Triruthenium and Triosmium Carbonium Derivatives

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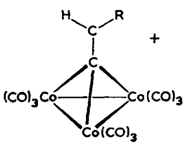
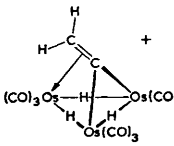
Summary The preparation and protonation of $H_2Os_3(CO)_9C{=}CH_2$ and other related complexes are reported.

OUR interest in the reactivity of co-ordinated olefins has led to the examination of the protonation of some trimetal–olefin derivatives. In recent communications Seyferth and his co-workers[1,2] reported the preparation and study of the cobalt carbonium salts (**1**).

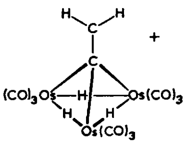
In the absence of direct evidence, Seyferth put forward the structure shown for complexes (**1**) but with considerable charge delocalisation into the CCo_3 cluster. We report here the preparation and study of the closely related osmium carbonium ion $[H_3Os_3(CO)_9C{-}CH_2]^+$ (**2**) which, on the basis of its ^1H n.m.r. spectrum, has structure (**A**) which contains an alternative bonding mode of the C = CH_2 fragment not considered by Seyferth.



(**1**)



(**2A**)



(**2B**)

Ethylene reacts with either $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ according to reaction (1). The two major products of

$$M_3(CO)_{12} \rightarrow H_2M_3(CO)_9(C{=}CH_2) + H_2M_3(CO)_9(CH{=}CH) \quad (1)$$

M = Ru or Os; (**3a**) M = Ru; (**3b**) M = Os; (**4**) M = Ru

this reaction are the isomers (**3**) and (**4**) formed by the transfer of two H atoms from the ethylene to the cluster with the concomitant formation of two M–C σ-bonds. The structure of (**3b**) in the solid has been confirmed by single crystal *X*-ray analysis[3] and the ^1H n.m.r. spectrum of this complex clearly suggests that this structure persists in solution.

Complex (**4**) is closely related to the complex $H_2Ru_3(CO)_9C_8H_{12}$ previously reported as one of the products of the reaction of either $H_4Ru_4(CO)_{12}$ or $Ru_3(CO)_{12}$ with cyclo-octadiene[4,5] and the ^1H n.m.r. spectrum is fully consistent with this suggestion. We therefore propose that complex (**4**) possesses the structure shown. The formation of these products sheds valuable insight into the way in which olefins interact with metal surfaces.

In acid, complex (**3**) undergoes reversible protonation to yield the cationic derivative (**2**) [reaction (2)]. Cation (**2**)

$$\underset{(\mathbf{3b})}{H_2Os_3(CO)_9(C = CH_2)} \underset{\longleftarrow}{\xrightarrow[\text{in } SO_2 \text{ or } CDCl_3]{CF_3CO_2H\dagger}} \underset{(\mathbf{2})}{[H_3Os_3(CO)_9\text{-}}(C{=}\ CH_2)]^+ \quad (2)$$

may also be prepared by hydride abstraction from $H_3Os_3(CO)_9CMe$[3] using $Ph_3C^+BF_4^-$ in SO_2. This cation is easily characterised on the basis of its ^1H n.m.r. spectrum which is temperature dependent in $CDCl_3$–CF_3CO_2H (2:1 v/v). The limiting spectrum at −10 °C shows two high-field singlets at τ 28·36 and 30·58 of relative intensity 1:2. At higher temperatures (*ca.* + 10 °C) coalescence of these signals occurs and at +70 °C a sharp singlet at τ 29·85 (3H) is observed. A sharp lower-field singlet at τ 2·31

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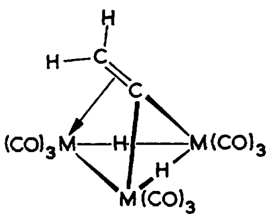
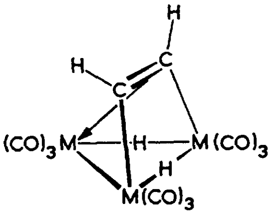
† *N.B.* In neat CF_3CO_2H another as yet uncharacterised trihydride is also formed.

(2H) (−10 °C) shows no variation with temperature (for solutions of the cation in liquid SO_2). The appearance of two hydridic resonances in the limiting spectrum (−10 °C) clearly shows that the protonated species (**2**) does not possess a symmetric topped structure (**B**) and it would appear that the less symmetric arrangement (**A**) is preferred. The reasons for this apparent change in structure are not clear but it is clear that in cation (**2**) the olefinic grouping is favourably disposed for π-bonding of the Chatt type to metal ion M_A and the complex may then be regarded as a 1,1-disubstituted derivative of ethylene.



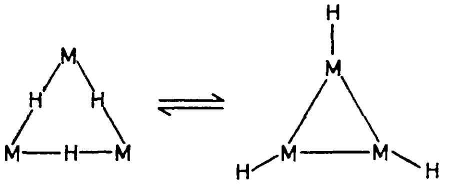
(**3**)



(**4**)

In CF_3CO_2D–$CDCl_3$, complex (**3**) adds D^+ to yield $[DH_2Os_3(CO)_9C{=}CH_2]^+$. The ^1H n.m.r. spectrum of this cation is similar to that of (**2**) except that the high field signal (70 °C) corresponds to 2H and on cooling this signal separates into two singlets of relative intensity 0·66H : 1·33H compared to the value of 2H for the low field signal at τ2·32. Exchange of H^+ with solvent is obviously slow and is similar to the protonation of triangular clusters reported previously. Using MeI as internal calibrant we were able to show that over prolonged periods (several days) in CF_3CO_2D some exchange of olefinic protons takes place although we have been unable to establish whether this exchange takes place *via* attack at the olefinic cation directly or *via* initial attack on the Os_3 cluster.

Temperature dependence of the ^1H n.m.r. spectrum of (**2**) may be interpreted in terms of a simple M–H–M bridge–terminal M–H interchange of the type in reaction (**3**), or alternatively *via* an intermediate of structure (**B**).



(3)

We have been unable to examine the protonation of the 1,2-disubstituted complex (**4**); however, protonation of the corresponding C_8H_{12} derivative $H_2M_3(CO)_9C_8H_{12}$(M = Ru or Os) readily occurs in CF_3CO_2H (or CF_3CO_2D) to produce the cation $[H_2RM_3(CO)_9C_8H_{12}]^+$ (R = H or D). The ^1H n.m.r. spectra of these cations are also temperature dependent and show behaviour similar to that observed for cation (**2**). Thus, for example, for M = Ru at −5 °C two signals at τ 26·45 and 31·76 of relative intensity 2 : 1 are observed. Above their coalescence temperature at +70 °C a single sharp line is observed at τ 28·20. This may be interpreted in terms of H exchange *via* a more symmetrical arrangement involving terminal M–H bonds or by rotation of the olefin.

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