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THE PROTONATION AND HYDROGEN TRANSFER PROCESSES IN ALKENE AND ALKYNE DERIVATIVES OF $Os_3(CO)_{12}$ AND $H_2Os_3(CO)_{10}$

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Summary

The complexes $H_3Os_3(CO)_9CMe$, $H_2Os_3(CO)_{10}$, $H_2Os_3(CO)_9L$ (L = PEt_3, PPh_3 or $AsPh_3$), $HOs_3(CO)_{10}CH{=}C(H)Ph$, and $Os_3(CO)_{10}HC_2Me$ undergo protonation in acid to yield $[H_4Os_3(CO)_9CMe]^+$, $[H_3Os_3(CO)_{10}]^+$ and $[H_4Os_3(CO)_{10}]^{2+}$, $[H_3Os_3(CO)_9L]^+$, $[H_2Os_3(CO)_{10}CH{=}C(H)Ph]^+$ and $[HOs_3(CO)_{10}HC_2Me]^+$, respectively.

The structures of these ions and their hydrido-ligand transfer reactions are described.

Although a great deal of information is available on the synthesis and structure of compounds derived from the reactions of the clusters $M_3(CO)_{10}X_2$ (M = Ru or Os, X = CO; M = Os, X = H) or $H_4Ru_4(CO)_{12}$ with alkenes or alkynes [1], there is little information on their reactions. In a previous communication [2] we reported the protonation of $H_2M_3(CO)_9(C{=}CH_2)$ (I) to yield the stabilised carbonium ion derivatives $[H_3M_3(CO)_9(C{=}CH_2)]^+$ (VI). We now describe an extension of these studies to the cluster compounds II-V.

The inter-relationship between clusters I—V is shown in Scheme 1. The ease with which hydrido ligands can migrate within the metal framework and with which hydrogen can be gained or lost is fundamental to the understanding of the chemistry of these compounds. It was with this in mind that the protonation experiments described below were undertaken.

The complex $H_3Os_3(CO)_9CMe$ (II) does not undergo protonation in CF_3CO_2H nor is there any evidence of H—D exchange for solutions of II in CF_3CO_2D. However, the ^1H NMR spectrum of a solution of II in HSO_3F shows three high-field hydride signals at τ 22.85 (br) s, 26.62 s and 26.81 ppm (br) s with relative intensities 1 : 2 : 1 (Table 1). Integration against the methyl resonance shows that these three signals correspond to a total of four protons. The species present

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SCHEME 1. Alkene and alkyne derivatives of $Os_3(CO)_{12}$ and their inter-relationship.

