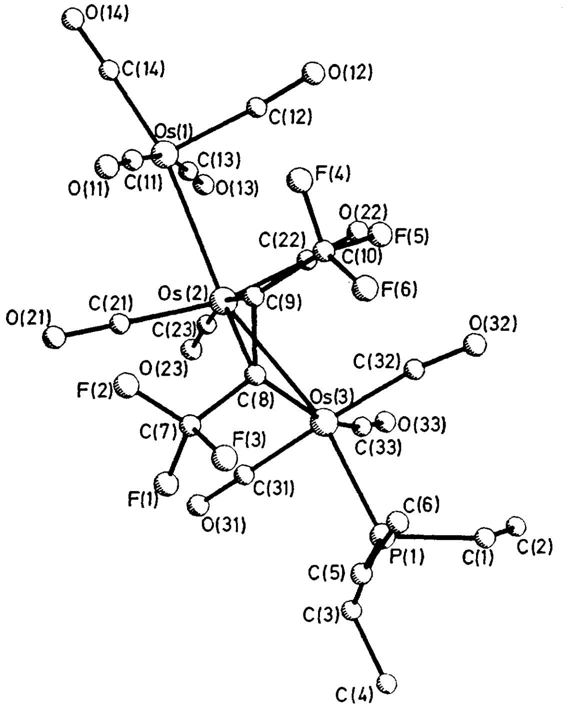

FIGURE. The molecular geometry of $[HOs_3(CO)_{10}(PEt_3)(CF_3CCHCF_3)]$ including the atom numbering scheme. Bond lengths: Os(1)—Os(2), 2·907(3); Os(2)–Os(3), 2·848(2); Os(3)–P(1), 2·363(6); Os(2)–C(8), 2·24(3); Os(2)–C(9), 2·20(3); Os(3)–C(8) 2·16(3); and C(8)–C(9), 1·41(4) Å; bond angles: Os(1)–Os(2)–Os(3), 162·3 (1) and Os(2)–Os(3)–P(1), 160·0(2)°.

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