Indirect Location of Hydride Ligands in Metal Cluster Complexes

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A quantitative procedure for indirectly locating hydride ligands bound to transition metals in cluster compounds is described. The method predicts hydride positions which can be and are compared with those determined by neutron (and *X*-ray) diffraction. Examples are presented of its use in determining hydride sites in cases where these ligands could not be located directly in the *X*-ray structure analysis. These results are contrasted to those obtained by other indirect techniques of hydride location.

VARIOUS techniques have been used to predict hydride positions in cluster compounds where direct location of the hydride ligands has proved impossible on the basis of *X*-ray crystallographic results. These qualitative techniques have relied on criteria such as metal–metal bond lengths,[1] electron counting,[2] ligand orientation,[3,4] and analysis of the ligand polyhedron [5-7] associated with the cluster. Potential-energy evaluations of hydride positions in mononuclear complexes have been used,[8] and this technique applied to a cluster complex.[9]

The stereochemical influence of the hydride ligand in transition-metal complexes has become well recognised; [10-13] it has been shown that hydride ligands occupy distinct co-ordination sites on metal atoms, and that they have finite steric requirements. These features of the behaviour of hydride ligands have been most clearly characterised by recent neutron-diffraction experiments.[13] Hydride ligands are frequently not located in the course of *X*-ray structure analyses of transition-metal hydride complexes, but the stereochemical influence of the hydride may still be revealed by examination of the non-hydrogen framework of the complex.

Hydride ligands have been found to occupy distinct co-ordination sites on metal atoms; they show metal–hydrogen bond lengths in the range 1.6—2.0 Å. In the case of bridging hydrides, the bridged M–M distance is typically *ca.* 0.15 Å longer than for the analogous unbridged M–M bond. These features permit a more quantitative approach to the indirect location of hydride ligands. The method described here uses a 'potential-energy' technique, similar to that independently developed by Ciani and co-workers [8,14] in order to define the most likely site for a hydride ligand in a cluster.

A computer program has been written which optimises hydride positions with specified connectivity. Thus, given the *X*-ray-determined spatial co-ordinates for the non-hydrogen framework of the cluster, it is possible to evaluate various postulated hydride sites on the cluster. The hydrogen may be bonded to 1, 2, or 3 metal atoms at specified bond lengths. Optimum positions are found for each postulated hydride site by minimisation of the potential energy of the intramolecular non-bonded interactions involving the hydride. Constraints are applied to ensure appropriate derived M–H bond lengths. The resultant potential energy enables a quantitative comparison to be made of the various possible hydride locations on the cluster.

TECHNIQUE

The information required by this procedure falls into four categories: (*i*) *X*-ray-determined atomic positional parameters for all non-hydrogen atoms within the cluster; (*ii*) parameters describing the non-bonded interactions between the hydride(s) and all other atomic types present in the cluster; (*iii*) the nature of the sites to be investigated, *i.e.* their connectivity (terminal, μ, or μ_3), and the atoms to which the hydride is thought to be bonded; and (*iv*) metal–hydride bond lengths appropriate to these sites, and permissible variations in these bond lengths.

The potential energy of a particular position is given by the sum of terms $V(r)$ [equation (1)] over all intramolecular non-bonded contacts involving the hydride in question; here $V(r)$ is in kcal mol^{-1},† r (in Å) is the interatomic separation

$$V(r) = \frac{a\exp(-br)}{r^d} - \frac{c}{r^6} \qquad (1)$$

involved, and a, b, c, d are dependent on the atomic type of the second atom in the H $\cdots$ X contact. The parameters which have been used in the work described below are given in Table 1 and are adapted from ref. 15. It should be noted that these parameters were initially developed in order to predict organic crystal structures and conformations. It is therefore unlikely that the given values for contacts of hydrogen with other atoms are a true reflection of the potential energies of the hydride non-bonded interactions, because of the differing steric requirements of alkyl and hydridic hydrogens. Nevertheless these parameters do serve to place the hydride's interaction with various atomic types on a common (if arbitrary) scale. Improvements in the parameters have not been necessary or possible as yet, but may be desirable in the future (see below). The M–H distances used in this work are given in Tables 2—4 and are taken from the neutron-

TABLE 1

Parameters used in calculation of non-bonded potential energies of interaction

Contact	*a*	*b*	*c*	*d*
Hydride	6 600	4.08	49.2	0
Carbon	44 800	2.04	125.0	6
Oxygen	42 000	2.04	132.7	6
Nitrogen	52 100	2.04	132.0	6
P/S	40 500	3.851	265.2	0
Metal	43 500	3.54	540	0

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† Throughout this paper: 1 cal = 4.184 J; all energies are given in kcal mol^{-1} multiplied by an arbitrary constant scale factor.

diffraction literature.[13] Where this is not possible values have been extrapolated on the assumption that M–H bond lengths follow the usual trends in metallic covalent radii.[16,17]

