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The Detection and Location of Hydrido Ligands in High Nuclearity Osmium and Ruthenium Carbonyl Clusters: A Critical Survey

Lutz H. Gade,[a] Brian F. G. Johnson,[b] and Jack Lewis[c]

[a]*Institut für Anorganische Chemie der Universität Würzburg,*
Am Hubland, D-97074 Würzburg, Germany

[b]*Department of Chemistry, University of Edinburgh, Kings Building,*
West Mains Road, Edinburgh EH9 3JJ, U.K.

[c]*University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.*

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Hydrido carbonyl clusters represent powerful molecular models for the co-adsorption of carbon monoxide and hydrogen on metal surfaces, a key step in several catalytic processes. Over the past two decades a considerable number of such species have been reported in the literature. In this paper, the structural chemistry of high nuclearity osmium and ruthenium hydrido carbonyl clusters is critically reviewed. Particular emphasis is placed on the limits of the various indirect methods of hydride location in clusters, and an alternative interpretation of the results of spectroscopic studies performed for samples of some Ru and Os clusters in solution is given.

INTRODUCTION

The location of metal bonded hydrido-ligands in mono- or polynuclear transition metal compounds is a particularly challenging task. Whereas the hydrido-ligands are virtually invisible in the electron density maps of X-ray structure analyses, their direct location by means of neutron diffraction analysis is feasible only in cases for which large single crystals are available. As a consequence, structural assignments are based mostly on indirect methods of location including a variety of spectroscopic techniques. Due to the limits of these methods, the data available for several (particularly high nuclearity) hydrido-carbonyl clusters have been either over- or even mis-interpreted. These »Flying Dutchmen« haunt the cluster literature. In this paper it is our intention to give an overview of the current state of the art in the area of high nuclearity ruthenium and osmium hydrido-carbonyl cluster chemistry and to critically review the published work in the light of the issues stated above. First of all, however, the relevance of this area of cluster chemistry to the better understanding of the chemisorption of CO and H on metal surfaces, a key step in heterogeneous catalysis, will be discussed.

HYDRIDO CARBONYL CLUSTERS: MODEL SYSTEMS FOR THE CHEMISORPTION OF »SYNTHESIS GAS« ON METAL SURFACES

The chemisorption of H_2 and CO on metal surfaces is one of the most extensively studied areas of surface science.[1–3] The role that the adsorption of these molecules (*e.g.* in »synthesis gas«) plays in various heterogeneous catalytic processes provides the underlying motivation for these research efforts. In particular, the hydrogen-nickel system is regarded as an excellent model for adsorption phenomena in general and has been the subject of a large number of publications in which many aspects of the dissociative chemisorptions of H_2 on various Ni-surfaces have been reported.[4] The dissociation equilibrium of adsorbed dihydrogen is very sensitive to the presence of co-adsorbates on the metal surface. A notable contribution to this problem is the study of the mutual effect that chemisorbed hydrogen and carbon monoxide on a Ni(100) surface have upon each other.[5] The presence of hydrogen apparently determines the adsorption pattern and thus the coordination mode of the CO molecules, while CO appears to induce the recombination of dissociated H-atoms.

The analytical methods employed have provided a detailed insight into the thermodynamic and kinetic aspects of chemisorption and surface reactions and allowed the proposal of structural models for some of these systems. However, given the current routine analytical methods available in this field, the structures of solid/fluid interfaces are not nearly as readily characterized as, for instance, those of molecular systems. More than a decade ago, Ertl and Muetterties proposed that the structural aspects of the chemisorption of small molecules on extended metal surfaces could be modelled by the interactions of main group fragments with discrete transition metal cluster molecules.[1,2,6] In the context of synthesis gas chemistry, the study of the structures and chemistry of hydrido carbonyl clusters has received particular attention. The determination of the crystal structures of these compounds by X-ray or neutron diffraction analysis has provided surface scientists with valuable data concerning the coordination (or adsorption!) geometry of CO and H on extended metal frameworks. A prominent early example of the interplay of cluster chemistry and surface science was the almost simultaneous location of the hydrido-ligands in $Cp_4Ni_4H_3$ by neutron diffraction analysis and the H atoms on a Ni(111) surface by LEED analysis.[1,7] In both systems, each hydrogen atom was shown to be μ_3 coordinated to the M_3-triangles.

In addition to the surface coordination of hydrogen atoms on cluster cores, the establishment of their location in interstitial sites of close packed metal atoms in clusters is of interest in connection with the behaviour of hydrogen »dissolved« in metals. The study of this phenomenon has been primarily inspired by the development of convenient hydrogen storage systems. The location of a hydrogen atom in the octahedral cavity of a discreet cluster was first demonstrated by Simon in the structure of $Nb_6I_{11}H$.[8] The original assignment was based on powder neutron diffraction data and was later confirmed by a single crystal neutron diffraction study of the deuteride.[9] More recently, Corbett and coworkers have shown that the zirconium monohalides, which have condensed cluster structures, readily incorporate hydrogen both into their octahedral cluster cavities and, depending on the stoichiometry, into their tetrahedral interstices.[10]

