Journal of Organometallic Chemistry, 198 (1980) C7—C10

Preliminary communication

FURTHER STABLE MODELS FOR CATALYTIC INTERMEDIATES. *cis*-HYDRIDO(ACETYL)-, *cis*-HYDRIDO(METHYL)-, AND *cis*-HYDRIDO(HYDROXYMETHYL)-OSMIUM(II) COMPLEXES

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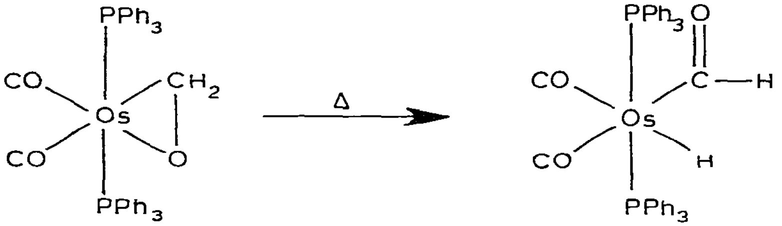
(Received July 8th, 1980)

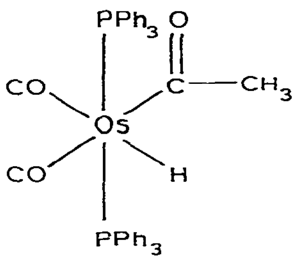
Summary

The synthesis and characterisation of the molecules *cis*-$OsH(CH_3CO)(CO)_2(PPh_3)_2$, *cis*-$OsH(CH_3)(CO)_2(PPh_3)_2$ and *cis*-$OsH(CH_2OH)(CO)_2(PPh_3)_2$, each of which models an intermediate postulated to occur in one of several metal-catalysed processes, are described.

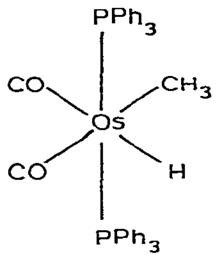
Transition metal complexes which have as a pair of adjacent ligands, a hydride and a carbon-bound ligand (alkyl, substituted alkyl, or acyl), are frequently discussed catalytic intermediates, but the examples of this type which have been thoroughly characterised are few in number [1]. This is because of the ease with which most of these compounds undergo reductive-elimination reactions (this reactivity is also the key to the catalytic effectiveness of these molecules), either by intramolecular [2] or intermolecular [1] mechanisms. We have recently described an osmium(II) complex with adjacent hydride and formyl ligands which arose from rearrangement of a *dihapto*-formaldehyde complex, $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ [3].



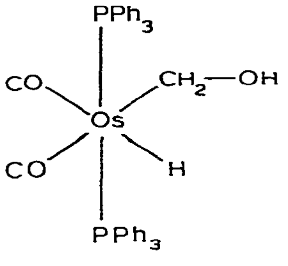
Both of the above compounds have relevance as models for intermediates involved in carbon monoxide hydrogenation. In an extension of this work we now describe three further molecules with a *cis*-arrangement of hydride and carbon-bound ligand. These are *cis*-hydrido(acetyl)dicarbonylbis(triphenylphosphine)osmium(II) (compound I); *cis*-hydrido(methyl)dicarbonylbis(triphenylphosphine)osmium(II) (compound II); *cis*-hydrido(hydroxymethyl)dicarbonylbis(triphenylphosphine)osmium(II) (compound III).



