Hydrogenation and Fluxional Behaviour of $H_2Os_3(CCH_2)(CO)_9$, a Vinylidene Complex derived from Ethylene

By ANTONY J. DEEMING* and MARK UNDERHILL

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

Summary Preliminary crystallographic data for the complex $H_2Os_3(CCH_2)(CO)_9$ derived from ethylene and $Os_3(CO)_{12}$ are given and the mechanisms of its fluxional behaviour and hydrogenation to give $H_3Os_3(CCH_3)(CO)_9$ are discussed.

RECENTLY we have reported the reaction of ethylene with $Os_3(CO)_{12}$ to give the compound $H_2Os_3(CCH_2)(CO)_9$.[1] In the ^1H n.m.r. spectrum, the lack of coupling between the non-equivalent hydrogens on the organic ligand suggested that the complex contained co-ordinated vinylidene (CCH_2) rather than co-ordinated acetylene (HCCH) which would have been analogous to the ligands formed from cyclic mono-olefins and $M_3(CO)_{12}$ (M = Ru or Os).[2] This has now been confirmed by an *X*-ray study[3] and preliminary data are given in the Figure. All three Os–Os bonds are different and the C_2 fragment is tilted away from the shortest of these bonds [$\angle$Os(1)–C(1)–C(2), 138°; $\angle$Os(2)–C(1)–C(2), 124°]. The positions of the hydrido-ligands have not been determined but they give separate signals in the ^1H n.m.r. spectrum. Because of this and the asymmetry of the molecule we suggest either structure (A) or (B). The bonding of the vinylidene group may be most simply envisaged as involving C(1)–Os(1) and C(1)–Os(2) σ-bonds and a simple mono-olefin type interaction between C(1), C(2), and Os(3).

The molecule is fluxional[1] with the exchange of H_c with H_d (E_a 20·4 kcal mol.$^{-1}$, $\Delta S^\ddagger$ 7·7 cal K^{-1} mol^{-1}; incorrectly quoted in ref. 1) occurring at a faster rate than that of H_a with H_b. For structure (A) alone a likely mechanism is the movement of H_b to the non-hydrogen-bridged Os–Os bond and thereby giving H_c–H_d exchange without H_a–H_b exchange, but hydride migrations would not readily explain the fluxional behaviour for structure (B). H_c–H_d exchange by movement of the ligand atoms with respect to the osmium triangle could also explain these data but we feel that this is less attractive since it requires dissociation of the Os(3)–ligand bond.

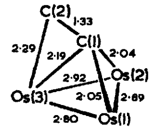
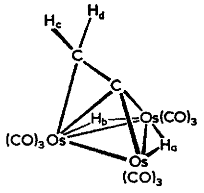
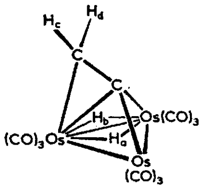


FIGURE. *Preliminary crystallographic data for the* Os_3C_2 *skeleton of* $H_2Os_3(CCH_2)(CO)_9$.



(A)



(B)

A nearly quantitative conversion into the ethylidyne complex $H_3Os_3(CCH_3)(CO)_9$ occurs on bubbling H_2 through a refluxing n-heptane solution of $H_2Os_3(CCH_2)(CO)_9$ (24 h). This product is the osmium analogue of $H_3Ru_3(CCH_3)(CO)_9$

prepared from α-$H_4Ru_4(CO)_{12}$ and ethylene,[4] and similarly shows two singlets of equal intensity in the ^1H n.m.r. spectrum (τ 5·55 and 28·58; $CDCl_3$). From a similar reaction of $H_2Os_3(CCH_2)(CO)_9$ with D_2 (n-octane; 24 h) we isolated a partially deuteriated ethylidyne complex, which was shown by its mass spectrum to contain $Os_3C_2H_4D_2(CO)_9$ together with significant quantities of $Os_3C_2H_3D_3(CO)_9$ and $Os_3C_2H_2D_4(CO)_9$. The ^1H n.m.r. spectrum is very similar to that of the H_2-adduct except that the methyl signal is broader and the ratio of intensities of methyl to hydride signals is 0·67 ± 0·01. Thus, as well as D_2-addition, there is considerable intermolecular exchange with D_2 and surprisingly this occurs preferentially at the organic ligand. This probably indicates that D_2-attack can occur at the ligand.

We thank the S.R.C. for a research studentship for M.U. and Johnson-Matthey Ltd. for a loan of osmium tetroxide.

(*Received, 5th March* **1973**; *Com.* **306.**)

[1] A. J. Deeming and M. Underhill, *J. Organometallic Chem.*, 1972, **42**, C60.
[2] A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **43**, C35.
[3] R. Baker, personal communication.
[4] A. J. Canty, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, 1972, 1331.