The first molecular cluster for which an interstitial H-atom was proposed is $[HRu_6(CO)_{18}]^-$.[11] The location of the hydrogen in the octahedral cavity of the cluster was originally deduced indirectly from the compact arrangement of the carbonyl ligands on the surface and the »anomalous« chemical shift of the hydride resonance in the ^{1}H-NMR spectrum of the cluster. The first direct locations of hydrido-ligands in molecular clusters were achieved for $[H_2Ni_{12}(CO)_{21}]^{2-}$, $[HNi_{12}(CO)_{21}]^{3-}$ [12] and $[HCo_6(CO)_{15}]^-$ [13] while shortly thereafter, the interstitial μ_6 coordination mode of the H-ligand in $[HRu_6(CO)_{18}]^-$ was confirmed by a neutron structure analysis.[14]

THE LOCATION OF HYDRIDO LIGANDS IN TRANSITION METAL CLUSTERS

The direct location of hydrido-ligands in transition metal clusters using X-ray diffraction analysis is only possible in exceptional cases.[15] This is a consequence of the difficulties associated with the location of hydrogen atoms (possessing no core electrons) in Fourier maps in the presence of »electron rich« heavy metal atoms. On the other hand, neutron diffraction is the method of choice for the direct detection of H-atom positions. Since the neutron scattering cross section of the hydrogen atom is of the same order of magnitude as those of the heavier transition metals, this method provides the opportunity to resolve not only the nuclear positions but also to obtain meaningful thermal parameters for each hydrogen atom. There are, however, two major drawbacks of this technique. Firstly, it involves equipment which is not readily available and, secondly, the technique requires relatively large crystals which may be difficult to obtain. Moreover, it is arguable whether the detailed structural information about the hydrogen atom which neutron structure analyses yield is required for an understanding of the structure of the ligand shell in many clusters. The time and expense of a single crystal neutron diffraction study are therefore not always justified. Neutron powder diffraction, on the other hand, has been successfully applied in the detection of hydrides in solids (*vide supra*) but has to date not entered the »armory« of standard methods in molecular carbonyl clusters chemistry. This is primarily due to the comparatively complicated nature (large number of structural parameters to be refined!) of the metal carbonyl structures.

Consequently, the location of the H-ligand(s) has been carried out by indirect methods for the majority of hydrido-clusters. Such locations are based on a variety of structural criteria such as the bond lengths of the H-bridged metal-metal vectors[16] and the steric effects of the »invisible hydride« on the surrounding ligand polyhedron.[17] This kind of reasoning is best exemplified by the pioneering work of Mays and Churchill on the hexaruthenium cluster $[H_2Ru_6(CO)_{18}]$.[18] In the octahedral cluster two opposite triangular faces were found to be significantly larger than the remaining six (d(Ru-Ru) = 2.954(3) Å *vs.* 2.867(5) Å). In addition, the disposition of the CO ligands around the core has systematic irregularities with ligands being distorted away from the enlarged equilateral faces. These structural features were regarded by the authors as indirect evidence for the μ_3-coordination of the hydrido ligands over the two expanded faces.

Another example of »indirect reasoning« is the proposal of the interstitial location of the hydrides in $[HNi_9Pt_3(CO)_{21}]^{3-}$.[19] The increased interlayer distance between two of the layers of metal atoms was thought to be a consequence of an interstitial location of the H-atom. This conclusion was based on the analogy of the system to $[HNi_{12}(CO)_{21}]^{3-}$ (characterized by single crystal neutron diffraction analysis) which showed a similar effect of the interstitial hydrido-atom on the metal core structure.[12]

More recently, McPartlin *et al.* have shown that the application of computer graphics to the analysis of the ligand shell of hydrido carbonyl clusters may provide a convenient short cut to the detection of »holes« in the ligand sphere, even for relatively complicated high nuclearity systems.[20] The method is based on the observation that hydrido-ligands have an appreciable size and thus steric effect on their surroundings in transition metal carbonyl hydrides. The indirect H-location methods derived from the X-ray crystallographic data have been put on a more quantitative basis by Orpen who has developed a »potential energy« method for the calculation of the position of hydrogen atoms coordinated to heavy transition metals.[21] This approach is an extension of a method originally developed for the prediction of organic crystal structures and optimisation of molecular conformations.[22] The basic information required is the set of X-ray-determined atomic positional parameters for all non-hydrogen atoms and the coordination mode to be investigated. A set of parameters describing the non-bonded interactions between the hydride and the non hydrogen atoms in the cluster, as well as the »typical« metal-H distance for the different coordination modes are initially to be defined. It has been found, that for a wide range of cluster geometries H-coordinates calculated by this method agree well with those determined in neutron diffraction studies.

The inherent weakness of the indirect methods discussed here is that unresolved disorder of the CO-ligand shell – frequently observed in the higher clusters – may lead to misinterpretations with regard to the packing of the carbonyls on the cluster surface, a point which will be discussed in more detail below.

THE STRUCTURES OF DECAOSMIUM AND DECARUTHENIUM HYDRIDO CLUSTERS: HYDROGEN ATOMS IN INTERSTITIAL TETRAHEDRAL SITES OR NOT?