Given these appropriate input data the procedure adopted is as follows: 26 initial estimates of the hydride position are generated in a 3 × 3 × 3 grid around the atom or atoms to which the hydride is postulated to be bound. These positions are refined by minimisation of a function, M [equation (2)], where the first summation is over all

$$M = \sum_i V(r_i) + \sum_k |(R_k - R)/S|^2 \qquad (2)$$

atoms within *ca.* 3.5 Å (exact radius chosen by the program for optimum efficiency) but not bonded to the hydride, and the latter summation is over atoms to which the hydride must be bonded; R_k is the interatomic distance to the kth of these atoms where R is the specified M–H distance and S the permissible error in this (usually *ca.* 0.05 Å). The function M is minimised by a conjugate-gradient technique adapted from that of Fletcher and Reeves.[18] This technique finds local minima of the function M for each of the 26 starting positions. The minimum obtained is rejected if unacceptable, *i.e.* if the M–H bond length is too far from that specified, or if there are unrealistically short non-bonded contacts. The acceptable minima are grouped into unique sets, each unique site further optimised, and the potential energy of each site is determined.

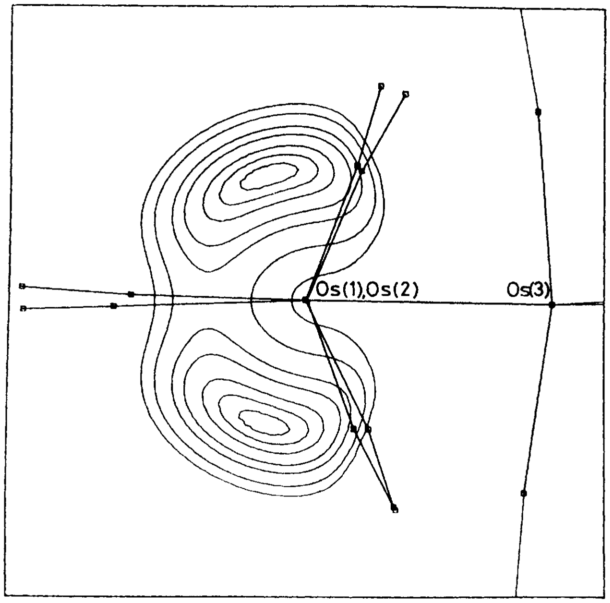

FIGURE 1 Contoured values of potential-energy function M [equation (2)], in the plane through the hydrides for $[Os_3H_2(CO)_{10}]$, with the X-ray determined non-hydrogen framework

The conjugate-gradient technique is especially appropriate because it is local minima that are of interest in this procedure. For instance, if there are several hydrides bridging an edge of a cluster, *e.g.* in $[Os_3H_2(CO)_{10}]$ (see below), multiple potential-energy minima will be associated with that cluster edge. The large number of initial hydride positions refined ensures location of all separated local minima. The best sites located on a cluster may be co-refined to allow for the interaction between neighbouring hydrides. By this means a self-consistent set of hydride positions may be generated in cases where several hydrides are known to be present (from spectroscopic or chemical evidence).

A contour plot of the function M, for an appropriate plane through the cluster, provides a useful visual check on the shape and singularity of the minima located. Figure 1 shows the contoured values of the function associated with the doubly bridged edge of $[Os_3H_2(CO)_{10}]$. An M–H bond length of 1.85(5) Å and potential-energy parameters as given in Table 1 were used. The plotted contours are for values of M in the plane perpendicular to, and bisecting, the bridged Os(1)–Os(2) vector, the X-ray-determined atomic positions are shown projected on to this plane. Figure 2 shows the neutron-determined structure of this compound [19] in a similar orientation. In this case the initial search for a bridging hydride on the Os(1)–Os(2) edge of the metal triangle yields two minima of approximately equal energy very close to the observed hydrogen positions (see Table 2).

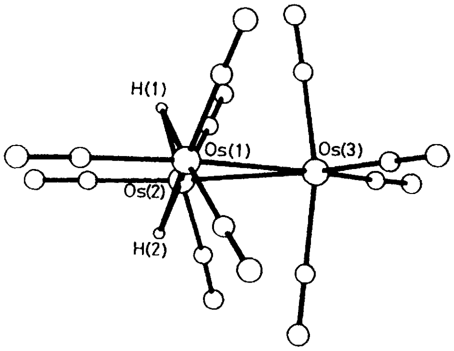

FIGURE 2 Neutron-determined structure of $[Os_3H_2(CO)_{10}]$ [19]

