Journal of Organometallic Chemistry, 159 (1978) C1—C4

Preliminary communication

THE INDIRECT LOCATION OF HYDRIDE LIGANDS IN METAL CARBONYL CLUSTERS

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(Received July 26th, 1978)

Summary

A semi-empirical method of predicting the location of hydride ligands in metal carbonyl cluster compounds using X-ray structural information is described. The hydride positions thus derived are compared with those obtained from neutron diffraction experiments and predictions made for previously ambiguous cases.

Direct location of hydride ligands in metal cluster compounds from X-ray data alone is difficult and the degree of precision attainable low. Accurate hydride positions may be obtained from neutron diffraction data but there are experimental problems, e.g. a large crystal must be grown. The stereochemical activity of the hydride ligand is well recognised and is clearly observable from X-ray structure determinations. Qualitative methods which have been used to predict hydride postions include electron counting, metal—metal bond lengths and other criteria [1,2].

The quantitative approach described here finds optimised hydride positions, given X-ray structural parameters for non-hydrogen atoms, such that the hydride is bonded to 1, 2 or 3 metal atoms at specified bond lengths. The optimised positions are at suitable minima of a "potential energy" defined by intramolecular non-bonded interactions between the hydride and other atoms. The potential function used is:

$$V(r) = ae^{-br}/r^{d} - c/r^{6}$$

where r is the interatomic distance and a, b, c and d are taken from ref. 3 or estimated; simpler functions (e.g. of the form $V(r) = a/r^6$) give hydride positions of similar accuracy.

Although there is evidence for variation in hydride "size" in certain environments [1], we find that terminal, μ_2 and μ_3 hydride sites in carbonyl clusters have similar "potential energies" as defined above. We allow for the interaction between hydride ligands (if several are known to be present) in order to ensure the compatability of proposed sites.

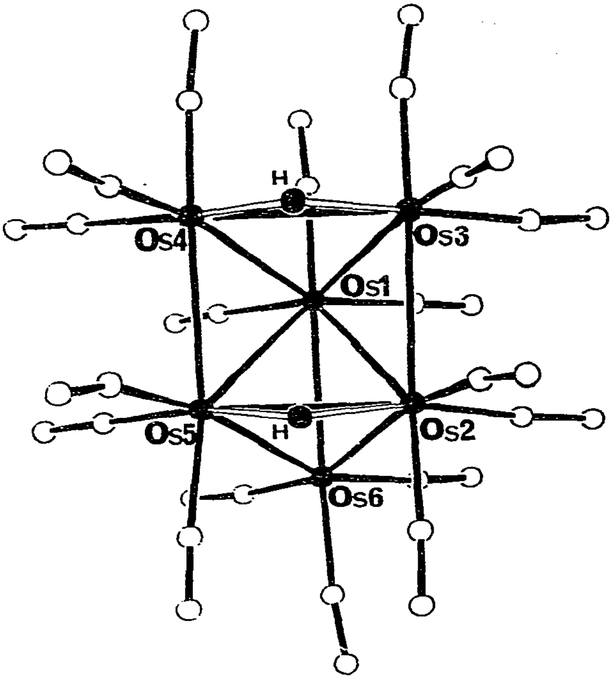

Fig. 1. $H_2Os_6(CO)_{18}$, showing predicted hydride locations for Os—H 1.85 Å. Os—Os bond lengths from ref. 6: Os(1)—Os(3) 2.849 Å, Os(1)—Os(4) Å 2.851, Os(2)—Os(3) 2.868 Å, Os(3)—Os(4) 2.965 Å, Os(4)—Os(5) Å, Os(2)—Os(5) 2.892 Å.

TABLE 1

POTENTIAL ENERGIES FOR POSSIBLE HYDRIDE POSITIONS

Compound	Atoms bonded to hydride			Site energy[a]
$H_2Os_6(CO)_{18}$	Os(2),	Os(5)		5.2
	Os(3),	Os(4)		4.5
	Os(2),	Os(3)		27.3
	Os(4),	Os(5)		28.0
	Os(3)[b]			85.3
	Os(4)[b]			43.6
	Os(1),	Os(3),	Os(4)[b]	81.5
$H_3Os_4(CO)_{11}C_6H_9$	Os(1),	Os(3)		3.3
	Os(2),	Os(4)		4.3
	Os(1),	Os(4)		5.2
	Os(1),	Os(2)		33.7
	Os(2),	Os(3)		37.9
	Os(3),	Os(4)		64.7

[a] Energies not on an absolute scale. [b] Sites suggested in refs. 6 and 7, all other terminal, μ_2 and μ_3 sites were also at unreasonably high energies.