The members of a series of clusters that have served as target molecules for indirect hydride location techniques are the decaosmium and decaruthenium species $[HOs_{10}C(CO)_{24}]^-$ (**1**),[23] $[H_2Os_{10}C(CO)_{24}]$ (**2**),[23,24] $[H_4Os_{10}(CO)_{24}]^{2-}$ (**3**),[25] $[H_5Os_{10}(CO)_{24}]^-$ (**4**),[25] $[HRu_{10}C(CO)_{24}]^-$ (**5**),[26] and $[H_2Ru_{10}(CO)_{26}]^{2-}$ (**6**),[27] (Figure 1). The apparent similarity of the carbonyl ligand distribution in **1**, **3** as well as the non hydrido species $[Os_{10}C(CO)_{24}]^{2-}$ (**7**),[28] origi-

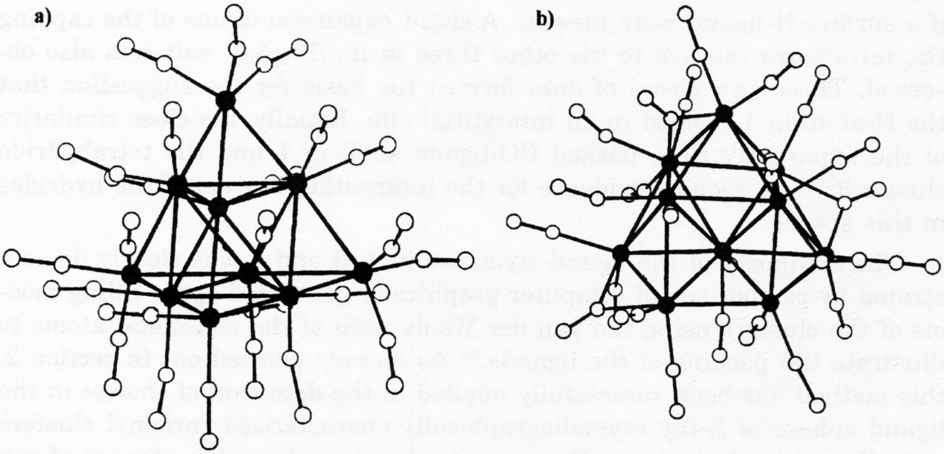

Figure 1. The metal carbonyl structure of the decanuclear osmium and ruthenium clusters: a) **1** – **5**, b) **6**.

nally led to the conclusion that the most reasonable position of the hydrogen atom in **1** and for at least three of the four hydrides in **3** was inside tetrahedral cavities of the metal cores of the clusters. The same argument was put forward for $[HRu_{10}C(CO)_{24}]^-$ [26] which was found to have an equally similar CO arrangement to that of the corresponding dianion $[Ru_{10}C(CO)_{24}]^{2-}$.[26,29] Hydrogen has been found in tetrahedral interstices for a number of solid state structures of binary hydrides MH_2 (CaF_2 structure)[30] as well as $ZrClH_x$ but had not previously been established in transition metal clusters.

In addition to these structural considerations, the spectroscopic data, particularly the ^{1}H-NMR chemical shifts, ^{187}Os-satellite patterns (in the Os clusters) and longitudinal relaxation times of the hydride signals, were interpreted as arising from interstitial occupancy and regarded as additional evidence for the proposed structures.

Comments on the Application of Indirect Hydride Location Methods in the Structural Analysis of the Tetrahedral M_{10}-Clusters of Ruthenium and Osmium

In 1982, $[HOs_{10}C(CO)_{24}]^-$, the first example of »a cluster compound with an interstitial hydrogen ligand in a tetrahedral site« was reported as the product of the protonation of $[Os_{10}C(CO)_{24}]^{2-}$ (**7**) with concentrated H_2SO_4.[23] For the dianion **7** the crystal structure analysis had revealed that the CO-ligands were symmetrically arranged approximately perpendicular to the four faces of the tetrahedral metal core. The monohydride **1** was found to have an almost identical ligand distribution to that of the dianion, with apparently none of the characteristic displacement of the carbonyls expected if a surface H-ligand were present. A slight expansion of one of the capping Os_4-tetrahedra relative to the other three in its $[Ph_4As]^+$ salt was also observed. These two pieces of data formed the basis for the suggestion that the H-atom in **1** resided in an interstitial site. Equally, the close similarity of the apparently close packed CO-ligand shell in **1** and the tetrahydrido cluster **3**[24] was seen as evidence for the interstitial location of the hydrides in this species.