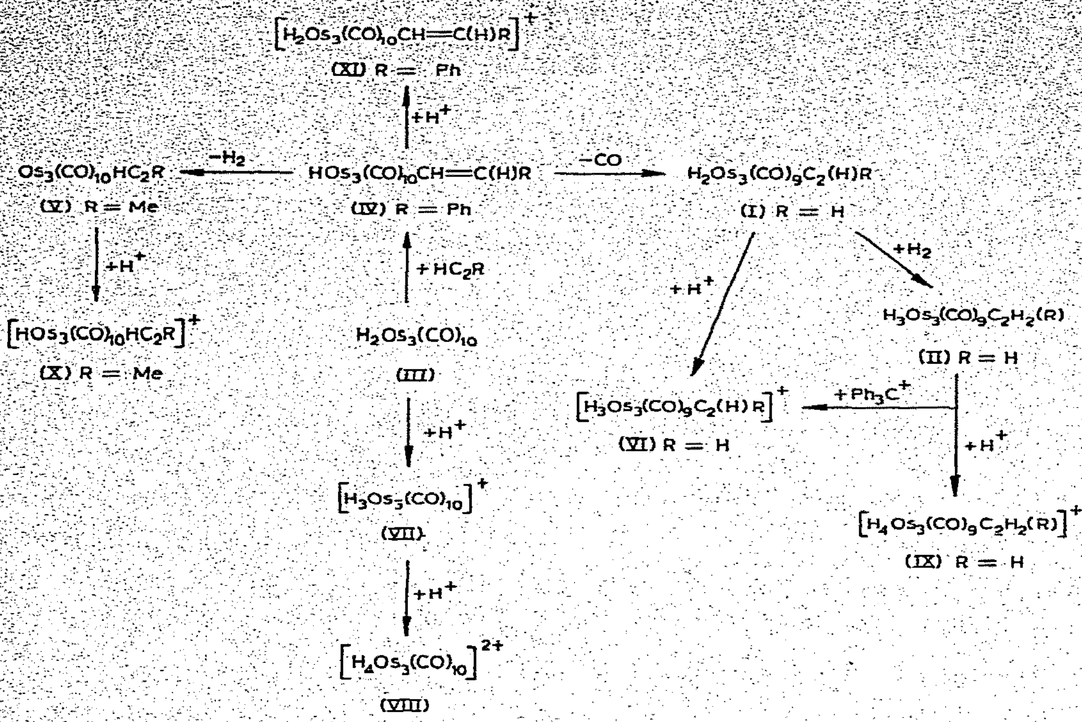


TABLE 1

^1H NMR SPECTRA OF PROTONATED SPECIES

Species	Solvent	Chemical shift τ [a] (ppm)
$[H_4Os_3(CO)_9CMe]^+$	HSO_3F (35°C)	4.65s (3H); 22.85(br)s (1H); 26.62s (2H); 26.81(br)s (1H);
$[H_3Os_3(CO)_{10}]^+$	CF_3CO_2H (35°C)	22.05(br)s, (2H); 24.20(br)s (1H)
$[H_4Os_3(CO)_{10}]^{2+}$	HSO_3F (35°C)	29.10s (4H)
$[H_3Os_3(CO)_9PEt_3]^+$	CD_2Cl_2/CF_3CO_2H (35°C)	21.18 (J(PH) 26.6 Hz); d (1H) 22.29 (J(PH) 6.3 Hz); d (1H) 24.41 (J(PH) 10.1 Hz); d (1H)
$[H_3Os_3(CO)_9PPh_3]^+$	CD_2Cl_2/CF_3CO_2H (35°C)	21.71 (J(PH) 4.4 Hz); d (1H) 21.93 (J(PH) 28.5 Hz); d (1H) 23.63 (J(PH) 9.3 Hz); d (1H)
$[H_3Os_3(CO)_9AsPh_3]^+$	CD_2Cl_2/CF_3CO_2H (35°C)	21.70s (1H) 22.90s (1H) 23.80s (1H)
$\overset{C,D}{H_2}Os_3(CO)_{10}[\overset{A}{CH}=\overset{B}{C}(H)Ph]^+$	CD_2Cl_2/CF_3CO_2H (40°C)	2.08dd ($1H^A$), $J(H^AH^B)$ 15 Hz, $J(H^AH^C)$ 2.5 Hz; 2.44s (5H), 3.50d ($1H^B$), $J(H^BH^A)$ 15 Hz; 27.78s ($1H^D$); 28.69d ($1H^C$), $J(H^CH^A)$ 2.5 Hz.
$[HOs_3(CO)_{10}HC_2Me]^+$	CD_2Cl_2/CF_3CO_2H (35°C)	2.81s (0.5 H); 3.04s (0.5 H); 7.58s (1.5H); 7.67s (1.5 H), 22.05s (1H)

[a] s, singlet; (br), broad; d, doublet; relative intensities in parentheses.

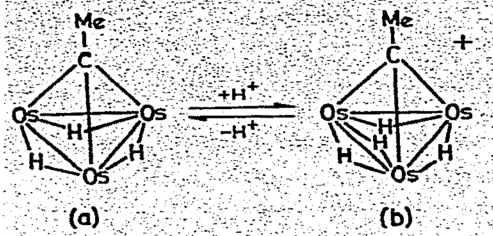


Fig. 1. Protonation of $H_3Os_3(CO)_9CMe$.

in solution is therefore considered to be $[H_4Os_3(CO)_9CMe]^+$ (IX). In the parent molecule II it is known [3] that the three hydrido ligands lie beneath the triangular plane of the three osmium atoms to form three Os—H—Os bridges (Fig. 1a). We therefore conclude that the incoming proton also bridges two osmium atoms to form a dihydrido-bridging system (Fig. 1b) similar to that postulated for $H_2Os_3(CO)_{10}$ [4]. Previously $H_2Os_3(CO)_{10}$ was the only example of such a bridging arrangement.