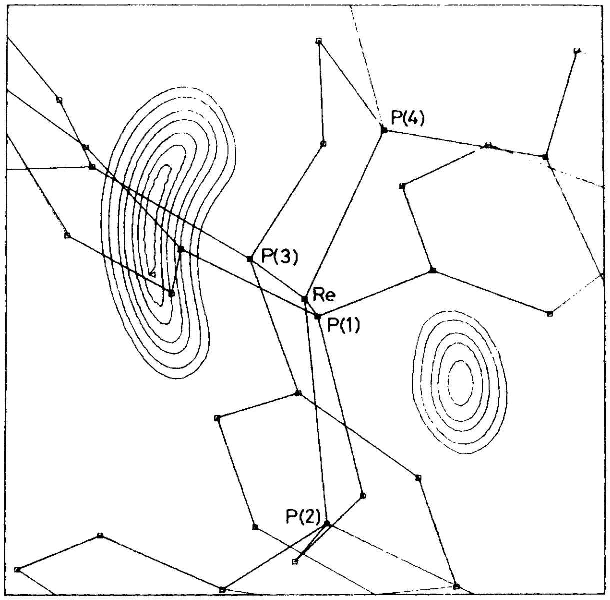

FIGURE 3 Contoured values of the potential-energy function M, in the hydride-containing plane of $[ReH_3(dppe)_2]$ with the X-ray-determined non-hydrogen structure projected on to this plane

Figure 3 shows the contoured values of M in the equatorial plane of a mononuclear pentagonal-bipyramidal rhenium complex, $[ReH_3(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane].[20] This figure illustrates the use of the plotting feature to analyse the complex potential-energy minima associated with polyhydride systems. The extended (and deeper) minimum results from the presence of two adjacent hydrides terminally bound to the rhenium atom, and shows why these are not differentiated by an initial search for terminal-hydride sites. Co-refinement of hydride positions at the isolated minimum and of two hydrides in the extended minimum yields estimates of all three hydride locations. These are in essential agreement with those predicted by another potential-energy method in the original *X*-ray analysis.[20] This co-refinement requires minimisation of *M* taking into account interhydride interactions omitted from the initial hydride search. All hydride positions in the complexes discussed below, containing more than one hydride, were co-refined in this way.

Testing the Procedure.—The procedure has been tested against all the suitable neutron-diffraction studies currently available in the literature, with considerable success (Table 2). In every case (except $[Rh_3H_3\{P(OMe)_3\}_6]$ [21]) the lowest-energy sites agree qualitatively with those observed directly in the neutron work.

Quantitative agreement is likewise good, the mean inaccuracy in hydride position being 0.05 Å for the 36 neutron-determined hydride ligands listed in Table 2. Only the non-hydrogen framework of the complex (as determined by neutron or *X*-ray diffraction) was used in these calculations. Clearly, some of these complexes {*e.g.* $[MnH(CO)_5]$} cannot be termed ' cluster ' or even polynuclear compounds: however, they do illustrate all observed modes of hydride coordination in cluster complexes. Good qualitative agreement has likewise been observed for all of the set of hydrido-clusters listed in Table 3, where hydride positions were directly determined from *X*-ray data by Fourier and/or least-squares refinement procedures. Quantitative assessment of the technique is not worthwhile here because of the low precision of hydride location in such studies.

TABLE 2

Neutron test cases

Compound	Ref.	Site type	M–H bond length (Å)		Site energy	Position error (Å)
			mean obs.[a]	used		
β-$[MnH(CO)_5]$	*b*	Terminal	1.601(10)	1.60(3)	7.46	0.026
$[Mo_2H(CO)_4(cp)_2(PMe_2)]$	*c*	μ	1.860(9)	1.86(5)	4.63	0.008
α-$[W_2H(CO)_9(NO)]$	*d*	μ	1.875(4)	1.87(5)	1.52	0.021
$[W_2H(CO)_8(NO)\{P(OMe)_3\}]$	*e*	μ	1.877(18)	1.87(5)	1.13	0.049
$[Ru_3H(CO)_9(CCBu^t)]$	*f*	μ	1.792(5)	1.79(5)	2.36	0.016
$[Os_3H_2(CO)_{10}]$	19	μ (2×)	1.850(5)	1.85(5)	0.69, 0.76 0.55, 0.50	0.033, 0.082 [g] 0.007, 0.025 [h]
$[Os_3H(CO)_{10}(C_2H_3)]$	52	μ	1.835(22)	1.835(50)	0.66,[g] 0.86 [h]	0.084,[g] 0.077 [h]
$[Os_3H_2(CO)_{10}(CH_2)]$	28	μ (2×)	1.820(27)	1.83(5)	1.86, 1.41	0.139, 0.027
$[Os_3H_2(CO)_9S]$	*i*	μ (2×)	1.829(8)	1.83(5)	2.14, 1.45	0.047, 0.026 [g]
$[Os_4H_3(CO)_{12}I]$	29	μ (3×)	1.788(21)	1.79(5)	3.64, 3.41	0.167, 0.002
$[Rh_3H_3\{P(OMe)_3\}_6]$	21	μ (3×)	1.765(17)	1.765(50)	1.24, 2.27, 2.27	0.201, 0.085, 0.337
$[Ru_4H_4(CO)_8\{P(OMe)_3\}_4]$ [j]	*k*	μ (8×)	1.773(3)	1.78(5)	3.05, 3.67, 2.88, 1.99, 3.09, 3.39, 2.82, 2.08	0.016, 0.056, 0.052, 0.006, 0.018, 0.047, 0.035, 0.027
$[Os_4H_3(CO)_{11}(HCCHPh)]$	33	μ (3×)	1.805(14)	1.81(5)	2.90, 2.95, 1.92	0.053, 0.112, 0.128
$[Re_3H_3(CO)_8(pop)_2]$ [l]	30	μ (3×)	1.812(18)	1.81(5)	2.27, 1.79, 1.40	0.146, 0.104, 0.165
$[Ni_4H_3(cp)_4]$	*m*	μ_3 (3×)	1.691(8)	1.69(5)	0.16, 0.19, 0.25	0.032, 0.043, 0.027
$[FeCo_3H(CO)_9\{P(OMe)_3\}_3]$	*n*	μ_3	1.734(4)	1.74(5)	2.24	0.021
$[N(PPh_3)_2][Co_6H(CO)_{15}]$	41	Interstitial		μ_3 1.74(5)	>32.5	
				μ 1.69(5)	>42.9	
$[AsPh_4][Ru_6H(CO)_{18}]$ [g]	40	Interstitial		μ_3 1.90(5)	>25.3	
				μ 1.79(5)	>41.7	

