Interconversion and Degradation of Acyl and Enolato-ligands in Triosmium Clusters†

By Kazi A. Azam and Antony J. Deeming

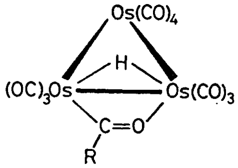
(*Department of Chemistry, University College London, 20 Gordon Street, London* WC1H 0AJ)

Summary The bridging acyl compounds $[HOs_3(COR)(CO)_{10}]$ (R = Ph, $PhCH_2$, n-C_5H_{11}, n-C_6H_{13}, or Pr^i), derived from aldehydes, and the bridging enolato-compounds $[HOs_3(OCH{=}CR_2)(CO)_{10}]$ (R = H, Me, or Ph), derived from ketens, give decarbonylated products at 150 °C, some by interconversion of these two forms.

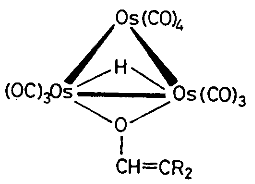
The ligand C_2H_3O can exist in the enolato ($M{-}OCH{=}CH_2$), the formylmethyl ($M{-}CH_2CHO$), the methoxycarbyne ($M{\equiv}C{-}OMe$), as well as the acyl (M–COMe) form, but previously the first three forms were not considered as being involved in the extensive transition metal chemistry of the acyl ligand. Our present results indicate that enolato-complexes should be seriously considered especially as possible intermediates in the reactions of metal carbonyl clusters containing acyls, for example in the hydroformylation of alkenes.[1]

$[Os_3(CO)_{12}]$, (I), reacts with various aldehydes in hydrocarbons at *ca.* 140 °C to give the bridging acyl compounds $[HOs_3(COR)(CO)_{10}]$, (II; R = Ph, $PhCH_2$, n-C_5H_{11}, n-C_6H_{13}, or Pr^i) in low to moderate (40%) yields.‡ The corresponding reaction with formaldehyde gives $[HOs_3(OMe)(CO)_{10}]$, presumably *via* compound (II, R = H) which is readily decarbonylated to $[H_2Os_3(CO)_{10}]$. We have indeed shown that formaldehyde reacts with this dihydride to give the methoxo-compound. Acetaldehyde also does not give (II) but only the same acetato-compound as formed from acetic acid.[2] Spectroscopic analysis (i.r., mass, and ^1H n.m.r.) of compounds (II) indicates the structure shown. In particular the lack of ν(CO) (acyl) above 1500 cm^{-1} implies a bridging mode for the acyl [for example: R = pentyl, ν(CO)(acyl) 1493 and 1479 cm^{-1} (Nujol)], and the AB quartet for CH_2Ph (up to 30 °C) and two sharp well resolved doublets for $CH(CH_3)_2$ (up to 120 °C) in the ^1H n.m.r. spectra show that the bridging ligand does not rapidly exchange between the two bridged osmium atoms as does the vinyl group in $[HOs_3(CH{=}CH_2)(CO)_{10}]$.[3]

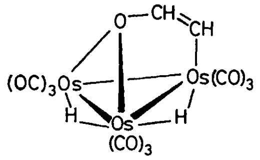
Compound (II, R = Pr^i) reacts with CO at 150 °C to give exclusively Pr^iCHO and (I).



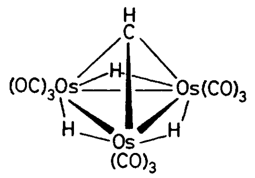
(II)



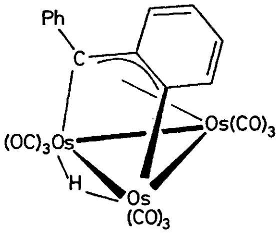
(III)



(IV)



(V)



(VI)

In an attempted alternative preparation of (II, R = Me), reaction of keten with $[H_2Os_3(CO)_{10}]$ gave $[HOs_3(OCH{=}CR_2)(CO)_{10}]$, (III, R = H) [$^1H$ n.m.r., $CDCl_3$, 30 °C: four equal intensity signals at δ 5·90dd, 3·98dd, 3·82dd, and

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† No reprints available.

‡ All new compounds gave parent molecular ions in their mass spectra and, except for a few contaminated by high-boiling hydrocarbons, satisfactory elemental analysis.

$-12{\cdot}35$s; J_{gem} 2·4, J_{cis} 5·8, and J_{trans} 13·0 Hz]. Similar compounds [III, R = Me (60%) or Ph (41%)] were also prepared from the corresponding substituted ketens. Compound (III, R = Me) smoothly and completely isomerises in [$^2H_8$]toluene at 150 °C in a sealed n.m.r. tube to compound (II, R = Pr^i).

While we have no direct evidence for thermal conversion of acyl into enolato ligands, compounds (II) can give decarbonylated products derived from the isomeric compounds (III) and *vice versa*. For example, compound (III, R = H) gives, in cyclohexane (81 °C; 65 h), traces of its isomer (II, R = Me) [^{1}H n.m.r., $CDCl_3$, 30 °C: $\delta(CH_3)$ 2·20s, $\delta(OsH)$ $-13{\cdot}93$s] and [$H_2Os_3(OCH{=}CH)(CO)_9$], (IV), formed by hydrogen atom transfer from the β-carbon of the enolato ligand, while the major product is [$H_3Os_3(CH)(CO)_9$], (V), [^{1}H n.m.r., $CDCl_3$, 30 °C: $\delta(CH)$ 9·27q, $\delta(OsH)$ $-19{\cdot}43$d, J 1·2 Hz] formed by decarbonylation of (II, R = Me) to give [$HOs_3Me(CO)_{10}$] as the most probable intermediate. Compounds (IV) and (V) are formed similarly from (II, R = Me), but (V) is not formed from (IV) even on extended heating at 150 °C. Other acyl compounds also give products apparently derived from the corresponding enolato form. Thus, compounds (II, R = $PhCH_2$, n-C_6H_{13}, or n-C_5H_{11}) give, by decarbonylation, [$H_2Os_3(OC_2HR')(CO)_9$] (R′ = Ph, n-C_5H_{11}, or n-C_4H_9) which are the direct analogues of compound (IV). The order of atoms of the ligand OCHCH in (IV) is known but not its mode of attachment to the metal atoms; the structure shown is only a possibility. Other products are formed by decarbonylation of acyl ligands: [$H_2Os_3(C_6H_4)(CO)_9$][4] from (II, R = Ph) and [$HOs_3(PhCC_6H_4)(CO)_9$], (VI), from (III, R = Ph) presumably by an initial isomerisation to its acyl isomer. Compound (VI) appears to be structurally equivalent to the known ruthenium compound.[5]

We are still trying to identify factors determining whether reaction takes place through forms (II) or (III) but clearly both isomers are important in this chemistry.

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