(I)



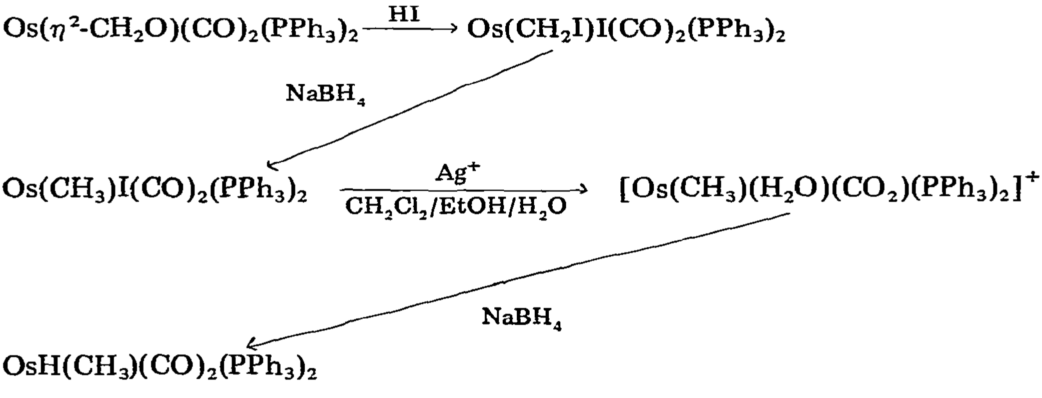
(II)



(III)

I results from the reaction of $Os(CO)_2(PPh_3)_3$ [4] with excess acetaldehyde in benzene solution under a tungsten-halogen lamp. The reaction occurs more slowly than with formaldehyde and no intermediate η^2-aldehyde complex is apparent as in the case with formaldehyde, the reaction instead proceeding directly to I. IR and ^1H NMR data for compounds I, II and III are presented in Table 1. Heating I in toluene under reflux for 1.5 hours leads to the formation of an intractable mixture which, nonetheless, contains significant amounts of $Os(CO)_3(PPh_3)_2$ (by IR spectrum) suggesting that some reductive elimination of methane has occurred. Thus I models the intermediates involved in the decarbonylation of aldehydes by complexes such as $RhCl(PPh_3)_3$ [5]. Other examples of *cis*-hydrido(acyl) compounds are confined to several tungsten compounds e.g., $WH(CH_3CO)(\eta^5\text{-}C_5H_5)_2$ [6], a partially characterised and unstable iridium compound $IrH(COEt)Cl(CO)(PPh_3)_2$ [7] and several compounds in which the acyl function is part of a chelating ligand [8].

II results from the following reaction sequence [9].



$$\begin{tikzcd}
Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \arrow[r, "HI"] & Os(CH_2I)I(CO)_2(PPh_3)_2 \arrow[dl, "NaBH_4"'] & \\
Os(CH_3)I(CO)_2(PPh_3)_2 \arrow[r, "Ag^+", "CH_2Cl_2/EtOH/H_2O"'] & {[Os(CH_3)(H_2O)(CO_2)(PPh_3)_2]^+} \arrow[dl, "NaBH_4"] & \\
OsH(CH_3)(CO)_2(PPh_3)_2 & &
\end{tikzcd}$$

(II)

II is a phosphine-substituted derivative of the very unstable $OsH(CH_3)(CO)_4$. Studies by Norton [1] have demonstrated that the instability of $OsH(CH_3)(CO)_4$ is a consequence of the availability of a facile dinuclear elimination

TABLE 1

IR [a] AND ^{1}H NMR DATA FOR OSMIUM HYDRIDES

Compound [b]	ν(CO) (cm^{-1})	ν(Os—H) (cm^{-1})	Chemical shift (τ) [c]
$OsH(CH_3CO)(CO)_2(PPh_3)_2$ I	2025, 1975 1585 (acetyl)	1907	15.08, t, 1H, Os—H, ^2J(H—P) = 20.5 Hz 8.87, s, 3H, CH_3CO
$OsH(CH_3)(CO)_2(PPh_3)_2$ II	2005, 1958	1890ms	16.72, t, 1H, Os—H, ^2J(H—P) = 23.5 Hz 10.68, dt, 3H, $—CH_3$, ^3J(H—P) = 8.0 Hz ^3J(H—H) = 2.5 Hz
$OsH(CH_2OH)(CO)_2(PPh_3)_2$ III	2020, 1965	1910	16.48, t, 1H, Os—H, ^2J(H—P) = 21.2 Hz 8.43, s, 1H, —OH 6.07, t, 2H, $—CH_2$-OH, ^3J(H—P) = 9.0 Hz

[a] Measured as Nujol mulls; all bands strong unless indicated otherwise. [b] Satisfactory elemental analyses obtained for all compounds. [c] In $CDCl_3$ solution.

mechanism. Such a process can presumably be blocked by the two bulky triphenylphosphine ligands in II. II is an air-stable solid with m.p. 173—177°C.