These observations led us to consider the protonation of the simple dihydrido species of $H_2Os_3(CO)_{10}$. This dihydride dissolves in cold trifluoroacetic acid to give a stable pale yellow solution. The ^1H NMR spectrum of this solution (Table 1) shows two high-field resonances at τ 22.05 (br) s, 2H and 24.20 ppm (br) s, 1H indicating that the species present is the trihydride $[H_3Os_3(CO)_{10}]^+$ (VII). In the stronger acid (HSO_3F) at the same temperature (35°C), a different NMR spectrum is obtained. In this case only one high-field signal is observed at τ 29.10 ppm s, 4H suggesting that a second protonation has occurred yielding $[H_4Os_3(CO)_{10}]^{2+}$ (VIII). The nature of these two ions is not clear since VIII is apparently fluxional whereas VII is not (at least at 35°C). In the parent molecule III one hydrogen is considered to lie above and one below the plane as shown in Fig. 2a, both bridge the same two osmium atoms Os(1) and Os(2). Therefore a possible struc-

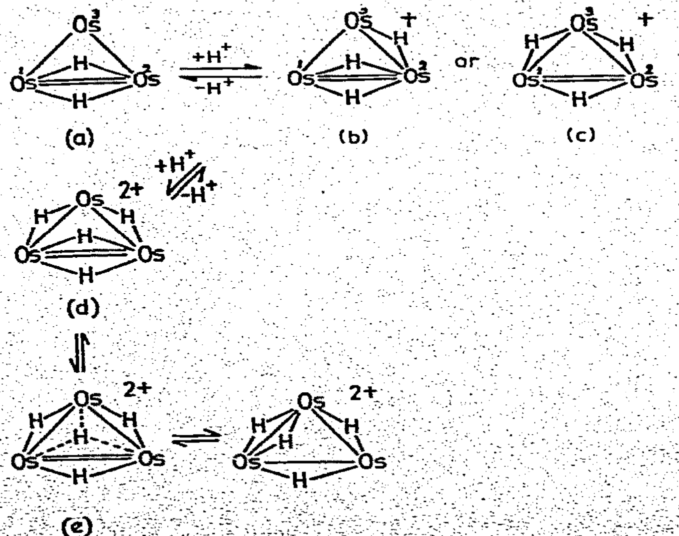
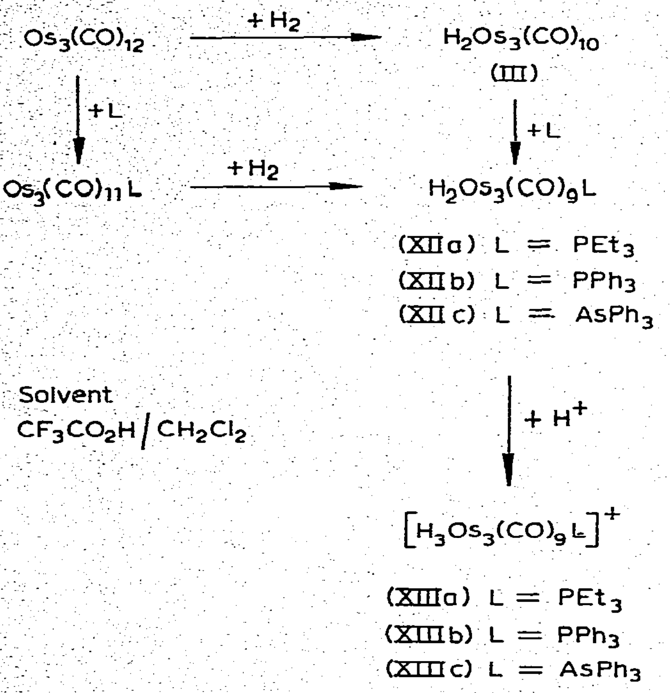


Fig. 2. Protonation of $H_2Os_3(CO)_{10}$ (carbonyl groups omitted for clarity).