The similarity of the ligand structure in **1**, **3** and **7** was clearly demonstrated by comparison of computer graphically generated space filling models of the clusters using the van der Waals radii of the non-metal atoms to illustrate the packing of the ligands.[20] As already pointed out in section 2, this method has been successfully applied in the detection of »holes« in the ligand sphere of X-ray crystallographically characterised carbonyl clusters as well as their derivatives. However, it relies heavily on the absence of any unresolved disorder of the carbonyl ligands which might obscure the ligand structure and thus conceal possible sites for the H-atoms on the metal surface. For example, the X-ray structural evidence put forward for the interstitial nature of the hydrido ligand in **1** can be explained by the presence of an external μ_2-H ligand coupled with a threefold disorder of the cluster in the $[Ph_4As]^+$ salt or a sixfold disorder in the $[Ph_3PMe]^+$ salt.[31] This alternative interpretation of the structure of **1** should be related to the recent results of a single crystal X-ray structure analysis of the dihydride **2**. With the knowledge of the results of a neutron diffraction study of **3** discussed below, Braga *et al.* deduced an external μ_2-coordination of the two hydrogen atoms which is partially obscured by a static disorder of the cluster in the crystal.[24]

Since the determination of the exact positions of the ligand atoms in clusters containing heavy atoms becomes less accurate and static or dynamic disorder in the ligand shell more likely with increasing nuclearity of the species, the indirect methods for hydride location become less reliable. Negative evidence for the surface location of H-ligands should therefore be treated with care!

Comments on the Interpretation of the Published ^{1}H-NMR Data

The ^{1}H-NMR chemical shifts of interstitial hydrido ligands have been found to vary widely. For H-atoms occupying the centre of an octahedral cavity in a cluster the $^1H_{(hydride)}$-NMR signals were detected at low field, such as $\delta = +23.2$ for $[HCo_6(CO)_{15}]^-$ [13] and $\delta = +16.4$ for $[HRu_6(CO)_{18}]^-$.[11,14] The observation of one of the two hydride signals in $[H_2Ru_8(CO)_{21}]^{2-}$ at $\delta = +6.9$ was therefore interpreted by Yamazaki *et al.* as being indicative of an interstitial location of one of the two hydrogen atoms in the cluster.[32] On the other hand, in larger transition metal clusters such as $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$, hydride resonances were found at »normal« high field positions ($\delta = -24.0$ and -18.0, respectively).[12] This is possibly a consequence of the highly asymmetric positions of the H-atoms in the interstitial sites which make them appear (and behave) like μ_3-coordinated ligands on »internal surfaces«. On the basis of the data accumulated to date, it appears impossible to reliably correlate ^{1}H-NMR shifts with the structural environment of transition metal bonded hydrogen.

The ^{1}H-chemical shifts of several high nuclearity hydrido osmium and ruthenioum clusters are summarised in Table I.

For these clusters, all of which have been proposed to contain interstitial hydrides, the chemical shifts of the hydrido nuclei lie well within the range normally found for μ_2- or μ_3-sites on the surfaces of Os- and Ru-clusters. Their chemical shift is thus not indicative of an abnormal environment of the H-ligands. An undecaruthenium hydrido cluster, $[HRu_{11}(CO)_{27}]^{3-}$, has also been reported.[27b] However, the conclusions concerning the hydride lo-

TABLE I

Hydride chemical shifts of decanuclear Os and Ru clusters

Cluster	$\delta(^1H)^a$	Reference
$[HOs_{10}C(CO)_{24}]^-$ (**1**)	−15.45	23
$[H_4Os_{10}(CO)_{24}]^-$ (**3**)	−16.48 (T = 293 K) −14.70, −19.08 (T = 198 K)^b	25
$[H_5Os_{10}(CO)_{24}]^-$ (**4**)	−15.9, −16.2^c	34
$[HRu_{10}C(CO)_{24}]^-$ (**5**)	−13.50	26
$[H_2Ru_{10}(CO)_{26}]^{2-}$ (**6**)	−14.80	27a

[a] values at T = 293 K in CD_2Cl_2; [b] rel. intensity 1:1; [c] rel. intensity *ca.* 4:1

cation derived for this cluster based on the comparison of the hydride chemical shift with that of $[HRu_6(CO)_{18}]^-$ are suspect since the τ and δ scales for the chemical shifts were apparently confused!

A series of clusters which have been studied by a whole range of sophisticated NMR spectroscopic methods are the $[H_{5-n}Rh_{13}(CO)_{24}]^{n-}$ (n = 1 – 4) anions.[33] In this case the $J(^{103}Rh\text{-}^1H)$ coupling pattern along with the studies of the ligand dynamics has not only established the interstitial (or at least »semi-interstitial«) location of the H-ligands but also their rapid migration inside the metal core.

As will be discussed in detail below, the ^{187}Os-satellite pattern of the hydride resonance in **1** may be explained in terms of a fluxional surface located hydride ligand. This implies that the assumption of an interstitial hydride is not essential in the interpretation of the ^{1}H- (as well as ^{13}C-) NMR spectra of $[HM_{10}C(CO)_{24}]^-$. Equally, the low temperature ^{1}H-NMR spectra of the tetrahydrido cluster **3** (two signals with an intensity ratio of approximately 1:1 at 198 K) are difficult to reconcile with a structural model which assumes the occupancy of three tetrahedral and one octahedral cavity in the metal, although the residual exchange observed even at very low temperatures may have obscured the actual situation.

Finally, the results of a series of T_1-measurements performed on a number of hydrido-clusters were thought to indicate an unusual location of the H-atoms.[35] In fact, »typical« ranges for the longitudinal relaxation times of interstitial hydrides in tetrahedral and octahedral sites were given; this, although the dynamic behaviour of the hydrides at the chosen temperatures was well established. Since, based on the data presented, it is impossible to distinguish between the effects that ligand mobility and chemical environment have on the relaxation behaviour of the hydrides, the study must be viewed as of little significance to the structural assignment.

