Direct Location of the Interstitial Hydride Ligand in $[HRu_6(CO)_{18}]^-$ by both *X*-Ray and Neutron Analyses of $[Ph_4As][HRu_6(CO)_{18}]$

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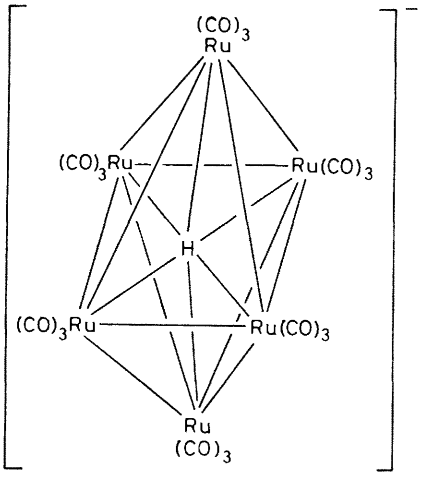
Summary The proposed interstitial location of the hydride ligand in $[HRu_6(CO)_{18}]^-$ has been established by *X*-ray and neutron analyses of $[Ph_4As][HRu_6(CO)_{18}]$

ALTHOUGH the interstitial nature of hydrogen in binary metal hydrides is well established,[1] the anion $[HRu_6(CO)_{18}]^-$ (**1**) was the first polynuclear carbonyl in which an interstitial hydrogen atom was detected.[2] For this compound



(1)

the possibility of the hydrogen ligand being on the exterior of the cluster was ruled out by the highly symmetrical overall structure, which was shown by *X*-ray analysis[2] to be almost identical to that in the dianion $[Os_6(CO)_{18}]^{2-}$ which has crystallographic D_3 symmetry.[3] Thus, no sign of the characteristic displacement of the close packed carbonyls necessary to accommodate an external hydrogen atom was observed and furthermore no $^{13}C-^{1}H$ n.m.r. coupling could be detected. The unusual low field signal (τ −6·41) in the ^1H n.m.r. spectrum was attributed to this novel hydrogen environment, but this assignment proved to be controversial. For example, recent neutron diffraction studies of the extended polynuclear carbonyls $[H_nNi_{12}(CO)_{21}]^{(4-n)-}$ [(2) $n = 1$, (3) $n = 2$] have shown that the

$[HNi_{12}(CO)_{21}]^{3-}$ $[H_2Ni_{12}(CO)_{21}]^{2-}$
(2) **(3)**

hydrogen ligands are also interstitial, being located in distorted octahedral cavities, but the ^1H n.m.r. spectra show the normal high field shifts (τ 34·0 and 28·0)[4] characteristic of transition metal hydrides. This prompted the conclusion, in a review published at the same time, that the hydrogen atom in (**1**) was not interstitial but that the large downfield shift exhibited in the ^1H n.m.r. spectrum was due to a hydrogen atom associated with a carbonyl ligand.[5] The authors made a similar assignment for $[HCo_6(CO)_{15}]^-$ (τ − 13·2) and proposed that a particularly low field ^1H n.m.r. shift in polynuclear carbonyls is diagnostic of a new class of cluster hydrides with direct carbonyl–hydrogen linkages. (A recent neutron analysis has shown that this cluster contains an interstitial hydrogen atom[6].) In addition, from consideration of the weakening effect of hydrogen ligands on M–M bonds, they concluded that interstitial hydrides would not occur in M_6 clusters except in the presence of μ_2- or μ_3-carbonyl ligands.

Recently with accurate *X*-ray data hydrogen atoms have been occasionally located directly in carbonyl clusters with up to four metal atoms.[7] Prompted by this, crystals of the anion (**1**) with a range of counter ions were prepared with the purpose of directly locating the H atom and confirming the original interstitial assignment. The $[Ph_4As]^+$ salt of (**1**) gave very good *X*-ray data which afforded ready location of the hydrogen atom at the centre of the Ru_6 octahedron, the positional and isotropic thermal parameters were successfully refined giving a mean Ru–H distance of 2·04 Å. Thus the interstitial site of the hydrogen ligand is confirmed beyond further question. This cluster is the first hexanuclear ruthenium species to be obtained with no external bridging ligand, so clearly octahedral clusters with interstitial hydride atoms are not too unstable to exist without the presence of bridging carbonyl ligands.

