# Hydride Fluxionality in High-nuclearity Osmium Carbonyl Clusters

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The $^1H$ n.m.r. spectra of monohydrido derivatives of decaosmium and higher-nuclearity clusters reveal satellites due to $^1J(^{187}Os–^1H)$ coupling; a study of the dynamic behaviour provides information about molecular structures in *solution*. The $^1H$ n.m.r. spectra of multihydrido decaosmium clusters, $[Os_{10}H_n(CO)_{24}X_y]^{m-}$ ($n = 4, m = 2, y = 0; n = 4, m = 1, y = 1; n = 5, m = 1, y = 0$; X = halide), show no such satellites and possible mechanisms for their behaviour in solution are discussed.

Hydrido ligands in transition-metal cluster complexes may adopt terminal,[1] μ-bridging,[2] $\mu_3$-capping,[3] or interstitial bonding modes.[4] Single-crystal *X*-ray structural analysis has been successful in the location of hydrogen atoms in a number of larger hydrido clusters in the solid.[5] However, in general, hydrogen atoms are usually located by indirect methods, such as consideration of the stereochemical arrangement of the ligands about metal atoms, M–M bond lengthening, and metal cluster face or cavity expansion.[6,7]

The unequivocal locations of hydrides are best established by neutron-diffraction studies,[8] as exemplified in the direct location of the hydride in the anion $[Ru_6H(CO)_{18}]^-$. Infrared spectroscopic studies have also been used to assign the positions of hydrides in both the solid and solution.[9,10]

In principle, $^1H$ n.m.r. spectroscopy can provide valuable information about the nature of the metal–hydrogen bond in hydrido clusters. Although chemical shift arguments have frequently been used to assign hydride environments in low-nuclearity hydrido clusters, such methods have met with little success in the higher-nuclearity clusters. In particular, wide variations in chemical shifts are associated with similar chemical environments.[11,12]

The characteristic splitting patterns observed in n.m.r. spectroscopy from coupling to spin ½ nuclei have been found to be important diagnostic aids in organometallic chemistry. Coupling to nuclei such as $^{31}P$ (100%), $^{195}Pt$ (33.7), $^{103}Rh$ (100), and $^{183}W$ (14.3) has provided valuable structural information.[13]

Reports of coupling to $^{187}Os$ (1.6%) are still comparatively rare[14,15] due to the scarcity of isotropically pure $^{187}Os$; the use of isotopically enriched samples is thus pre-empted. Several values of $^1J(^{187}Os–^1H)$ have been reported,[16–18] for mono- and multi-hydrido osmium clusters. We now report the use of high-resolution $^1H$ n.m.r. spectroscopy to observe the coupling at natural abundance of $^{187}Os$ ($I = \frac{1}{2}$, 1.6% natural abundance) to hydride in a range of high-nuclearity osmium clusters.

**Table.** $^1H$ N.m.r. data for the hydrido-osmium clusters (**1**)—(**8**)

| Complex | Chemical shift (δ)[a] | $^1J(^{187}Os–^1H)$/Hz |
|---|---|---|
| (**1**) $[N(PPh_3)_2][Os_{10}H^{13}C(^{13}CO)_{24}]$ | −15.3 | 15.9,<br>26.6[b] |
| (**2**) $[PPh_3Me][Os_{11}HC(CO)_{27}]$ | −19.1 | 14.1,<br>38.2,<br>49.9 |
| (**3**) $[Os_{10}HC(CO)_{24}\{Au(PPh_3)\}]$ | −20.4 | 15.4,<br>26.2 |
| (**4**) $[N(PPh_3)_2][Os_{10}HC(CO)_{22}(NO)I]$ | −17.5 | 13.8,<br>25.9 |
| (**5**) $[Os_{10}H_2C(CO)_{24}]$ | *c* | |
| (**6**) $[N(PPh_3)_2]_2[Os_{10}H_4(CO)_{24}]$ | −16.48<br>−14.70,<br>−19.08[d] | |
| (**7**) $[N(PPh_3)_2][Os_{10}H_5(CO)_{24}]$ | −15.9,<br>−16.2 | |
| (**8**) $[N(PPh_3)_2][Os_{10}H_4(CO)_{24}I]$ | −16.05,<br>−17.14 | |

[a] Measured at 400 MHz and 25 °C unless otherwise stated, in $CD_2Cl_2$. [b] $J$(C–H) 2.00 Hz. [c] No signals observed using $^1H$ n.m.r. ($CD_3COCD_3$), due to poor solubility, or using magic angle spinning $^1H$ n.m.r. due to the long nuclear relaxation time of (**5**). [d] At −80 °C in $CD_2Cl_2$.