DANGERS OF ANALOGIES: THE STRUCTURES OF $[H_{2-x}M_6(CO)_{18}]^{x-}$ (M = Ru, Os; x = 0,1)

The example *par excellence* for the fallacies that conclusions by analogy may produce is the series of hexametal clusters $[H_{2-x}M_6(CO)_{18}]^{x-}$ (M = Ru, Os; x = 0,1). As mentioned above, the first hydrido cluster from this series to be characterised by X-ray crystallography was $[H_2Ru_6(CO)_{18}]$.[18] The Ru_6-octahedron contains two enlarged *trans* faces which are μ_3-bridged by the two hydrido-ligands. The monohydrido cluster $[HRu_6(CO)_{18}]^-$, on the other had, has an interstitial hydride within its octahedral metal framework, a fact which was established by neutron crystallography.[14] The corresponding osmium cluster contains the hydrido ligand in a μ_3-bridging mode across one of its triangular faces.[36] Finally, the dihydrido-cluster $[H_2Os_6(CO)_{18}]$ was found to have a completely different metal core geometry, a monocapped square-based pyramid with two long basal Os-Os bonds which are thought to be μ_2-bridged by the two H-atoms.[37]

This example not only demonstrates the potential pitfalls of analogies in cluster chemistry but also shows that the position of a hydride ligand is very sensitively dependent upon the metal, *i.e.* electronic factors in the cluster framework. A largely neglected aspect in the whole discussion is the role that the other ligands, in this case the carbonyls, might play. The influence of the hydride upon their disposition in a molecule has been discussed in most of the cases mentioned in this paper. The way CO....CO and CO...metal interactions in the cluster conversely influence the coordination of the H-ligands is far less well understood. The results of the investigations into mixed CO/H_2 chemisorption on metal surfaces cited in the first section should, however, inspire a closer examination of this aspect of the structural chemistry of clusters.

THE DIRECT LOCATION OF THE HYDRIDES IN $[H_4Os_{10}(CO)_{24}]^{2-}$ BY NEUTRON DIFFRACTION ANALYSIS

In order to resolve the problem of the position of the hydrido ligands in $[H_4Os_{10}(CO)_{24}]^{2-}$ (**3**), a neutron structure analysis of the $[(Ph_3P)_2N]^+$ salt was carried out by McPartlin *et al.*[38] It revealed that all four hydrogen atoms are in fact located on the surface of the metal core (Figure 2). Two hydrides occupy μ_3-positions while the other two were found to be in μ_2-positions at the edges of the M_{10}-tetrahedron (one being disordered between two neighbouring edge positions).

The nearly close packed distribution of the carbonyl ligands around the μ_3-H atoms in **3** gives rise to some remarkably short C....H contact distances. Incipient C....H interaction may also be deduced from the concerted slight

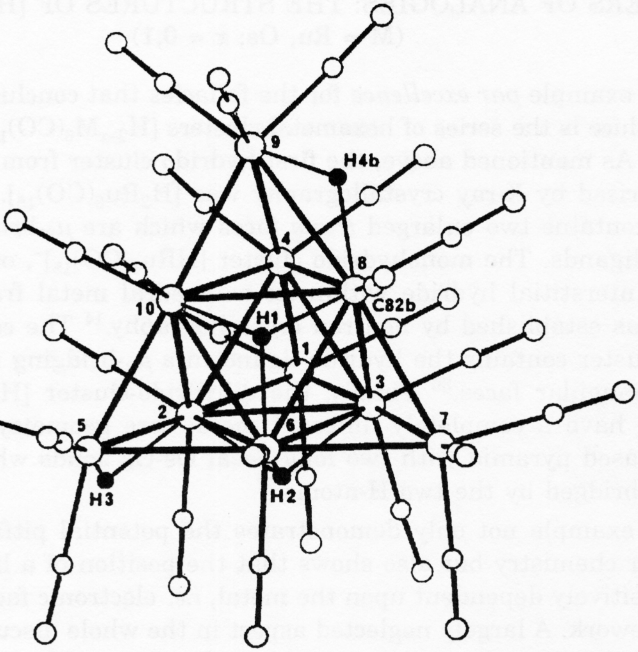

Figure 2. The position of the hydrido ligands in one of the two disordered isomeric forms of **3** (from Ref. 38).

displacement of the oxygen atoms of the carbonyl ligands away from the occupied μ_3-sites (a feature which is absent in the non-bridged faces of the tetrahedral cluster).

In view of the surface location of the hydrides as established in the neutron diffraction analysis, several questions arise. Firstly, what might have determined the precise position of the H-atoms in the crystal and why is only one of them disordered between two sites? Secondly, what is the structure of the cluster in solution?

In their analysis of the crystal structure of the neutral dihydrido-cluster $[H_2Os_{10}C(CO)_{24}]$ Braga *et al.* have related the position of the indirectly located hydrido atoms to the packing of the cluster units in the crystal.[24] Their conclusion is that the choice of the sites of the H-ligands might be under »intermolecular control«. A convincing case for this postulate is certainly more easily based on the highly symmetrical packing of a neutral cluster than in the case of salts such as the $[(Ph_3P)_2N]^+$ salt of **3**. Nonetheless, it is likely that intermolecular interactions in crystalline $[(Ph_3P)_2N]_2[H_4Os_{10}(CO)_{24}]$ contribute substantially to the actual situation as is described above.