TABLE. The M–H distances in $[HRu_6(CO)_{18}]^-$ (from *X*-ray/neutron refinement) together with those reported for the other interstitial hydrides.

Interstitial hydride	*d* (M–H)/Å	^1H n.m.r. shift (τ)
$[HCo_6(CO)_{15}]^-$	1·80—1·87(2)[a]	−13·2[a]
$[HRu_6(CO)_{18}]^-$	2·03—2·06(1)	−6·4
(**3**)	long 2·00(av.)[b] short 1·84(av.)	28·0[b]
(**2**)	long 2·22(av.)[b] short 1·72(av.)	34·0[b]
$[H_2Rh_{13}(CO)_{24}]^{3-}$	[c]	36·7[d]
$[H_3Rh_{13}(CO)_{24}]^{2-}$	[c]	39·3[d]

[a] Ref. 6. [b] Ref. 4. [c] These hydrides are not truly interstitial; the position of the H atoms in square pyramidal sites on the surface, has been deduced from *X*-ray analyses (ref. 10). [d] Ref. 10.

In view of the very large difference in the ^1H n.m.r. shift observed for the intersitial hydride in this octahedral cluster compared to those for the hydrogen atoms in the extended clusters (**2**) and (**3**) it was important to obtain a more accurate location of the hydrogen atom within the Ru_6 octahedron of (**1**). Neutron data† were collected with a larger crystal of the $[Ph_4As]^+$ salt and a combined refinement of single set of positional and thermal parameters using the *X*-ray and neutron data was carried out by the method described by Sheldrick.[8] The results together with data reported for other interstitial hydrides are shown in the Table, and the overall structure of (**1**) is shown in the Figure.

The range of ^1H n.m.r. shifts for the four interstitial polynuclear carbonyl cluster hydrides that are known (Table) varies from τ − 13·2 to 34, a wide range compared to that of the hundreds of other reported compounds of the later

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† *Crystal data*: $C_{42}H_{21}AsO_{18}Ru_6$, *M* 1495·1, monoclinic, space group $P2_1/n$, $a = 16·393(5)$, $b = 19·426(7)$, $c = 15·023(5)$ Å, $\beta = 100·64(2)°$, $U = 4,701·8$ Å^3, $D_c = 2·11$ g cm^{-3}, $Z = 4$, Mo-K_α radiation $\lambda = 0·71069$ Å, μ(Mo-K_α) = 24·45 cm^{-1}, neutrons, $\lambda = 1·2641$ Å, $\mu = 0·65$ cm^{-1}. The structure was initially solved from the *X*-ray data alone, and then refined to current residuals of $R = 0·073$, $R_w = 0·079$ (*X*-ray), and $R = 0·091$, $R_w = 0·087$ (neutron) for 4480 *X*-ray ($\sin\theta/\lambda > 0·45$) and 2261 observed neutron data [$F > 5\sigma(F)$].

There is a slight disorder (0·906 . 0·094) of the $[HRu_6(CO)_{18}]^-$ anion similar in nature to that present for one of the two independent anions of the $[(Ph_3P)_2N]^+$ salt (C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, accepted for publication). The two orientations of the cluster are related by rotation about an axis through the centre of the cluster so that the H atom is unaffected by the disorder.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

