

Preliminary communication

Oxidative addition reactions in cluster complexes of osmium:
intracluster reactions of benzyne and a novel 'phenyl' complex.

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(Received May 26th, 1972)

SUMMARY

The structures of $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_3)(\text{C}_6\text{H}_4)$, $\text{HOs}_3(\text{CO})_8(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$ and $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_3)$ are described, the latter illustrating an intracluster reaction of the coordinated benzyne ligand.

Oxidative addition reactions of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and of triphenylphosphine with $\text{Os}_3(\text{CO})_{12}$ have been described¹. Three further X-ray structural analyses are now summarised which essentially complete the characterisation of the reaction products.

$\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_3)(\text{C}_6\text{H}_4)$, [(VI) of the Table given in ref. 1; a typographical error has interchanged the number of carbonyl groups in (V) and (VI)] crystallises in the triclinic system with the Delaunay reduced cell, $a = 17.313$, $b = 11.878$, $c = 10.638\text{\AA}$, $\alpha = 95.87^\circ$, $\beta = 96.93^\circ$, $\gamma = 110.77^\circ$; space group $P\bar{1}$; $Z = 2$. 2804 independent reflexions ($F_{\text{obs}}^2 \geq 3.0 \sigma(F_{\text{obs}}^2)$) have been observed by four-circle automatic diffractometry (Mo- K_α) and Fourier and least squares methods have determined and refined atomic parameters ($R = 0.08$ at present without absorption correction of the observed data). The stereochemistry is illustrated in Fig. 1; present e.s.d.'s to be associated with the bond lengths are approximately 0.002\AA (Os–Os), 0.010\AA (Os–P), 0.04\AA (Os–C) and 0.05\AA (C–C) and (C–O).

$\text{HOs}_3(\text{CO})_8(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$, (IV), crystallises with $a = 20.981$, $b = 13.179$, $c = 31.422\text{\AA}$, $\beta = 112.25^\circ$; the space group is $C2/c$ with $Z = 8$. The stereochemistry, illustrated in Fig. 2, results from atomic parameters defined by the analysis of 2410 independent reflexions ($F_{\text{obs}}^2 \geq 3.0 \sigma(F_{\text{obs}}^2)$); four-circle diffractometry, (Mo- K_α); $R =$

J. Organometal. Chem., 40 (1972)

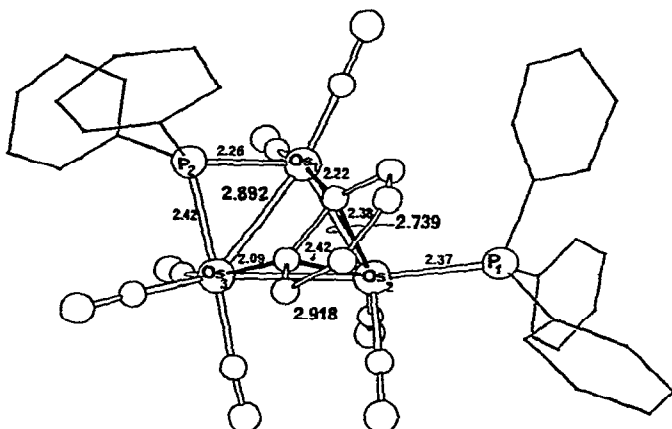


Fig. 1. Stereochemistry of $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_3)(\text{C}_6\text{H}_4)$ (VI).

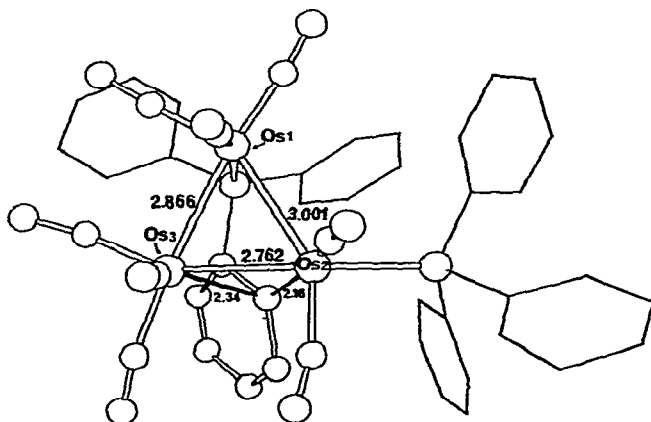


Fig. 2. Stereochemistry of $\text{HOs}_3(\text{CO})_8(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$ (IV).