THE INTERPRETATION OF ^{1}H- AND ^{13}C-NMR DATA: DYNAMIC BEHAVIOUR OF THE HYDRIDO LIGANDS IN $[HOs_{10}C(CO)_{24}]^{-}$ (**1**) AND $[H_4Os_{10}(CO)_{24}]^{2-}$ (**3**).

The ^{13}C-NMR spectrum of **1** in the ^{13}CO chemical shift region recorded at 300 K is shown in Figure 3 (the carbide resonance is observed as a singlet at considerably higher frequencies, δ = 409.0).[39]

The spectrum consists of five signals with an intensity ratio of 1:1:2:3:1 which are split into a high frequency set of three (1:1:2) and a lower frequency set of two (3:1) signals. It can be interpreted unambiguously in terms of a C_{3v} molecular symmetry on the timescale of the experiment, assuming rapid tripodal rotation of the apical $Os(CO)_3$-units which is a fast process even at 170 K. The original interpretation of this effective C_{3v} symmetry of **1** was that the hydride resided within a tetrahedral interstitial site,[40] however, in view of the arguments put forward in the sections above, it is necessary to reconsider the data, and we are therefore obliged to consider the possibility that the H-ligands in **1** (as well as its Ru-analogue **5**) are located on the surface of the metal core.

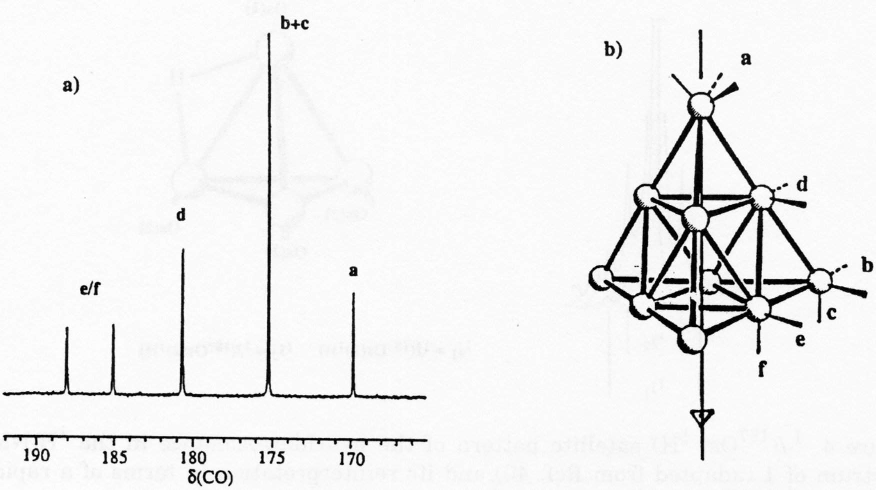

Figure 3. a) ^{13}C-NMR spectrum of **1** recorded at 300 K; b) labeling of the CO ligands for the assignment of the spectrum (adapted from Ref. 39).

The only possible position in which a static surface-located hydride may confer C_{3v} symmetry on **1** and **5** is in a symmetrical μ_3-coordination site above one of the exposed faces of the central octahedron (*i.e.* in the centre of one of the surfaces of the cluster core), as found in the solid state for two of the four hydrido atoms in **3**. However, such an interpretation of the ^{13}C-NMR spectra may be discounted in the case of **1** and, by implication, **5** with reference to the reported ^{1}H-NMR spectrum of **1**.[40] Associated with the hydride resonance at $\delta = -15.3$ are two sets of ^{187}Os-satellites ($I = 1/2$, 1.96% natural abundance) with an intensity ratio of *ca.* 1:3 and $^{1}J(^{187}\mathrm{Os}\text{-}^{1}\mathrm{H})$ coupling constants of 26.6 and 15.9 Hz respectively. Clearly, μ_3-coordination of the hydride as proposed above would lead only to one set of satellites since all three of the osmium atoms in this site are equivalent. We are therefore led to consider the location of the H-ligand on the surface of one of the capping tetrahedra of the metal core, and in this situation the ^{187}Os-satellite pattern suggests the association of the hydride with three equivalent osmium atoms in addition to the apical one. This is consistent with the ^{13}C-NMR spectrum since static location of the hydrido ligand on a face (μ_3-) or edge (μ_2-) of a tetrahedral cap would lead at best to C_s symmetry, whilst its equal association (on the NMR time scale) with the three osmium atoms at the base of a cap and with that at a vertex would clearly result in the required effective C_{3v} symmetry (Figure 4).