## Results and Discussion

The $^1H$ n.m.r. spectrum of $[Os_{10}HC(CO)_{24}]^-$ (**1**) shows two $^1H–^{187}Os$ couplings of 15.9 and 26.6 Hz (Table) with the satellite intensities being in the ratio of 3:1.[17] This is as expected for a hydride in a tetrahedral environment (Figure 1). The possibility of couplings to $^{13}C$ in either the carbide or the carbonyl ligands was eliminated by recording the $^1H$ n.m.r. spectrum of an enriched sample (16% $^{13}C$) of (**1**). The largest observed coupling to $^{13}C$ was *ca.* 2 Hz.

The $^{13}C$ n.m.r. spectrum of the $^{13}C$-labelled sample of (**1**) demonstrated that all of the carbonyls *and* the carbide (+409 p.p.m.) had been enriched. The $^{13}C$ n.m.r. spectrum exhibits five lines in a ratio 1:1:2:3:1 (Figure 2) in $CD_2Cl_2$ at 20 °C, which

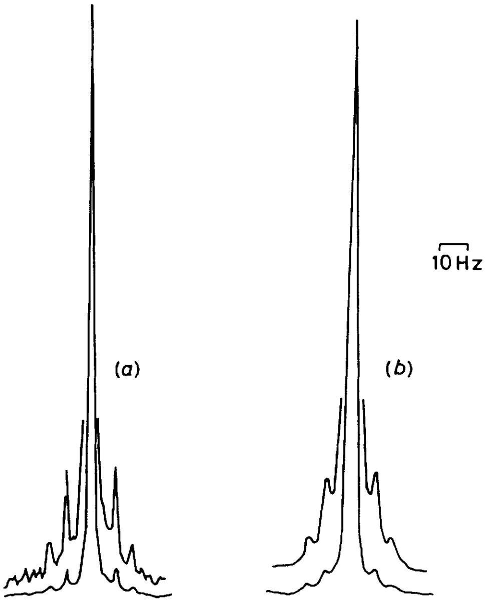

**Figure 1.** The $^1H$ n.m.r. spectra of compound (**1**) in $CD_2Cl_2$ with (*a*) $^{13}C$ at natural abundance and (*b*) $^{13}C$ enriched to *ca.* 16%

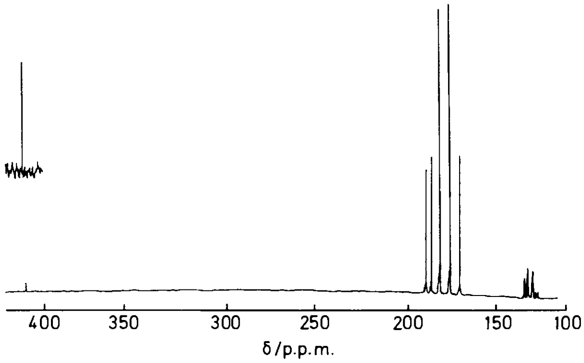

**Figure 2.** The $^{13}C$ n.m.r. spectrum of $[N(PPh_3)_2][Os_{10}H^{13}C(^{13}CO)_{24}]$ (**1**) in $CD_2Cl_2$ at 20 °C (250 MHz)

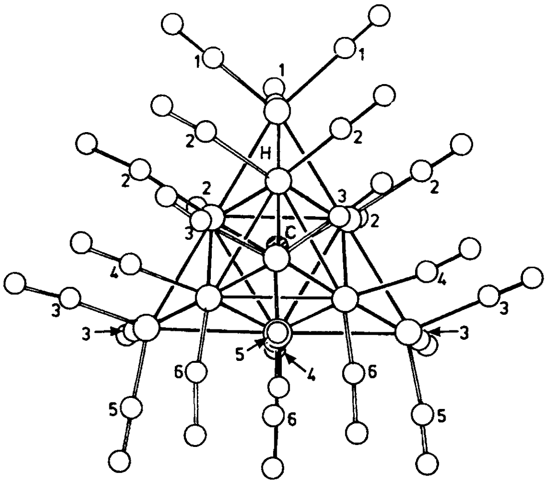

**Figure 3.** Structure of $[N(PPh_3)_2][Os_{10}HC(CO)_{24}]$ (**1**)

remains unchanged on cooling to −80 °C. The solid-state structure indicates *six* unique carbon environments, in a ratio of 1:1:2:1:2:1 (Figure 3). It is evident from the $^{13}C$ n.m.r. spectra of compound (**1**) that two peaks are coincident.

Carbon-13 n.m.r. data for $[N(PPh_3)_2][Os_{10}H^{13}C(^{13}CO)_{24}]$ (**1**)

| Expected peaks | Intensity | | δ/p.p.m. |
|---|---|---|---|
| | Calc. | Obs. | |
| 1 | 3 | 3 | 170.45 |
| 2 | 6 | 6 | 181.33 |
| 3 | 6 | | 175.88 |
| 4 | 3 | 3 } 9 | 185.78 |
| 5 | 3 | | 175.88 |
| 6 | 3 | 3 | 188.8 |

This supports the results of crystallographic studies that demonstrated a slight expansion of the tetrahedral site[4] containing the interstitial hydrido atom.

