

Synthesis and X-ray Analysis of the Hydrido-carbido-monoanion $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$; a Cluster Compound with an Interstitial Hydrogen Ligand in a Tetrahedral Site

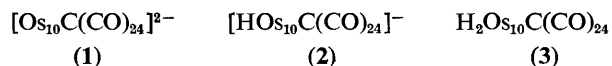
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Protonation of the carbido-dianion $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ with conc. H_2SO_4 gives $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ and $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$; from X-ray analyses of the $[\text{Ph}_4\text{As}]^+$ and $[\text{Ph}_3\text{MeP}]^+$ salts of the hydrido-monoanion, which show a structure with a close-packed carbonyl distribution virtually identical to that of the dianion, it may be deduced that this is the first example of an H-ligand in a tetrahedral site of a polynuclear carbonyl species.

We recently reported the synthesis and structural characterisation of the dianion $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ (1) and proposed that since the carbonyl ligands lie approximately perpendicular to the large faces of the Os_{10} tetrahedron, this cluster may be a good model for a monolayer of carbon monoxide chemisorbed onto a metal surface.¹ A study of the reactions of (1) with simple molecules should therefore allow some of the properties of clusters to be more realistically compared with those of the bulk metal; such studies are crucial in assessing the validity of cluster/surface analogies.



Protonation (conc. H_2SO_4) of the dianion (1) in donor solvents gives a mixture of (1), $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ (2), and $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ (3) but the actual product distribution is highly dependent on the basicity of the solvent, as has been found for other carbonyl hydride systems.² For example, whereas acidification in tetrahydrofuran (THF) gives an equilibrium

mixture of (1), (2), and (3), acidification in MeCN gives initially the monoanion (2) and finally a precipitate (quantitative) of the dihydride (3). Protonation in non-donor solvents such as CH_2Cl_2 or CHCl_3 gives only the monoanion (2) which may be isolated in quantitative yields as the $[\text{PPN}]^+$, $[\text{Ph}_4\text{As}]^+$, or $[\text{Ph}_3\text{MeP}]^+$ salts.

Solutions of the hydrido-monoanion (2) are brown and the carbonyl i.r. spectrum[†] is more complicated than that of the dianion (1) and is similar (in pattern) to those[†] of the iodo-monoanion $[\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}]^-$ and $\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}_2$ in which the addition of the I^+ ligands has caused an opening up of the metal polyhedron.

[†] $\nu(\text{CO})$ (cm^{-1} , CH_2Cl_2): $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ (1) (ref. 1) 2033 s and 1986 s; $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ (2) 2062 s sh, 2057 vs, 2019 m, 2009 s, and 2002 w sh; $[\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}]^-$ (ref. 3) 2065 s, 2057 vs, 2017 m, and 2004 s; $\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}_2$ (ref. 3) 2084 sv, 2076 m, 2308 s, 2027 m, and 2011 w sh.

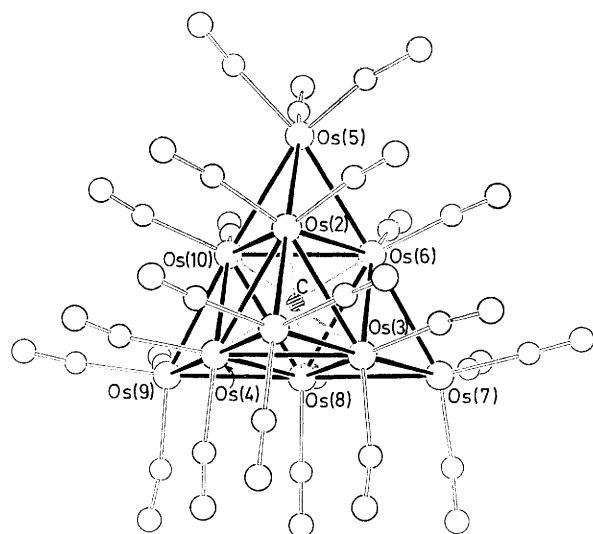


Figure 1. The structure of the $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ anion (2) in the $[\text{Ph}_3\text{MeP}]^+$ salt. Important Os-Os bond lengths (Å) are: (1)-(2) 2.791, (1)-(3) 2.823, (1)-(4) 2.835, (2)-(3) 2.884, (2)-(4) 2.893, (2)-(5) 2.793; (2)-(6) 2.890, (2)-(10) 2.890, (3)-(4) 2.890, (3)-(6) 2.892, (3)-(7) 2.837, (3)-(8) 2.870, (4)-(8) 2.871, (4)-(9) 2.822, (4)-(10) 2.881, (5)-(6) 2.810, (5)-(10) 2.832, (6)-(7) 2.805, (6)-(8) 2.885, (6)-(10) 2.892, (7)-(8) 2.776, (8)-(9) 2.769, (8)-(10) 2.904, (9)-(10) 2.813, maximum e.s.d. 0.001 Å.