[a] E.s.d.s in observed bond length from $\sum_i |(d_i - \bar{d})|/n(n-1)$: this means asymmetric M–H–M systems will have large apparent e.s.d.s. [b] S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davidson, *Inorg. Chem.*, 1969, **8**, 1928. [c] J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 6610. [d] J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. A. Andrews, D. L. Tipton, and R. Bau, *J. Amer. Chem. Soc.*, 1974, **96**, 6621. [e] R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey, and R. Bau, *J. Amer. Chem. Soc.*, 1976, **98**, 4491. [f] M. Catti, G. Gervasio, and S. A. Mason, *J.C.S. Dalton*, 1977, 2260. [g] Based on *X*-ray co-ordinates. [h] Based on neutron co-ordinates. [i] B. F. G. Johnson, J. Lewis, D. Pippard, P. R. Raithby, G. M. Sheldrick, and K. D. Rouse, *J.C.S. Dalton*, 1979, 616. [j] Two independent molecules. [k] A. G. Orpen and R. K. McMullan, unpublished work. [l] pop = $(C_2H_5O)_2POP(OC_2H_5)_2$. [m] G. Huttner and H. Lorenz, *Chem. Ber.*, 1974, **107**, 996; T. F. Koetzle, R. K. McMullan, R. Bau, D. W. Hart, R. G. Teller, D. L. Tipton, and R. D. Wilson, *Adv. Chem. Ser.*, 1978, **167**, 61. [n] R. G. Teller, R. D. Wilson, R. K. McMullan, T. F. Koetzle, and R. Bau, *J. Amer. Chem. Soc.*, 1978, **100**, 3071.

DISCUSSION

The method described above clearly succeeds, in all but one case (see below), in finding accurate estimates of hydride positions in a wide range of cluster compounds. The quantitative agreement between predicted and observed neutron results is good for most cases. Despite the somewhat naive use of arbitrary, isotropic potential-energy parameters (further discussed below) the method has proved very flexible and reliable, giving a quantitative prediction of hydride location for a wide range of cluster and ligand types and geometries.

Given the results of these tests, it is possible to make some generalisations as to the characteristics of ' good ' hydride positions. Observed energies for various coordination types are given below, values being taken from Tables 2 and 3. In all cases studied (with the exception of $[Rh_3H_3\{P(OMe)_3\}_6]$) the method unambiguously predicts the lowest energy set of hydride positions to be those actually present in the cluster complex. Acceptable values for the various site types are likely to fall within, or close to, the ranges given in Table 4. However, errors in light-atom positions, as derived from *X*-ray studies, can be the cause of fairly large errors in the predicted hydride positions, and possibly anomalously high site energies. In general, as illustrated by the details given in Tables 2—5, there is a clear differentiation in energy between the true and false hydride sites. As shown in Table 4, there is some systematic variation in observed site energies, so that $E(\text{terminal}) \gtrsim E(\text{bridging}) \gtrsim E(\text{face bridging})$. This variation is in general small compared with the difference between true and false sites in a particular molecule.

TABLE 3

X-Ray test cases

Compound	Ref.	Site type	M–H (Å) [a] used	Site energy
$[Ru_3H_3(CO)_9(CCH_3)]$	*b*	μ (3×)	1.79(5)	1.84, 2.32, 1.84
$[Mn_3H_3(CO)_{12}]$	5	μ (3×)	1.73(5)	8.78, 8.58, 5.66
$[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$ [c]	44	μ (3×)	1.79(5)	1.57, 1.52, 1.59
$[Fe_2H_3\{CH_3C(CH_2PPh_2)_3\}_2]$	*d*	μ (3×)	1.75(5)	0.32, 0.37, 0.38
$[Os_3H_2(CO)_{10}(PPh_3)]$	*e*	Terminal	1.68(5)	2.23
$[Fe_3H(CO)_9(SC_3H_7)]$	*f*	μ	1.75(5)	10.59
$[Ru_4H_4(CO)_{10}(dppe)]$	*g*	μ (4×)	1.79(5)	3.58, 0.73, 3.12, 1.91
$[Ru_3H(CO)_9(C_6H_9)]$	*h*	μ	1.79(5)	3.09
$[Ru_3H(CO)_{10}(CNMe_2)]$ [i]	1	μ (2×)	1.79(5)	1.59, 1.64
$[Co_4H_4(cp)_4]$	*j*	μ_3 (4×)	1.74(5)	0.05, 0.03, −0.07, 0.07

The agreement was good in each case.