ture for VII is that of Fig. 2b in which the incoming H^+ has attacked a vacant Os—Os edge. However, there is an alternative (Fig. 2c), which is also compatible with the observed spectrum. In this a proton is considered to be associated with each Os—Os edge, and would necessitate the transfer of one of the original hydrido ligands from the Os(1)—Os(2) edge to one of the two remaining edges Os(1)—Os(3) and Os(2)—Os(3). The transfer of groups within cluster units on protonation is not unusual and, for example, CO migration has been observed on protonation of $Os_3(CO)_{12}$ to yield $[HOs(CO)_5]^+$. In an attempt to differentiate between these two possibilities, we have examined the protonation of the monosubstituted complexes $H_2Os_3(CO)_9L$ [L = PEt_3 (XIIa); L = PPh_3 (XIIb) and L = $AsPh_3$ (XIIc)] which were prepared by the routes shown in Scheme 2, and have been

SCHEME 2. Preparation and protonation of $H_2Os_3(CO)_9L$ (L = PEt_3, PPh_3 or $AsPh_3$).



fully characterised by the usual analytical and spectroscopic techniques. The ^1H NMR spectrum of XIIa exhibits a doublet at τ 20.91 ppm (J(P—H) 6.9 Hz) which shows no temperature dependence over the range −60 to +60°C. This implies that the two hydrido ligands are equally disposed to the phosphine ligand which could occupy an equatorial position on Os(1) (Fig. 3); the ^{13}C NMR spectrum supports this view. Thus six signals are observed (Fig. 3, ppm relative to TMS): 186.7 (CO(a), 2), 185.3 (CO(b), 1), 184.6 (CO(c), 1), 183.4 (CO(d), 2), 180.1 (CO(e), 1) and 177.1 (CO(f), 2). The signal at 183.4 ppm shows coupling to the ^{31}P nuclei with J(P—C) 4 Hz. On ^1H decoupling, this signal and that at 177.1 ppm broaden and collapse, clearly indicating that these signals are associated with carbonyls CO(d) and CO(f). On addition of CF_3CO_2H to a solution of XIIa in CD_2Cl_2 the ^1H NMR spectrum changes and three

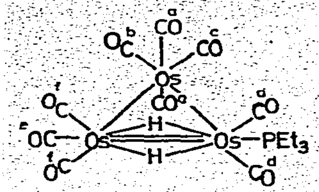


Fig. 3. Probable structure of $H_2Os_3(CO)_9PEt_3$. The assignments for CO(a), CO(d) and CO(f) are definite; those for CO(b), CO(c) and CO(e) are speculative.

doublets are observed in the high field region at τ 21.18 ppm (J(P—H) 26.6 Hz), τ 22.29 ppm (J(P—H) 6.3 Hz) and τ 24.41 ppm (J(P—H) 10.1 Hz). This information is best interpreted in terms of structure a of Fig. 4 in which each of the three hydrido ligands spans an edge of the Os_3 triangle. The alternative structure (Fig. 4b) would be expected to give rise to two hydrido signals only if the assumption is made that proton H(3) lies just about in the plane of the triangle. The corresponding PPh_3 and $AsPh_3$ derivatives show similar behaviour (Table 1). Structure a of Fig. 4 is obviously closely related to structure c of Fig. 2 and thus lends supports to our preference for structure 2c for $[H_3Os_3(CO)_{10}]^+$.

Some additional support for structure c of Fig. 2 comes from the behaviour of $H_2Os_3(CO)_{10}$ in CF_3CO_2D. Addition of CF_3CO_2D to $H_2Os_3(CO)_{10}$ in CD_2Cl_2 results in rapid and total exchange of H for D. Since the possibility of triprotonation of one Os—Os edge is remote, the most feasible mechanism of H—D exchange involves the rapid and reversible formation of an intermediate of a similar structure to Fig. 2e. The incoming D^+ which attacks one of the vacant Os—Os edges (say Os(2)—Os(3)) causes the displacement of one of the original H ligands from the Os(1)—Os(2) edge to the remaining vacant edge Os(1)—Os(3) giving rise to the intermediate of type c (Fig. 2). Loss of H^+ then occurs to produce $HDOs_3(CO)_{10}$ and so on.

