

Fluxional Behaviour of Some Cluster Complexes of Osmium Containing C_6H_4 as Ligands

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Summary The C_6H_4 ligands in the complexes $Os_3H(C_6H_4)(PMe_2)(CO)_9$ (A) and $Os_3(C_6H_4)(PMe_2)_2(CO)_7$ (B), synthesised from $Os_3(CO)_{12}$ and PMe_2Ph , undergo rapid rotation relative to the Os_3 ring, a process which necessitates a carbonyl transfer between osmium atoms in the case of complex (B) [$\Delta G(T_c)^\ddagger$ values are 13.6 and 13.9 kcal mol⁻¹ for (A) and (B) respectively].

carbonyl stretching region and hence, most probably, a directly analogous structure to that established for $Os_3(C_6H_4)(PPh_2)_2(CO)_7$ by an X-ray study (Figure 1).¹ The C_6 ring

We have recently reported¹ a novel reaction in which a carbon-hydrogen bond of a PPh_3 ligand co-ordinated to one osmium atom in a cluster molecule is activated by an adjacent osmium atom to give a bridging ligand system containing an osmium-carbon σ -bond and subsequent cleavage of phosphorus-carbon bonds results in complexes containing bridging C_6H_4 or C_6H_5 as ligands. The relevance of this work to the activation of organic molecules at metal surfaces has been noted.¹

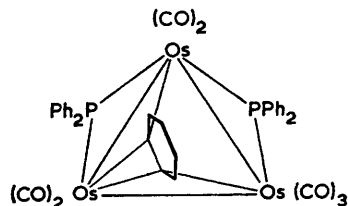


FIGURE 1. Structure of $Os_3(C_6H_4)(PPh_2)_2(CO)_7$.

We now report some related work on the ligand PMe_2Ph . The complexes $Os_3(CO)_{12-x}(PMe_2Ph)_x$ ($x = 1, 2$, or 3) were prepared by reaction of $Os_3(CO)_{12}$ with the ligand in refluxing toluene. After separation of the mixture on alumina these complexes were further heated in refluxing nonane to give new products, of which we were able to separate two: $Os_3H(C_6H_4)(PMe_2)(CO)_9$ (A) as stable yellow crystals [from $Os_3(CO)_{11}(PMe_2Ph)$] and $Os_3(C_6H_4)(PMe_2)_2(CO)_7$ (B) as stable orange-red crystals [from $Os_3(CO)_{10}(PMe_2Ph)_2$]. Complex (B) has an almost identical i.r. spectrum in the

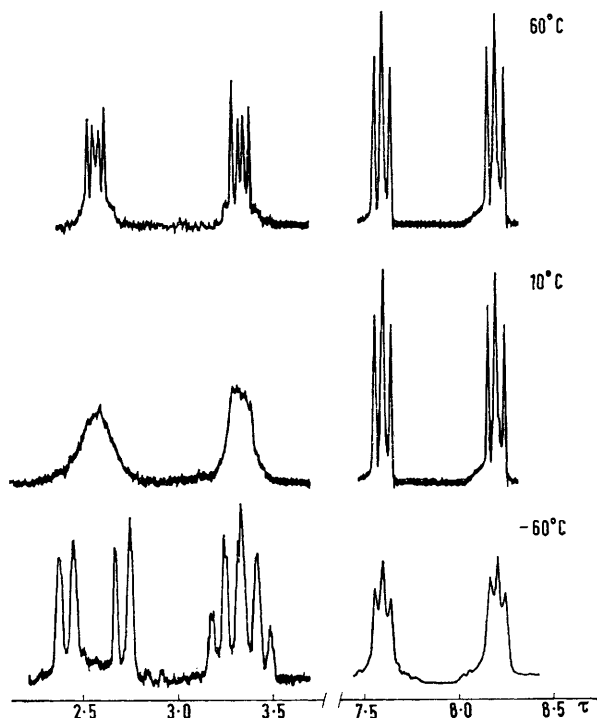


FIGURE 2. N.m.r. spectra for complex B.

is involved in bonding through two carbon atoms to all three metal atoms with the plane of the ring approximately perpendicular to the plane of the three osmium atoms.

Consequently for complex (B) one would predict that the four methyl groups and the four hydrogen atoms of the C_6H_4 ligand should be all magnetically non-equivalent. However, the n.m.r. spectrum in $CDCl_3$ at room temperature is too simple for this structure in the absence of a dynamic process. The spectrum (Figure 2) shows that the

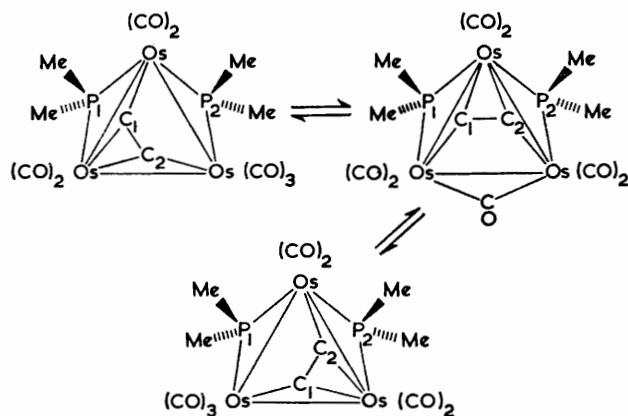


FIGURE 3. Proposed mechanism for complex B. C_1 and C_2 represent the two carbon atoms of the C_6H_4 ligands bonded to the metal atoms.

PMe_2 ligands are effectively equivalent. However, the methyl groups on each phosphorus atom are non-equivalent, the triplet patterns being due to virtual coupling with the ^{31}P nuclei. A similar situation with respect to the phosphido-bridges is found in $Fe_2(PMe_2)_2(CO)_6$.² The AA'XX' spectrum for the C_6H_4 ligand at room temperature would be consistent with this ligand being a symmetrically *ortho*-

disubstituted derivative of benzene. The apparently symmetrical nature of the ring must be due to a rapid process since on cooling below the coalescence temperature [$T_c = 5^\circ C$, $\Delta G^\ddagger(T_c) = 13.9 \text{ kcal mol}^{-1}$] the C_6H_4 group shows a clearly resolved ABXY spectrum while the methyl signals broaden and remain broad at -90° .

Making the reasonable assumption that the PMe_2 bridges remain intact throughout, we propose that the mechanism for the process (Figure 3) involves a rotation of the C_6H_4 ring with respect to the Os_3 ring with a simultaneous carbonyl transfer from one osmium atom to another; however, we have no evidence to show whether the bridged carbonyl species is an intermediate or a transition state nor whether the organic ring is undergoing free rotation rather than an oscillation as shown in Figure 3. By this process $C(1)$ and $C(2)$ undergo exchange as do the phosphido-groups, and thus we can account for the changes in the n.m.r. spectrum with temperature as described above. Complex (A) is of unknown structure but the C_6H_4 ligand gives a very similar n.m.r. spectrum showing similar temperature dependence to that of complex (B) [$T_c = 4^\circ C$, $\Delta G^\ddagger(T_c) = 13.6 \text{ kcal mol}^{-1}$].

It is interesting that the rate of these processes is similar to that of ethylene rotation in platinum³ or rhodium⁴ complexes in which the olefin rotates about the metal-olefin axis. Our studies may be relevant to the behaviour of unsaturated species at a metal surface where at least three metal atoms could be involved in bonding to the organic portion, and we believe that processes similar to those we have described might well occur under such conditions.

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