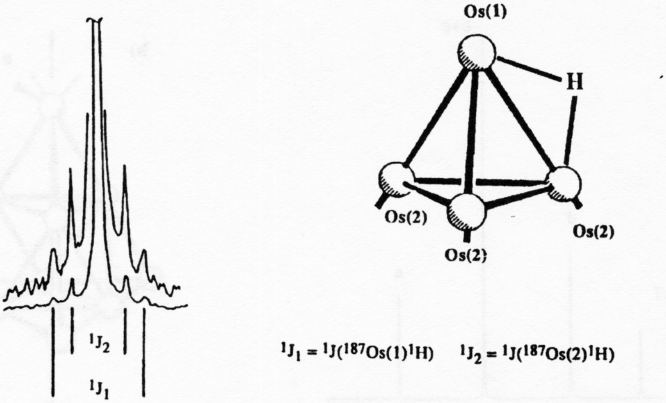

Figure 4. $^{1}J(^{187}\mathrm{Os},\ ^{1}\mathrm{H})$ satellite pattern of the hydride resonance in the ^{1}H-NMR spectrum of **1** (adapted from Ref. 40) and its reinterpretation in terms of a rapidly migrating H ligand.

Returning to the ^{187}Os satellite pattern, the coupling constant of 15.9 Hz for the more intense satellites is unusually small for a static hydride in an osmium cluster (typical values are between 26 and 40 Hz, although the amount of published data is by no means extensive).[40,41] It is, however, comparable to the average $^{1}J(^{187}\mathrm{Os}\text{-}^{1}\mathrm{H})$ found for rapidly exchanging systems such as $H_4Os_4(CO)_{12}$(^1J(^{187}Os-^{1}H) = 14.4 Hz at 298 K and 30.5 Hz at 168 K). We therefore have to consider a model in which the hydrido-ligand is surface located and rapidly »rotating« around the three equivalent edges and faces of one of the capping tetrahedra, a situation which generates the observed overall symmetry, and is in adition consistent with the ^{1}H-NMR data. The ^1J(^{187}Os-^{1}H) of 26.6 Hz is attributed to the coupling to the vertex osmium nucleus whilst the splitting of the set of satellites with threefold intensity corresponds to the average coupling to the three chemically equivalent osmium nuclei as depicted in Figure 4. Such a rotation of the hydride would not be surprising considering the above-mentioned observation that the apical $M(CO)_3$ units are undergoing rapid tripodal rotation with which the hydride motion may be concerted. This is therefore the alternative model to that originally proposed (based on the assumption of the interstitial location of the H-atom). The ^{13}C-NMR spectrum of **1** shown in Figure 3 thus conceals some residual motion of both the hydrido and carbonyl ligands, and indeed, the spectra recorded above these temperatures reveal a development of these motions.

A series of ^{13}C-NMR spectra of **1** recorded in $C_2D_2Cl_4$ up to 416 K is shown in Figure 5a. The initial effect of increasing the temperature is the exchange broadening of all resonances in the spectrum followed by coalescence above 380 K. The appearance of the spectra suggests that the three signals at $180 < \delta < 190$ (those due to the edge-$Os(CO)_2$ units) and the two

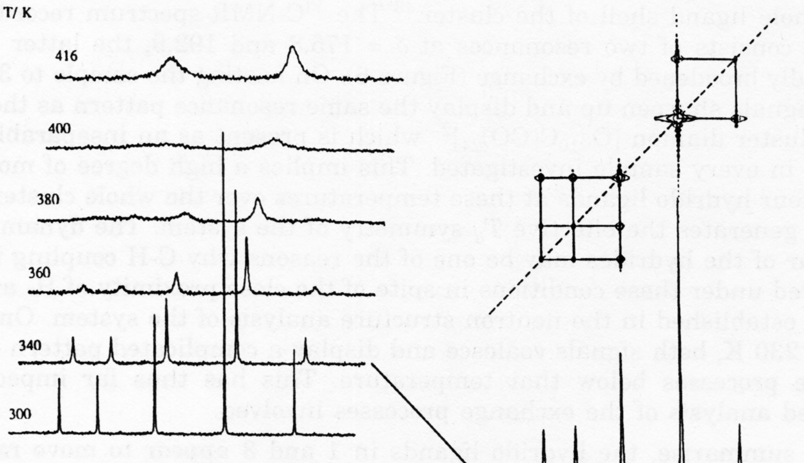

Figure 5. a) A high temperature ^{13}C-NMR series of **1**; b) ^{13}C-EXSY spectrum of **1** recorded at 340 K (adapted from Ref. 39).

signals at lower frequency (the $M(CO)_3$ carbonyls) internally coalesce, but that there is no visible exchange between the two sets of signals. This results in the emergence of two broad resonances at 416 K (δ = 173.6, 182.9), each due to the 12 CO-ligands and indicative of a transformation of the effective point symmetry from C_{3v} to T_d.

In order to unambiguously establish the exchange network for the ^{13}CO resonances of **1**, a $\{^1H\}^{13}$C-EXSY spectrum was recorded at 340 K and is shown in Figure 5b. The pattern is consistent with the deductions made from the one dimensional VT-spectra in that only cross peaks attributable to exchange between the two apical $M(CO)_3$ sites or the three $M(CO)_2$-edge sites are observed but not between these two environments. In addition, both processes appear to be correlated. Since CO exchange between the vertex positions cannot occur without involving the edge sites, the only possible explanation is the exchange of the hydride between all possible positions on the cluster surface, and if this were a rapid process, the expected effective symmetry at high temperatures would be T_d, as is observed. In this way the migration of the hydride over the surface of the cluster core is indirectly probed by the observation of its effect on the effective point symmetry of the system. It should be pointed out that the observed behaviour of the hydride in **1** is closely related to that of Hg-Y-fragments (Y = Cl, Br, I, CF_3) attached to Os_{10}-cores.[42] This is an example for the usefulness of the isolobal analogy in this area of chemistry.