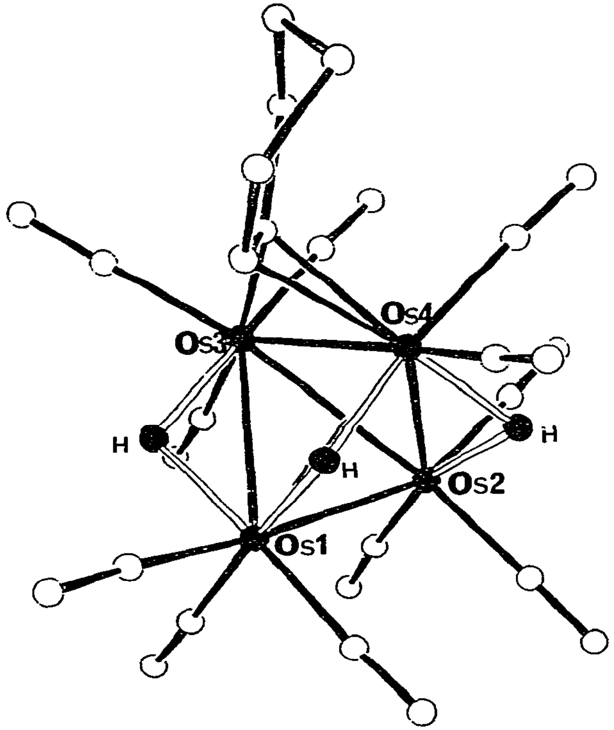

Fig. 2. $H_3Os_4(CO)_{11}C_6H_9$, showing predicted hydride location for Os—H 1.85 Å. Os—Os bond lengths from ref. 8: Os(1)—Os(2) 2.794 Å, Os(1)—Os(3) 2.984 Å, Os(1)—Os(4) 2.953 Å, Os(2)—Os(3) 2.938 Å. Os(2)—Os(4) 2.817 Å, Os(3)—Os(4) 2.793 Å.

The procedure has been tested for a number of neutron diffraction structures of metal carbonyl hydrides ($HMn(CO)_5$, $HFeCo_3(CO)_9[P(OMe)_3]_3$, $HW_2(CO)_9NO$, $HW_2(CO)_8NO[P(OMe)_3]$, $HMo_2(PMe_2)(C_5H_5)_2(CO)_4$, $HRu_3(CO)_9(C{\equiv}CBu\text{-}t)$, $HOs_3(CO)_{10}C_2H_3$, $H_2Os_3(CO)_{10}$, $H_2Os_3(CO)_9S$) [4] with good agreement: all predicted positions are within 0.1 Å of those directly located. Good qualitative agreement has been obtained with all of a larger number of X-ray studies where direct (if imprecise) location of hydrides was possible (notably $H_3Mn_3(CO)_{12}$ and $H_2Os_3(CO)_{10}PPh_3$ [5] and others in ref. 2).

Application of this procedure to clusters of higher nuclearity has produced unambiguous results in cases where hydride positions were not previously clear. For example in $H_2Os_6(CO)_{18}$ various hydride sites have been suggested [6,7]. By the above method we predict two μ_2 sites on opposite edges of the base of the capped tetragonal pyramidal cluster (Fig. 1). For $H_3Os_4(CO)_{11}C_6H_9$ [8] three μ_2 sites are predicted, but not on the three longer edges of the tetrahedral cluster (Fig. 2). In all examples studied there is a very clear differentiation between the energies of actual hydride sites and those of all other optimised hypothetical sites, as illustrated in Table 1.

We thank B.P. Ltd. and Gonville and Caius College, Cambridge for financial support. The calculations were carried out on the Cambridge University IBM 370/165 computer with programmes written by the author.

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