

New Mode of Bonding of a Vinyl Ligand to an Osmium Cluster: the X-Ray Crystal Structure of $[\text{HOs}_3(\text{CO})_{10}(\text{CF}_3\text{CCHCF}_3)]$

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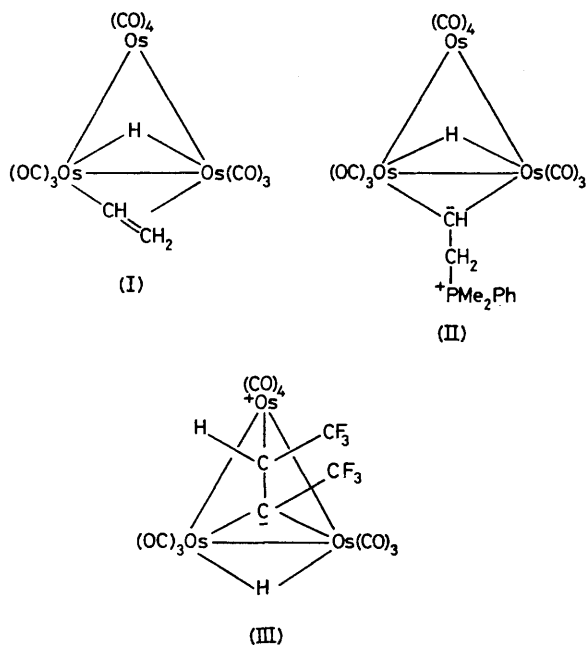
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Summary The reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ in hexane at room temperature leads to the formation of $[\text{HOs}_3(\text{CO})_{10}(\text{CF}_3\text{CCHCF}_3)]$; a single crystal X-ray analysis reveals that the organic fragment is bonded to all three Os atoms.

THE reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with acetylene at room temperature leads to the formation of $[\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_2)]$ (I).^{1,2} The vinyl ligand in this complex bridges one edge of the Os_3 triangle and bonds in an unsymmetrical σ , π fashion. Addition of PMe_2Ph to a pentane solution of (I) at room temperature results in attack of the nucleophile at the vinyl group to give (II). This reaction has been reported to be specific to phosphorus donors.^{3,4}



In an attempt to increase the reactivity of the vinyl ligand in (I) towards nucleophiles we have treated $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$. In hexane solution at room temperature reaction is essentially complete after 12 h, and gives a single yellow crystalline product (III) which was shown by mass spectroscopy to have the stoichiometry $[\text{HOs}_3(\text{CO})_{10}(\text{CF}_3\text{CCHCF}_3)]$ analogous to (I). The ^1H n.m.r. spectrum of (III) at -80°C ($\text{C}_6\text{D}_5\text{CD}_3$) exhibits a multiplet peak centred at δ 2.9 due to the CH proton and a singlet resonance at δ -13.4 due to the bridging hydride ligand.

The ^{19}F n.m.r. spectrum (30°C , C_6D_6) shows two equal intensity resonances (q, 57.93 p.p.m.; m, 59.51 p.p.m., at high field relative to CCl_3F) due, respectively, to the CCF_3 and CHCF_3 atoms. The i.r. spectrum of (III) in hexane solution, however, [$\nu(\text{CO})$ 2120w, 2097sh, 2088vs, 2076m, 2058w, 2044s, 2038s, 2025sh, 2018s, 2013s, 2006sh, 1999w, and 1961m cm^{-1}] is quite different from that of (I) and a single crystal X-ray analysis was therefore undertaken to ascertain its structure.

The crystals are triclinic, space group $P\bar{1}$, with $a = 16.63$, $b = 16.06$, $c = 8.68 \text{ \AA}$, $\alpha = 93.1$, $\beta = 93.3$, $\gamma = 116.4^\circ$, $Z = 4$. Cell dimensions and intensities were obtained on a Philips four-circle diffractometer (Mo- K_α radiation) from a crystal $0.2 \times 0.2 \times 0.4 \text{ mm}$ ($\mu = 197 \text{ cm}^{-1}$) out to $\theta_{\text{max}} = 23^\circ$. The structure was solved by the heavy-atom method and R for the Os atoms alone was 16.8%. All other atoms (except H) were unequivocally located from Fourier maps, and a final Fourier difference map showed no remaining regions of significant electron density. The current R is 12.3% for 3681 reflexions with $I > 1.65\sigma(I)$. The relatively high value of R is partly due to the lack of an absorption correction, and partly to the fact that the crystal suffered radiation damage with a consequent broadening of diffraction peaks.†

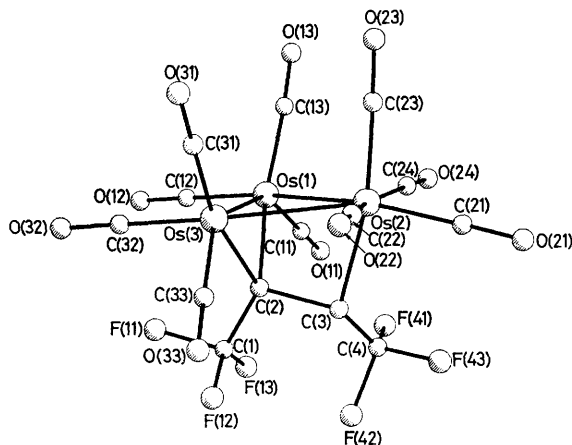


FIGURE. Os(1)–Os(2), 2.90; Os(2)–Os(3), 2.91; Os(1)–Os(3), 2.78; Os(2)–C(3), 2.19; Os(1)–C(2), 2.11; Os(3)–C(2), 2.06; C(1)–C(2), 1.64; C(2)–C(3), 1.63; C(3)–C(4), 1.54 Å; \angle C(1)–C(2)–C(3), 106° ; \angle C(2)–C(3)–C(4), 124° .

The molecular geometry is shown in the Figure which includes some important bond parameters. The two independent molecules are very similar, the only significant difference being 20° in the C(1)–C(2)–C(3)–C(4) torsion

† 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.

angles. Mean values for the dimensions of the two molecules are quoted. The geometry of the C atom chain suggests that one H atom is attached to C(3) and the other H atom presumably occupies a bridging position between Os(1) and Os(3) on the opposite side of the Os₃ triangle to that occupied by the vinyl ligand. The CO groups are all linear with Os·····O distances ranging from 2.96 to 3.25 Å (mean 3.07 Å). The standard deviation in the position of an Os atom is 0.003 Å and in the position of C, O, or F atoms *ca.* 0.1 Å.

A particularly noteworthy feature of this structure is the bond between C(3) and Os(2) which gives Os(2) a geometry which has not been observed previously in any triangular osmium cluster. The structural differences between (I) and (III) may be rationalised by considering the effect of substituting CF₃ groups for H atoms in (I). This presumably increases the susceptibility of C(3) to nucleophilic attack and hence leads, in the absence of other electron

donors, to the formation of a bond between C(3) and the Os(CO)₄ group acting as a weak nucleophile. In valence bond terms the structure may therefore be formally represented as in (III) which is closely related to that previously proposed for (II).^{3,4}

Complex (III) reacts rapidly with Ph₃P at room temperature to give at least three products. The structure of these products and the reaction of (III) with other nucleophiles is under study.

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