0.08 (no absorption correction; the e.s.d.'s in the bond lengths are essentially the same as those above).

The unidentified yellow compound (X), obtained by the decomposition of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ in xylene under reflux (see text of ref. 1), is shown (Fig. 3) to be $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_3)$. Its crystals are also monoclinic with $a = 13.715$, $b = 16.786$, $c = 19.175\text{Å}$, $\beta = 95.42^\circ$; space group $P2_1/c$; $Z = 4$. The structure was defined by the analysis of 3123 independent reflexions ($F_{\text{obs}}^2 \geq 3.0 \sigma(F_{\text{obs}}^2)$); four-circle diffractometry (Mo- $K\alpha$); $R = 0.054$ without absorption correction; e.s.d.'s average 0.002Å (Os-Os) 0.008Å (Os-P) 0.03Å (Os-C) and 0.04Å (C-C and C-O)).

The coordination of the benzyne ligand by the osmium atoms in (II) and (VI) is seen to be very similar. (X) can be thought to be formed by the intracuster oxidative

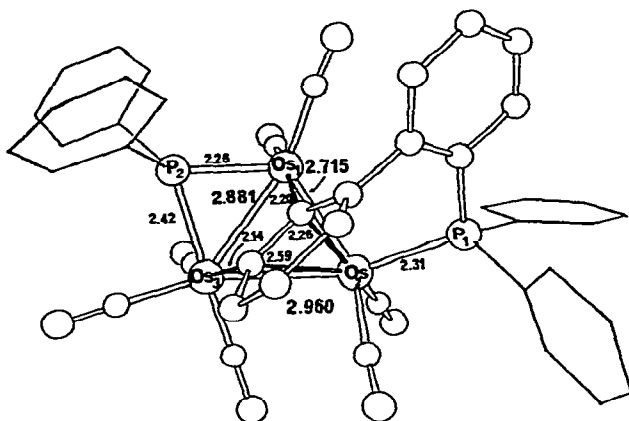


Fig. 3. Stereochemistry of $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_3)$ (X).

addition of benzyne to a β carbon–hydrogen bond of the terminal phosphine ligand of (VI).

The mean carbon–carbon bond length in the coordinated benzyne ligand in (II), (VI) and (X) is 1.42\AA , there being no significant deviation from this mean value for any bond at the present stage of refinement.

The dihedral angle between the planes containing the osmium atoms and the mean plane of the aryne in the three benzyne complexes is $69 \pm 3^\circ$. This conformation reflects the osmium atoms, Os(1) and Os(3), being approximately coplanar with the benzyne ligand with a mean Os–C bond length of 2.16\AA ; the mean $\text{Os}_2\text{–C}$ (aryne) bond length is 2.39\AA . The stereochemistry of each coordinated carbon atom is thus closer to trigonal pyramidal than tetrahedral.

The structure of (IV) is unusual in that it shows the metallation of a β -carbon hydrogen bond of a triphenylphosphine ligand by two adjacent osmium atoms; the complex can be regarded as a precursor of (I), (II) and (VI). The Os–C–Os bond angle of 74° is significantly smaller than that observed in $\text{Os}_3(\text{CO})_8(\text{PPh}_2)(\text{Ph})(\text{PPhC}_6\text{H}_4)$, (I); as such it is similar to bridge bond angles found in electron deficient complexes and is discussed elsewhere².

The rare gas rule and the stereochemistry of the metals suggest that the hydride ion is terminally bound to Os(1) in complexes (VI) and (X); that in (IV) is presumed to bridge Os(2) and Os(3). As yet, we have no reasonable explanation for the considerable variations observed in the metal–metal bond distances in these complexes.

We are grateful to the Science Research Council for support of these studies.

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