[a] Figures in parentheses show permissible error in bond length, *S* in equation (2), used. The actual deviation from prescribed M–H bond length was usually <0.01 Å. [b] G. M. Sheldrick and J. P. Yesinowski, *J.C.S. Dalton*, 1975, 873. [c] C_{3v} isomer. [d] P. Dapporto, S. Midollini, and L. Sacconi, *Inorg. Chem.*, 1975, **14**, 1643. [e] M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, 1977, **16**, 2397. [f] R. Bau, B. Don, R. Greatrex, R. J. Haines, R. A. Love, and R. D. Wilson, *Inorg. Chem.*, 1975, **14**, 3021. [g] M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, 1978, **17**, 1980. [h] G. Gervasio, D. Osella, and M. Valle, *Inorg. Chem.*, 1976, **15**, 1221. [i] Two molecules. [j] G. Huttner and H. Lorenz, *Chem. Ber.*, 1975, **108**, 973.

In one case above (Table 3, $[Rh_3H_3\{P(OMe)_3\}_6]$) two alternative sets of positions for the three hydrides (one on each edge of the triangular cluster), of approximately equal energy, were observed. One set (given in Table 2) gave positions fairly close to those observed. However the technique does not work satisfactorily and it is instructive to examine why not. The observed non-bonded distances between the hydride and P and Rh atoms in the neutron study [21] show some unusually short Rh ··· H non-bonded contacts [H(3) ··· Rh(1) 2.47, H(1) ··· Rh(2) 2.7 Å]. These could not be reproduced given the parameters used for Rh here. Secondly, and more importantly, the co-ordination geometry of the four-co-ordinate Rh atoms is square planar, as might be expected for a diamagnetic rhodium(I) d^8 complex. However, this geometry does not correspond to 'close packing' of the ligands around the metal. In contrast, the approach adopted here explicitly favours the ligand arrangement expected on steric grounds (*i.e.* tetrahedral co-ordination in this case). This problem is aggravated by the fact that there are only six non-hydrogen ligands defining this square-planar geometry, two per Rh atom. The derived low-energy sites have angles about the Rh atoms nearer to those of tetrahedral than square-planar geometry. In view of these difficulties no attempt has been made to reproduce the observed co-ordination in compounds where the non-hydrogen framework is even more sparse {*e.g.* the polyhydride complexes $[Re_2H_8L_4]$,[22] $[OsH_4L_3]$,[23] $[MoH_2(cp)_2]$,[24] $[TaH_3(cp)_2]$ ($cp = \eta\text{-}C_5H_5$),[25] recently studied by neutron diffraction}.

TABLE 4

Site energies

Site type	Range	Average	Number
Terminal	2.2—7.5	4.8	2
Edge bridging	0.2—10.6	2.76	41
Face capping (μ_3)	−0.07—2.24	0.37	8

Inaccuracy and Improvements.—The most obvious causes of inaccuracy may be divided into three categories.

(*a*) Quite large errors in light- (non-hydrogen-) atom positions, especially for clusters of the second- and third-row transition elements, as derived from *X*-ray structure analyses. In view of this problem we expect, and see, for $[Os_3H_2(CO)_{10}]$ and $[Os_3H(CO)_{10}(C_2H_3)]$ (Table 2), more accurate results with neutron-determined atomic positions than with *X*-ray. In addition, disorder in the cluster (involving the metals and/or ligands), which is unfortunately not uncommon, can prevent useful application of this technique {*e.g.* for $[N(PPh_3)_2][Cr_2H(CO)_{10}]$ [26] and $[N(PPh_3)_2][W_2H(CO)_{10}]$ [27]}, unless an accurate, unique set of molecular parameters can be derived.

(*b*) Asymmetry of the M–H–M and HM_3 systems for bridging hydrides. This is not taken into account by the program, which forces all M–H bond lengths towards a common, specified, value. It is for two of the most asymmetric cases reported {*viz.* $[Os_3H_2(CO)_{10}(CH_2)]$ [28] and $[Os_4H_3(CO)_{12}I]$ [29]} that agreement is indeed amongst the poorest; the connectivity of the predicted hydride sites is however correct.

(*c*) Poor assessment of parameters describing the M–H distances and non-bonded interactions. Metal–hydride bond lengths are well characterised [13] for a growing number of metals and co-ordination geometries (Table 2) and this does not appear to be a major problem. It is not yet feasible to determine an empirical set of parameters to better fit the observed hydride positions, although in time this might become possible. It is also rather unreasonable to expect all carbon atoms, for instance, to be well modelled by a single set of parameters regardless of their chemical environments. Despite these problems, this technique has proved very reliable in predicting hydride positions.