In the $[\text{Ph}_4\text{As}]^+$ salt the anion (2) has exact C_{3v} symmetry with the C_3 axis through Os(5) . . . C(carbido). Unique Os-Os bonds (Å): (1)-(2) 2.838, (1)-(4) 2.781, (2)-(4) 2.870, (2)-(5) 2.811, (2)-(6) 2.900, (3)-(4) 2.884, maximum e.s.d. 0.002 Å. Mean Os-C (carbido) 2.04 Å in both salts.

From X-ray analyses[‡] of both the $[\text{Ph}_4\text{As}]^+$ and $[\text{Ph}_3\text{MeP}]^+$ salts, the anion $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ has been shown to have the structure illustrated in Figure 1. Interestingly the addition of the H-ligand to the $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ dianion has not produced an opening up of the metal core, as observed in $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$,³ nor any significant displacement of the close-packed carbonyl ligands.

Comparison of the structure of the dianion (1) [Figure 2(a)] with that of the monohydride (2) [Figure 2(b)] shows their remarkable similarity. It is well established that attachment of hydrogen atoms to the metal surface of a cluster compound produces a marked and characteristic displacement of the carbonyl ligands and this is frequently used to deduce the H-ligand co-ordination site.^{4,5} For example the μ_3 -hydride ligand in $[\text{HOs}_6(\text{CO})_{18}]^-$ was readily inferred⁵ from the marked 'bending back' of the carbonyl ligands from one face of the Os_6 octahedron giving a distorted hexagonal ring (diameter ca. 5.5 Å) of carbonyl carbon atoms above the bridged metal triangle, Figure 3(a). In contrast, the carbonyl ligands in the monohydride (2) remain almost perpendicular to the faces of the metal core as in the dianion (1). Consequently the C atoms of the CO ligands form a close packed network of virtual T_d symmetry surrounding the cluster surface, Figure 3(b).

The ^1H n.m.r. signal at 25.45 τ ($[\text{PPN}]^+$ salt, CDCl_3 , 20 °C) indicates that the H-ligand in (2) is directly bonded to the

[‡] Crystal data: $[\text{C}_{24}\text{H}_{20}\text{As}][\text{C}_{25}\text{HOs}_{10}\text{Os}_{10}]$, hexagonal, space group $P6_3mc$, $a = 16.660$, $c = 12.070$ Å, $Z = 2$, $I/\sigma(I) > 3.0$, θ -range 3–25°, present R value 0.0539 for 1205 reflections. The $[\text{Ph}_4\text{As}]^+$ cation is disordered.

$[\text{C}_{18}\text{H}_{16}\text{P}][\text{C}_{25}\text{HOs}_{10}\text{Os}_{10}]$, triclinic, space group $P\bar{1}$, $a = 16.211$, $b = 15.052$, $c = 12.016$ Å, $\alpha = 85.30$, $\beta = 96.38$, $\gamma = 111.43^\circ$, $Z = 2$, $I/\sigma(I) > 3.0$, θ -range 3–25°, present R value = 0.0503 for 6724 reflections.

The atomic co-ordinates for these structures are available 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.

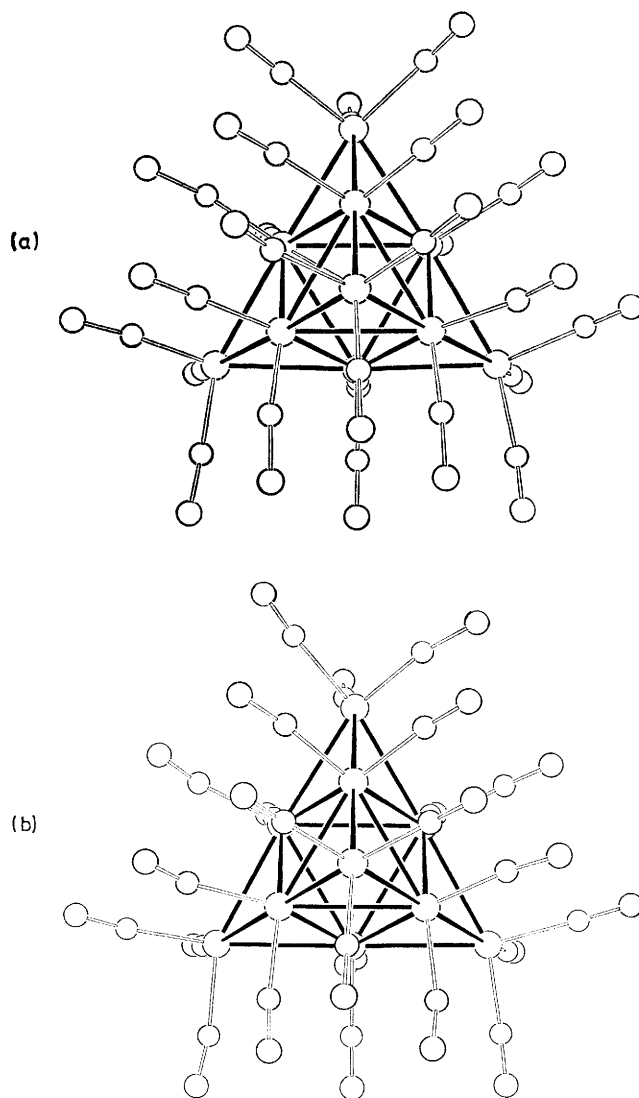


Figure 2. Comparison of the structures of (a) the $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ dianion (1) and (b) the $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ hydrido-monoanion (2).