Whereas an excess of HX (X = Cl, Br, I) with $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ leads to the halomethyl compounds $Os(CH_2X)X(CO)_2(PPh_3)_2$ as described above, one equivalent of acid leads to formation of the intermediate hydroxymethyl compounds. Thus $Os(CH_2OH)Cl(CO)_2(PPh_3)_2$ results from $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ with one equivalent of HCl. Reduction of the hydroxymethyl ligand to a methyl group using $NaBH_4$ has been demonstrated by Graham for the rhenium compound $Re(CH_2OH)(CO)(NO)(\eta^5\text{-}C_5H_5)$ [10]. Reaction of $Os(CH_2OH)Cl(CO)_2(PPh_3)_2$ with $NaBH_4$ in CH_2Cl_2-EtOH, however, results in hydride substitution at osmium yielding the novel hydrido(hydroxymethyl) complex $OsH(CH_2OH)(CO)_2(PPh_3)_2$ (compound III). The IR spectrum shows ν(OH) as a sharp band of medium intensity at 3560 cm^{-1} which is shifted to 2630 cm^{-1} (m, sharp) in the D_2O-exchanged sample. This compound provides a good example not only of the elusive hydroxymethyl ligand, previously reported only for $Re(CH_2OH)(CO)(NO)(\eta^5\text{-}C_5H_5)$ [10,11], but in addition, with the adjacent hydride ligand III precisely models the sort of intermediate often postulated [12] in the last step of the reduction of CO to MeOH. However, the stability of III is such that heating under reflux in degassed toluene in the presence of excess PPh_3 for 2 hours fails to promote a clean reductive elimination of methanol and leads to an intractable mixture of products.

We thank the New Zealand Universities Grants Committee for grants towards instrumental facilities and the award of a Postgraduate Scholarship to C.E.L.H.

References

1 J.R. Norton, Accounts Chem. Res., 12 (1979) 139.
2 L. Abis, A. Sen and J. Halpern, J. Amer. Chem. Soc., 100 (1978) 2915.
3 K.L. Brown, G.R. Clark, C.E.L. Headford, K. Marsden and W.R. Roper, J. Amer. Chem. Soc., 101 (1979) 503.
4 B.E. Cavit, K.R. Grundy and W.R. Roper, J. Chem. Soc. Chem. Commun., (1972) 60; D.H. Farrar, K.R. Grundy, N.C. Payne, W.R. Roper and A. Walker, J. Amer. Chem. Soc., 101 (1979) 6577.
5 J. Tsuji, in I. Wender and P. Pino (Ed.), Organic Syntheses via Metal Carbonyls, Vol. 2, Wiley, New York, 1977, p. 595.

6 B.R. Francis, M.L.H. Green, T. Luong-thi and G.A. Moser, J. Chem. Soc. Dalton, (1976) 1339.
7 G. Yagupsky, C.K. Brown and G. Wilkinson, J. Chem. Soc. (A), (1970) 1392.
8 J.W. Suggs, J. Amer. Chem. Soc., 100 (1978) 640; T.B. Rauchfuss, J. Amer. Chem. Soc., 101 (1979) 1045.
9 C.E.L. Headford and W.R. Roper, details to be published.
10 J.R. Sweet and W.A.G. Graham, J. Organometal. Chem., 173 (1979) C9.
11 C.P. Casey, M.A. Andrews, D.R. McAlister and J.E. Rinz, J. Amer. Chem. Soc., 102 (1980) 1927.
12 E.L. Muetterties and J. Stein, Chem. Rev., 79 (1979) 479.