For an investigation of the properties of **3** in solution, ^{13}C-NMR spectroscopy was likewise thought to be the most appropriate method, since it permitted the observation of the effect that the presence of H-ligands has on the whole ligand shell of the cluster.[43] The ^{13}C-NMR spectrum recorded at 295 K consists of two resonances at δ = 175.8 and 192.9, the latter being markedly broadened by exchange (Figure 6). On heating the sample to 375 K, both signals sharpen up and display the same resonance pattern as the carbido cluster dianion $[Os_{10}C(CO)_{24}]^{2-}$ which is present as an inseparable impurity in every sample investigated. This implies a high degree of mobility of all four hydrido ligands at these temperatures over the whole cluster core which generates the effective T_d symmetry of the system. The dynamic behaviour of the hydrides may be one of the reasons why C-H coupling is not observed under these conditions in spite of the close proximity of H- and C-atoms established in the neutron structure analysis of the system. On cooling to 230 K, both signals coalesce and display a complicated pattern of exchange processes below that temperature. This has thus far impeded a detailed analysis of the exchange processes involved.

To summarise, the hydrido ligands in **1** and **3** appear to move rapidly through the shell of the coordinated carbon monoxide. This is a behaviour reminiscent of the observed mobility of chemisorbed hydrogen on metal surfaces exposed to »synthesis gas«. As far as the experimental method employed is concerned, it has been found that for the probing of the hydride mobility in symmetrical high nuclearity carbonyl clusters the indirect moni-

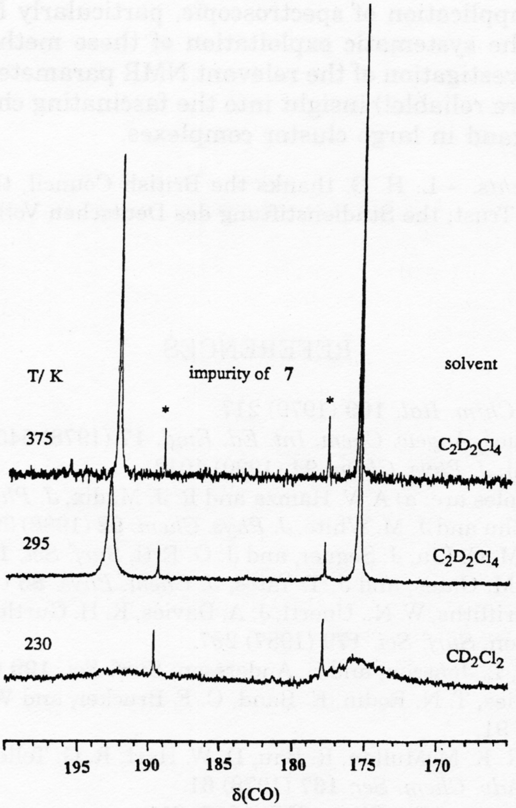

Figure 6. Variable temperature series of ^{13}C-NMR spectra of **3**.

toring of its effect on the CO shell as a whole by means of ^{13}C-NMR spectroscopy may be the method of choice. As the amount of accumulated data increases an even more specific interpretation of the spectroscopic results will be feasible.

CONCLUSIONS

Nowadays, the difficulties associated with the location of hydrido-ligands in clusters are more apparent than ever before. The case histories referred to in this paper, some of which have already found their way into current textbooks, should serve as caveats in future investigations. While it appears unlikely that improvements in the area of X-ray crystallographic methods will provide more definitive information for the indirect H-location techniques in the near future, there is certainly still a considerable untapped potential in the application of spectroscopic, particularly NMR, methods to these systems. The systematic exploitation of these methods coupled with the theoretical investigation of the relevant NMR parameters should provide a deeper (and more reliable!) insight into the fascinating chemical behaviour of the hydrido ligand in large cluster complexes.

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SAŽETAK

Detekcija i lociranje hidrido-liganada u visokonuklearnim karbonilnim klusterima osmija i rutenija: kritički osvrt

Lutz H. Gade, Brian F. G. Johnson i Jack Lewis

Hidrido-karbonilni klusteri vrlo su važni molekulski modeli za koadsorpciju ugljikova monoksida i vodika na metalne površine, koja je ključni korak u nizu katalitičkih procesa. U posljednje dvije dekade u literaturi je objavljen znatan broj takvih modela. U ovom radu dan je kritički pregled strukturne kemije visokonuklearnih hidrido-karbonilnih klustera osmija i rutenija. Posebno su naglašena ograničenja različitih posrednih metoda lociranja hidrida u klusterima. Dana je i alternativna interpretacija rezultata spektroskopskih istraživanja uzoraka nekih rutenijevih i osmijevih klustera u otopini.