Controversies and Predictions.—$[Mn_3H_3(CO)_{12}]$. One of the X-ray cases given in Table 5, $[Mn_3H_3(CO)_{12}]$, has been a subject of some controversy. The non-hydrogen ligand polyhedron of this triangular cluster is a nearly regular anticubo-octahedron. It has been suggested[6] that the most appropriate way to ' fit ' the hydrides into this ligand polyhedron is into the large square faces of the polyhedron, of necessity out of the equatorial Mn_3 plane. This proposal contradicts the X-ray results[5] which show a nearly planar arrangement of the H_3Mn_3 core of the molecule. Application of this potential-energy technique yields results in close agreement with the X-ray-(difference-Fourier-) determined positions. The calculated hydride positions show deviations from the plane of the Mn_3 triangle of the same order as the X-ray results [which are of low precision for the hydride location, the estimated standard deviation (e.s.d.) in the average Mn–H bond length being 0.07 Å]. The largest dihedral angle between the Mn_3 triangle and Mn–H–Mn plane is for Mn(1)–H(1)–Mn(2): the angle from the X-ray co-ordinates is 25.6° and from the calculated hydride co-ordinates is 25.2°. This assignment of hydride positions is supported by the neutron work on $[Re_3H_3(CO)_8(pop)_2][pop = (C_2H_5O)_2POP(OC_2H_5)_2]$,[30] where the ligand polyhedron is anticubo-octahedral, as for $[Mn_3H_3(CO)_{12}]$, and the hydride positions show similar slight distortions from coplanarity with the M_3 triangle.

This case illustrates the problems associated with non-quantitative approaches to hydride location. The approximation of the observed ligand arrangement to a regular geometrical polyhedron leads to a false conclusion regarding the positions of the hydride ligands.

TABLE 5

Predictive cases

Compound	Ref.	Cluster geometry	Sites tested	M–H (Å) used	Site energies
$[Os_6H_2(CO)_{18}]$ (Figure 5)	34	Capped square pyramidal	μ (2×)	1.83(5)	1.24,* 0.96 *
			terminal (2×)	1.68(5)	22.9, 24.5
			μ_3	1.95(5)	26.02
$[Os_4H_3(CO)_{11}(C_6H_9)]$ (Figure 4)	31	Tetrahedral	μ (3×)	1.83(5)	3.40,* 1.38,* 3.23 *
			μ_3 (2×)	1.95(5)	10.45, 20.20
			μ (other)	1.83(5)	37.97, 28.92
$[Os_6H(CO)_{18}]^-$	34	Octahedral	μ_3	1.95(5)	0.37 *
			μ_3 (four other)	1.95(5)	8.7, 10.3, 9.4, 10.4
$[Ru_4H_4(CO)_{12}]$	42	Tetrahedral	μ (4×) (D_{2d})	1.79(5)	2.63,* 3.64,* 3.57,* 3.15 *
			μ_3 (4×)	1.90(5)	5.7—7.3
			μ (two other)	1.79(5)	29.3, 32.33
$[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$ (C_2 isomer)	44	Tetrahedral	μ (3×)	1.79(5)	2.65,* 1.97,* 2.11 *
			μ (three other)	1.79(5)	27.6, 32.8, 37.6
$[N(PPh_3)_2]_2[Os_4H_2(CO)_{12}]$	46	Tetrahedral	μ (2×) (D_{2d})	1.83(5)	1.89,* 4.04 *
			μ (four other)	1.83(5)	27.31–40.41
$[Os_4H_4(CO)_{12}]$	43	Tetrahedral	μ (4×) (D_{2d})	1.83(5)	3.69,* 3.00,* 3.54,* 3.27 *
			μ (two other)	1.83(5)	27.81, 27.29
$[Os_3PtH_2(CO)_{10}\{P(C_6H_{11})_3\}]$	45	Tetrahedral	μ (2×)	1.85(5)	1.16,* 1.19 *
			μ (four other)	1.85(5)	11.0—38.4
$[Os_3H_2S_2(CO)_7(CS)]$ (2 molecules)	37 (Figure 6)	Bent	μ (4×)	1.83(5)	0.92,* 1.00,* 1.00,* 1.10 *
$[N(PPh_3)_2][Os_3H(CO)_9S]$	49	Triangular	μ	1.83(5)	2.70 *
			μ (two other)	1.83(5)	23.9, 24.1
$[Re_2H_2(CO)_6(Ph_2PCH_2PPh_2)]$	50	Dimeric	μ (2×)	1.85(5)	0.38,* 0.24 *
$[Os_3CoH_3(CO)_{12}]$	47	Tetrahedral	μ (3×)	1.83(5)	2.27,* 2.51,* 3.18 *
$[Os_5H_2(CO)_{16}]$	48	Edge-bridged tetrahedral	μ (2×)	1.83(5)	0.88,* 1.51 *

* Site predicted to be present, all others false.