The diprotonated species VIII may be considered to possess structure d of Fig. 2. Since there are no available vacant Os—Os edges in this structure, the fluxional behaviour that VIII undergoes is perhaps surprising because hydride transfer reactions in metal clusters are usually associated with the migration of the bridges to a vacant edge. However, equilibration could occur via a triply-bridging hydrido intermediate of type e shown in Fig. 2 as first postulated by Knight and Mays [6]. If this assumption is correct, then the rigidity of complex VII is more readily understood since such a mechanism might be expected to be less readily available to a species which can more easily attain a complete Os—H—Os edge bridging state (e.g. Fig. 2c). It might be argued on these grounds that a similar mechanism should be available to $[H_4Os_3(CO)_9CMe]^+$. This is so, but in this case proton migration to the centre

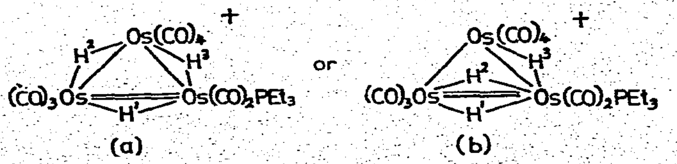


Fig. 4. Protonation of $H_2Os_3(CO)_9PEt_3$.

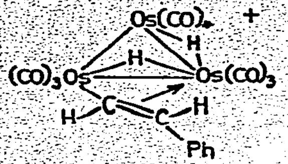


Fig. 5. Protonation of $HOs_3(CO)_{10}CH{=}C(H)Ph$.

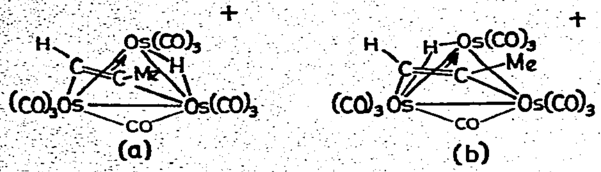


Fig. 6. Protonation of $Os_3(CO)_9CH{=}CMe$.

of the Os_3 triangular plane would be restricted to one face only, giving rise to a higher activation energy. Unfortunately, however, we are not able to examine the ^1H NMR spectrum of this compound over a higher temperature range. Addition of water to solutions of VII or VIII in acid causes the precipitation of the original complex III indicating that no major structural change in the $Os_3(CO)_{10}$ unit has occurred during these experiments.

The complex $HOs_3(CO)_{10}CH{=}C(H)Ph$ (IV) in CD_2Cl_2 readily undergoes protonation on addition of CF_3CO_2H. In the ^1H NMR spectrum, two resonances are observed in the high field region at τ 27.78 s, 1H and τ 28.69 ppm d, 1H. The pattern of hydrido signals (see Table 1) shows that (i) the two hydrido ligands are inequivalent and (ii) one proton couples to the $CH{=}C(H)Ph$ ligand. These and the other data (Table 1) indicate that the species present is $[H_2Os_3(CO)_{10}\text{-}CH{=}C(H)Ph]^+$ (XI) having the structure shown in Fig. 5 and that H^+ attack has occurred at the Os_3 unit rather than at the unsaturated organo-group.

The spectrum of the solution obtained by dissolving $Os_3(CO)_{10}CH{=}CMe$ (V) in CD_2Cl_2/CF_3CO_2H (2:1 v/v) (Table 1) is consistent with the formation of two isomeric species of formula $[HOs_3(CO)_{10}HC_2Me]^+$, possessing structures a and b of Fig. 6. In each case the incoming proton occupies an Os—Os edge. No evidence of H transfer was observed at +30°C.

Throughout this discussion we have not considered terminal Os—H intermediates but on the occasions that we envisage edge—edge transitions such a possibility may occur. Finally, these studies lead us to the following conclusions: (i) Protonation of these Os_3 clusters readily occurs in CF_3CO_2H provided that a vacant Os—Os edge is available; (ii) diprotonation can also occur even at an occupied edge but only in stronger acid, e.g. FSO_3H; (iii) in all cases protonation occurs on the metal unit and no evidence for H^+ addition to the bound organo-group has been found; and (iv) it would appear that a cluster containing more H ligands than polyhedral edges can undergo low energy fluxional behaviour thereby indicating that filled edge—vacant edge transitions are not the only mechanism that may operate.

Experimental

^{13}C and ^{1}H NMR spectra were recorded on a Varian Associates XL-100 spectrometer at 25.2 and 100 MHz respectively; chemical shifts are relative to Me_4Si. All compounds were prepared by published methods [7—10].

Acknowledgements

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