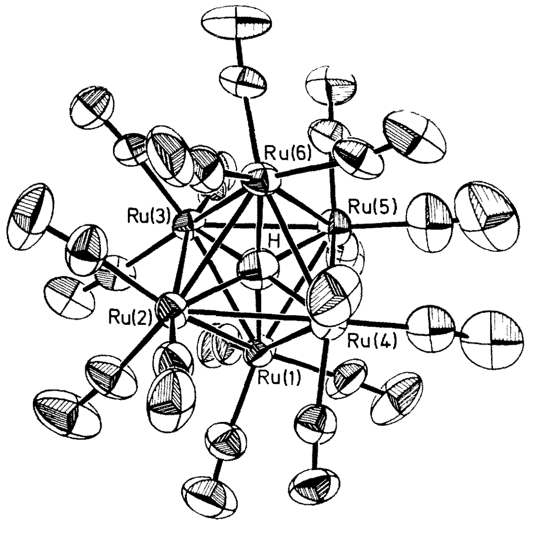

FIGURE. The structure of the dianion $[HRu_6(CO)_{18}]^-$ from the neutron analysis of the $[Ph_4As]^+$ salt. Ruthenium hydride bond lengths are: Ru(1)–H, 2·033(11); Ru(2)–H, 2·034(11); Ru(3)–H, 2·039(12); Ru(4)–H, 2·055(12); Ru(5)–H, 2·028(11); Ru(6)–H 2·034(11) Å.

transition elements where, in spite of a variety of modes of hydride bonding, this shift lies in the range τ 10—69 with very few exceptions.[9] Clearly ^1H n.m.r. spectroscopy alone cannot be used as a diagnostic test for the position of an H-atom in a polynuclear cluster as interstitial hydrides are very sensitive to the exact symmetry of the surrounding metals. In (**1**) and in $[HCo_6(CO)_{15}]^-$ a nearly O_h symmetry is observed for the metals together with almost equal M–H distances; this environment is associated with large downfield shifts of the ^1H n.m.r. resonance. However, the hydride ligands in the D_{3d} cavities of the extended clusters (**2**) and (**3**) are in less symmetrical positions being much closer in each case to the central hexa-metal plane than to the outer triangular metal set (Table), so that in (**2**) the hydride may be considered as triply bridging three nickel atoms and only very weakly bonded to the other three.[4] The unsymmetrical bonding of the H-atoms in (**2**) and (**3**) is accompanied by ^1H n.m.r. signals in the normal upfield region (Table). It seems consistent with this trend that the 'interstitial' H-atoms in the extended cluster $[H_nRh_{13}(CO)_{24}]^{(5-n)-}$ ($n = 2$, and 3), which are in incomplete octahedral (*i.e.* square pyramidal) sites on the surface of the clusters have ^1H n.m.r. shifts at the even higher τ values of 36·7 and 39·3.[10]

Many transition metals absorb hydrogen to produce non-stoicheiometric hydrides in which the hydrogen atoms occupy octahedral sites within the close-packed metal array. This is always accompanied by an expansion of the metal lattice; for example, an octahedral site in the cubic close-packed structure of palladium metal has a radius of 1·94 Å, but the radius of this site increases to 2·04 Å in $PdH_{0\cdot7}$.[11] Of the three polynuclear carbonyl species $[H_nRu_6(CO)_{18}]^{n-2}$ ($n = 0, 1, 2$) the dianion, with no hydride ligands, has an octahedral site radius of 2·02 Å. The introduction of an interstitial hydride ligand increases this to 2·04 Å in (**1**), and in the neutral $H_2Ru_6(CO)_{18}$ molecule,[12] where the two hydrogens are on the outside of the cluster, there is a further expansion of the octahedral hole giving a mean radius of 2·05 Å. This casts doubt on any assumption that increase in the metal–metal distances is merely a reflection of the 'size' of the interstitial hydrogen atom. Significantly the mean Ru–C distance in $[Ru_6(CO)_{16}C]^{2-}$ is 2·05 Å,[13] very similar to the mean Ru–H bond length observed in $[HRu_6(CO)_{18}]^-$. From the limited data available for external Ru–H bridging bond lengths it seems that a value of *ca.* 1·8 Å is typical; for example the eight μ_2-H–Ru lengths in $H_4Ru_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$ average 1·76(5) Å.[7] This supports the conclusion that the space available in an 'unexpanded' Ru_6 octahedral hole of radius 2·02 Å would be more than adequate to accommodate an interstitial hydride. Thus it seems probable that the expansion in M–M bond lengths produced by external μ-H ligands and those produced by interstitial H-atoms are related and are electronic in origin.

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