$[Os_4H_3(CO)_{11}(C_6H_9)]$. The X-ray analysis of this tetrahedral cluster complex[31] (Figure 4) shows a pattern of three long and three short M–M distances. Unusually, they fail to conform to the principle that hydride-bridged M–M vectors are longer than those not so bridged. This potential-energy technique successfully predicts the location of the hydrides spanning three edges of the cluster with M–M distances given in the legend for Figure 4. The predicted arrangement of hydride ligands[32] is confirmed by a neutron-diffraction study of an analogous complex $[Os_4H_3(CO)_{11}(HCCHC_6H_5)]$[33] showing a very similar ligand arrangement and pattern of M–M distances. This case demonstrates the care that must be taken in applying simple bond-lengthening arguments to more complex cluster geometries. Presumably in such clusters (*e.g.* tetrahedral, octahedral, *etc.*) all M–M vectors are bridged by other metal atoms. This, and other poorly understood electronic factors, might distort the metal framework, making the simple criterion of M–M bond length less useful for higher clusters.

$[Os_6H_2(CO)_{18}]$. This cluster shows a complex structure (Figure 5) based on a capped square-pyramidal Os_6 unit.[34] Several hydride locations, including a variety of face bridging[34] [to Os(1), Os(3), and Os(4)], edge-bridging[34] [Os(2)–Os(5), Os(3)–Os(4)], and terminal sites [bonded to Os(3) and Os(4)][35] have been suggested and are evaluated here (Table 5).

The results clearly indicate two bridging sites (Figure 5) as being both mutually compatible and of appropriate energy (Table 5). The other proposed sites are all of considerably higher energy and are clearly inappropriate. The edge-bridged structure has indeed been postulated on theoretical grounds for the formally analogous B_6H_8 system.[36]

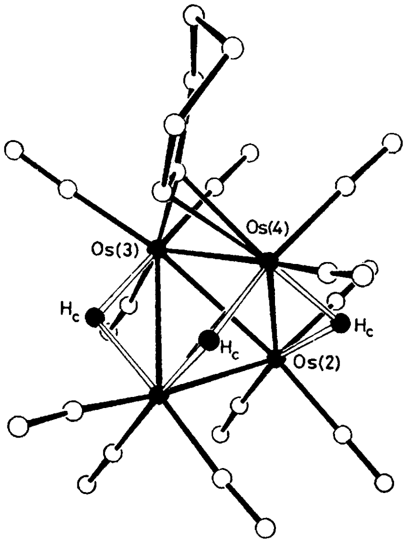

FIGURE 4 *X*-Ray-determined structure of $[Os_4H_3(CO)_{11}(C_6H_9)]$ with hydrides in calculated positions (H_c); bond lengths are Os(1)–Os(2) 2.794, Os(1)–Os(3) 2.984, Os(1)–Os(4) 2.953, Os(2)–Os(3) 2.938, Os(2)–Os(4) 2.817, and Os(3)–Os(4) 2.793 Å

$[Os_3H_2S_2(CO)_7(CS)]$ (2Os–Os). This polynuclear complex (Figure 6) presented considerable difficulties in interpretation of an unusual ^1H n.m.r. spectrum,[37] which showed hydride–hydride coupling, rarely found for cluster complexes.[38] The observed AB pattern was not readily explicable on the basis of the *X*-ray analysis [37] which failed to locate the hydrogen atoms. Application of this quantitative approach yielded clear indication of two sites bridging the two Os–Os bonds (Figure 6). These positions give an H–Os(1)–H angle of *ca.* 162°, *i.e.* the hydrides are mutually *trans*. This geometry, unusual for a trinuclear hydride cluster, explains the ^1H–^1H coupling, therefore resolving the problems described above.

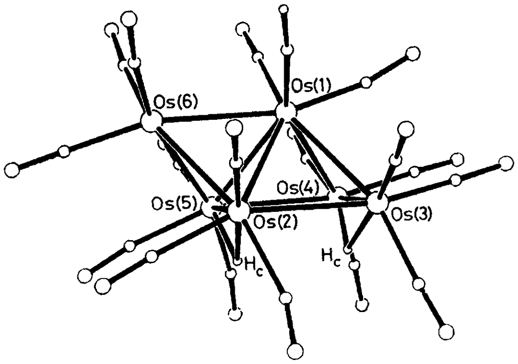

FIGURE 5 *X*-Ray-determined molecular structure of $[Os_6H_2(CO)_{18}]$, with hydrides in calculated positions (H_c); bond lengths Os(1)–Os(3) 2.849, Os(1)–Os(4) 2.851, Os(2)–Os(3) 2.868, Os(1)–Os(2) 2.828, Os(1)–Os(5) 2.829, Os(1)–Os(6) 2.850, Os(2)–Os(5) 2.892, Os(2)–Os(6) 2.805, Os(3)–Os(4) 2.964, Os(4)–Os(5) 2.860, and Os(5)–Os(6) 2.805 Å

Interstitial Hydrides.—This recently characterised [13] class of cluster complexes clearly presents further difficulties in location of the hydride from *X*-ray data alone. This procedure, relying as it does on non-bonding interactions, cannot work when applied to a hydride buried in a cluster where there can be no such interactions. It can provide negative evidence, however, assessing the likelihood of a site on the exterior of the cluster, but it is not possible to check all possible modes of co-ordination of the 'missing' hydrogen atom(s), such as binding to a CO group, as has been postulated.[39]

