

Preliminary communication

Dehydrogenation of organic and inorganic molecules by reaction with $\text{Os}_3(\text{CO})_{12}$

A.J. DEEMING and M. UNDERHILL

Department of Chemistry, University College London, 20 Gordon Street, London WC 1 (Great Britain)

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There has been a recent report¹ that the dihydride $\text{H}_2\text{Ru}_3(\text{C}_8\text{H}_8)(\text{CO})_9$ is formed in the reaction of bicyclo[3,2,1] octa-2,6-diene (C_8H_{10}) with $\text{Ru}_3(\text{CO})_{12}$, the two hydrogen atoms being abstracted from one of the two olefinic groups. We have observed related reactions in osmium chemistry in our work on the activation of carbon-hydrogen bonds by transition metal cluster complexes. Complexes of the type $\text{H}_2\text{Os}_3\text{X}(\text{CO})_9$ can be obtained by reaction of $\text{Os}_3(\text{CO})_{12}$ with both organic and inorganic molecules of type H_2X ($\text{H}_2\text{X} = \text{H}_2\text{S}$, C_6H_6 or C_2H_4) where X is capable of both triply bridging the three osmium atoms and of acting as a four electron donor to the metal cluster.

We first came across this behaviour in our attempts to prepare $\text{Os}(\text{CO})_3\text{Vp}$ ($\text{Vp} = o$ -vinylphenyldiphenylphosphine) which would be analogous to the known iron and ruthenium complexes². However, we were unable to isolate any monomers from the reaction of Vp with $\text{Os}_3(\text{CO})_{12}$ in *n*-octane at 125° , isolating instead a complex of apparent formula $\text{Os}_3(\text{CO})_8\text{Vp}$, complex (I). The NMR spectrum (see Table 1) showed this to be a

TABLE 1
NMR DATA^a

Complex	Solvent	Hydride signals ^b τ	Other signals τ
(I)	CDCl_3	26.8 d; $J(\text{P-H}) = 25.4^c$ 30.8 d; $J(\text{P-H}) = 10.3^c$	2.68 m } 3.20 m } $\text{Ph}_2\text{PC}_6\text{H}_4\text{C}_2\text{H}$
(II)	$\text{CD}_3\text{C}_6\text{D}_5$	28.13 d } 31.83 d } $J(\text{H-H}) = 1-2$	3.90 s } 4.43 s } C_2H_2
(III)	CDCl_3	28.96 s	2.13 m } 3.14 m } C_6H_4 '(AA'BB' spectrum) ^d
(IV)	CH_2Cl_2	30.70 s	

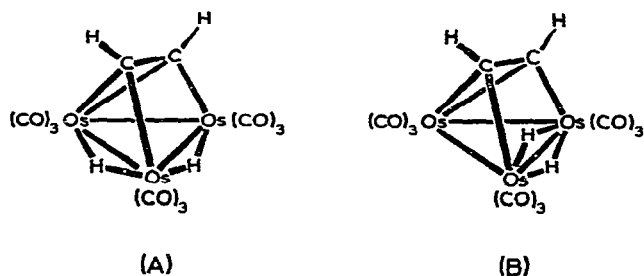
^a Complexes (I)–(IV) were also characterised by elemental analysis and IR spectra and showed parent ions in their mass spectra. ^b s = Singlet; d = doublet; m = multiplet; J -values in Hz. ^c Some further fine structure is apparent but not clearly resolved. ^d Thus the C_6H_4 ligand appears to be symmetrical.

dihydride and the lack of signals in the regions expected for either free or coordinated vinyl groups² indicated the formulation $\text{H}_2\text{Os}_3(\text{Ph}_2\text{PC}_6\text{H}_4\text{C}_2\text{H})(\text{CO})_8$; the remaining vinyl hydrogen signal is probably close to or obscured by the phenyl signals. We suggest that the vinyl group has been dehydrogenated to give what is formally an acetylenic ligand triply bridging three osmium atoms. We subsequently examined the reactions of $\text{Os}_3(\text{CO})_{12}$ in *n*-octane with ethylene at 125° which gave $\text{H}_2\text{Os}_3(\text{C}_2\text{H}_2)(\text{CO})_9$, (II), and with benzene in a sealed glass tube at 180° which gave $\text{H}_2\text{Os}_3(\text{C}_6\text{H}_4)(\text{CO})_9$, (III). The *o*-phenylene group probably bonds to the three osmium atoms through two carbon atoms as shown by an X-ray study for C_6H_4 in a related complex³.

The reaction of $\text{Os}_3(\text{CO})_{12}$ in *n*-octane at 125° with H_2S gave $\text{H}_2\text{Os}_3\text{S}(\text{CO})_9$, (IV), which is related to the complexes described above except that here group X bonds to the Os_3 ring through a single atom. The complex $\text{H}_2\text{Ru}_3\text{S}(\text{CO})_9$ is known^{4,5} but was not prepared directly from H_2S and $\text{Ru}_3(\text{CO})_{12}$ as we have since shown to be possible.

The intermediates in these reactions could be of the type $\text{HOs}_3(\text{HX})(\text{CO})_{10}$ since related complexes are known to be formed in the reaction of $\text{Os}_3(\text{CO})_{12}$ with compounds containing only one available hydrogen⁶. We are at the moment looking for evidence for intermediate vinyl and phenyl complexes in the reactions of ethylene and benzene respectively.

Of the complexes $\text{H}_2\text{Os}_3\text{X}(\text{CO})_9$ all show single hydride signals in the NMR spectra at room temperature and on cooling to -50° except the C_2H_2 complex which shows the non-equivalence of all four hydrogen atoms. However, the singlets at τ 3.90 and 4.43 coalesce to a singlet at 72° and above. ($E_a = 20.4 \text{ kcal}\cdot\text{mol}^{-1}$; $\Delta S^\ddagger = -38 \text{ e.u.}$). If the hydride ligands were exchanging at the same rate as the C_2H_2 protons one would expect a coalescence temperature of 96° . The hydrides must be exchanging by a slower process since even at 115° broad but separate hydride signals are observed. A discussion of the mechanism of these exchange processes is premature since we have yet to establish whether the complex contains $\text{CH}-\text{CH}$ or $\text{C}-\text{CH}_2$ fragments. The lack of coupling between the two hydrogens as shown in the NMR spectrum might suggest $\text{C}-\text{CH}_2$ but by analogy with the *o*-phenylene complex and the earlier ruthenium work¹ we at present favour structure (A), rather than structure (B) which is inconsistent with the NMR spectrum. However, we cannot say whether the C_2H_2 complex is structurally unique in the series or whether the



apparent equivalence of the hydride ligands in the other complexes is due to similar but more rapid intramolecular processes. The latter may actually be the case since some related C_6H_4 complexes are known to be fluxional⁷.

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