metal core and, as it cannot be accommodated on the cluster surface, we conclude that it is interstitial. Several examples of interstitial H-atoms in octahedral sites of polynuclear carbonyls have recently been reported.⁶⁻⁹ However, in (2) the only octahedral site is occupied by the carbido-atom so this hydride appears to be the first example of a carbonyl cluster with an H-atom in a tetrahedral site. § The M-H bond lengths of interstitial hydride ligands in octahedral sites have been found to lie in the range 1.72 to 2.22 Å.⁹ For an H-atom in one of the capping tetrahedra of (2) the Os-H bond length is estimated to be 1.75 Å. This value is similar to the Os-H distances found from neutron diffraction studies of non-interstitial hydrido-osmium carbonyl clusters which range from 1.659 to 1.883 Å.⁹

As the clusters (1) and (2) have similar metal atom and carbonyl ligand geometries, with virtual T_d symmetry, the change from the simple two band i.r. spectrum of (1) to the more complex pattern of (2) is attributable to the introduction of the H-ligand (formally H^+) into one of the four tetrahedral interstitial sites thereby reducing the symmetry from T_d to C_{3v} .

§ A number of earlier transition metals are known to form binary dihydrides with a fluorite type of structure in which the hydrogen atoms are located in tetrahedral sites: W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, 'Metal Hydrides,' Academic Press, New York, 1968.

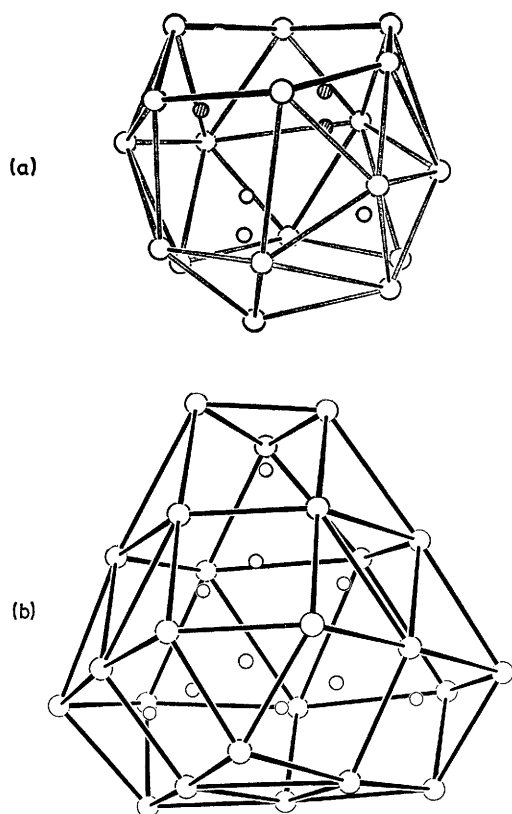


Figure 3. The distribution of the carbon atoms (large circles) of the CO ligands round the metal core (small circles) in (a) $[\text{HOs}_8(\text{CO})_{18}]^-$ (the μ_3 -hydrogen ligand is above the shaded Os atoms), and (b) $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$.

The monoanion (**2**) in the $[\text{Ph}_4\text{As}]^+$ salt has exact C_{3v} symmetry with the crystallographically unique Os_4 capping group having a mean Os–Os bond length of 2.856 Å, 0.018 Å ($> 20\sigma$) longer than the mean value for the three other, symmetry related, Os_4 groups. The three smaller Os_4 capping groups have a mean Os–Os bond length of 2.838 Å which is close to the mean value of 2.835 Å for the capping groups in the dianion (**1**).¹ It has been shown that octahedrally located interstitial H-atoms produce a slight expansion of the enveloping metal polyhedron.^{8,8} The small, but highly significant,

enlargement of the unique Os_4 capping group in the $[\text{Ph}_4\text{As}]^+$ salt is therefore further evidence for the interstitial nature of the H-ligand in (**2**) which is apparently located in this tetrahedral cavity on the crystallographic C_3 axis.

In the $[\text{Ph}_3\text{MeP}]^+$ salt the H-ligand appears to be disordered over two principal sites. Two Os_4 capping tetrahedra are equal in mean Os–Os bond lengths (2.852 Å) and significantly larger than the other two Os_4 tetrahedra (mean Os–Os 2.844 and 2.843 Å).

The stability of (**2**) is similar to that of the interstitial hydride⁶ $[\text{HCo}_6(\text{CO})_{15}]^-$, *i.e.* salts of (**2**) are moderately soluble and stable in non-co-ordinating solvents, but in the presence of solvents such as THF, MeCN, MeOH, or H_2O deprotonation readily takes place. However this type of behaviour is not general for polynuclear carbonyls containing embedded hydrogen atoms, for example $[\text{HRu}_6(\text{CO})_{18}]^-$ will not deprotonate even under severe conditions.⁸

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