Applying this procedure to the neutron-determined clusters $[Ru_6H(CO)_{18}]^-$ and $[Co_6H(CO)_{15}]^-$ yields conclusive indications that there are no metal-bound sites available on the exterior of these octahedral clusters. In the case of $[Ru_6H(CO)_{18}]^-$, despite there being a long (2.960, *cf.* mean Ru–Ru 2.895 Å) Ru–Ru vector,[40] there are no associated μ or μ_3 sites with energy lower than 41.6 or 25.3 units respectively. For $[Co_6H(CO)_{15}]^-$ there was speculation [41] that the longest edge of the octahedral cluster was hydride bridged. However the energy of such a site and the μ_3 sites spanning this edge are again unreasonably high, being 42.9 and 32.5 units respectively.

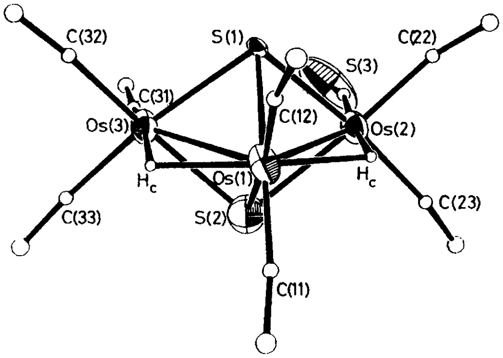

FIGURE 6 *X*-Ray-determined structure of $[Os_3H_2S_2(CO)_7(CS)]$ showing the calculated hydride positions (H_c)

Other Examples.—Other less controversial hydride-site assignments are confirmed by this work (Table 5); in particular, the edge-bridging sites proposed for $[Ru_4H_4(CO)_{12}]$ [42] and $[Os_4H_4(CO)_{12}]$ [43] are found to have typical bridging energies, alternative μ_3 face-bridging sites [38] being of higher energy, as might be expected. The two isomers of $[Ru_4H_3(CO)_{12}]^-$,[44] of C_2 and C_{3v} symmetry, indeed show the predicted hydride arrangements (the hydrides were actually located in the *X*-ray study of the C_{3v} isomer). The bridging site assignments for $[Os_3PtH_2(CO)_{10}\{P(C_6H_{11})_3\}]$,[45] $[Os_4H_2(CO)_{12}]^-$,[46] $[Os_3CoH_3(CO)_{12}]$,[47] $[Os_5H_2(CO)_{16}]$,[48] $[Os_3H(CO)_9S]^-$,[49] and $[Re_2H_2(CO)_6(Ph_2PCH_2PPh_2)]$ [50] are confirmed, and the μ_3 face-bridging site in $[Os_6H(CO)_{18}]^-$ [34] likewise found reasonable.

Conclusion.—It is interesting to analyse exactly why the method works! It would seem unlikely that the non-bonded interactions are the primary factors in determining hydride positions in clusters, although packing forces of this type are thought to influence ligand (and cluster) geometries.[6,51] The conformation of flexible ligands, and in particular their more peripheral atoms, may indeed reflect the hydride geometry in this way. The stereochemistry of metals in cluster compounds is dominated by octahedral co-ordination which is a highly favoured configuration in terms of packing six ligands around a central atom. Therefore, this technique, in explicitly assuming a close-packed arrangement of ligands around any metal centre when searching for a site, implicitly takes into account the favoured co-ordination geometry of the metal(s) to which the hydride is bound. Other ' close-packed ' co-ordination geometries, *e.g.* tetrahedral, trigonal, and trigonal bipyramidal, would seem unlikely to present problems. Those for which steric considerations less successfully mimic electronic factors (*e.g.* square planar and square pyramidal) could, and do, cause difficulties (*e.g.* $[Rh_3H_3\{P(OMe)_3\}_6]$ above), especially when the non-hydride ligand polyhedron is poorly defined. The technique in its predictive role relies, of course, on current knowledge of M–H bond lengths. It works as well as it does because these are fairly well defined and vary relatively little for a given co-ordination type and metal.

In conclusion, the empirical method described here has been very successful, both in agreeing with experimental data and in the prediction of unknown sites for hydrides, within the limitations described above. Clear-cut predictions have been possible in cases where qualitative arguments have been unable to provide unambiguous assignments of hydride positions.

In association with accurate *X*-ray single-crystal data, this method could be of considerable utility in using limited neutron data sets for the study of hydride co-ordination in cluster complexes by combined refinement of the *X*-ray and neutron data.[52] This quantitative means of inferring hydride positions from the *X*-ray-determined non-hydrogen framework of the molecule enables the prediction of (and hence collection of) the neutron data most relevant to characterising the hydride positions. Likewise hydrides could be included in calculated positions in *X*-ray studies; such a procedure has been shown [53] to be of utility in structure analysis of even third-row transition elements.

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