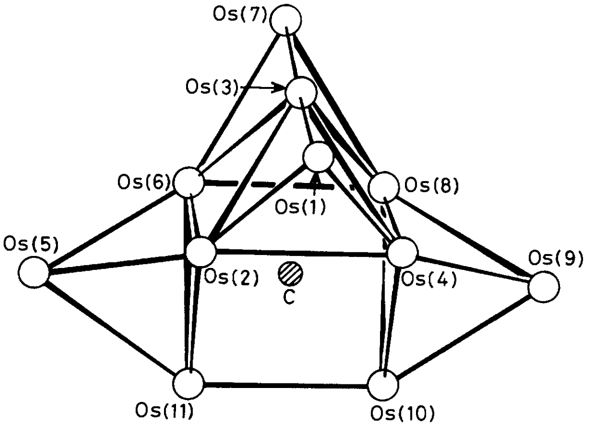

**Figure 4.** Structure of $[PPh_3Me][Os_{11}HC(CO)_{27}]$ (**2**)

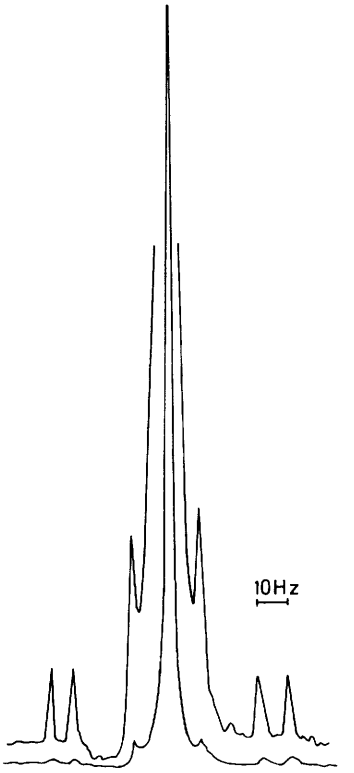

**Figure 5.** The $^1H$ n.m.r. spectrum (400 MHz) of $[PPh_3Me]$-$[Os_{11}HC(CO)_{27}]$ (**2**) in $CD_2Cl_2$ at 18 °C. Number of pulses: 760. Sweep width: 600 Hz. Acquisition time: 13.65 s

The salt $[PPh_3Me][Os_{11}HC(CO)_{27}]$ (**2**) has recently been characterised by a single-crystal *X*-ray study[19] and shown to adopt a bicapped square-based pyramidal structure sharing its square base with a trigonal prism which is also bicapped on its triangular faces (Figure 4). Although the hydride was not located in the solid-state structure it was suggested (on the basis of the lengthening of the Os–Os metal bonds) that it occupied a tetrahedral interstitial site in one of the two tetrahedra capping the square-based pyramid. The osmium satellites of (**2**) would be expected to be in a different intensity ratio to those of (**1**), since there are three unique osmium atoms in the capping tetrahedron. The $^1H$ n.m.r. spectrum of (**2**) in $CD_2Cl_2$ at room temperature (r.t.) exhibits three $^{187}Os$–$^1H$ couplings of 14.1, 38.2, and 49.9 Hz, with the satellite intensities being in a ratio of 2:1:1 (Figure 5). This is expected, since two osmium atoms in the trigonal prism are identical [Os(2) and Os(4)], but those capping the square-based pyramid and the capping tetrahedron are unique [Os(3) and Os(1)]. So the observed satellites are consistent with a hydride in a tetrahedral environment. As for

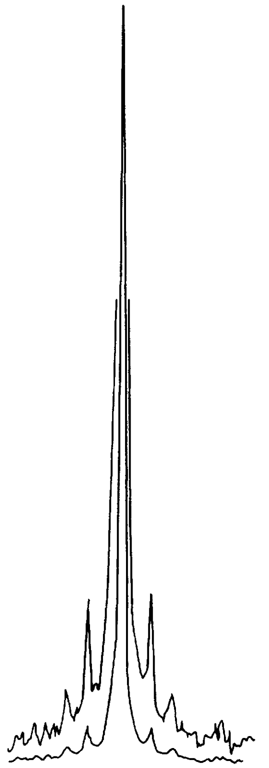

**Figure 6.** The $^1H$ n.m.r. spectrum of (250 MHz) $[Os_{10}HC(CO)_{24}\{Au(PPh_3)\}]$ (**3**) in $CD_2Cl_2$ at 20 °C. Number of pulses: 920. Sweep width: 600 Hz. Acquisition time: 5.32 s

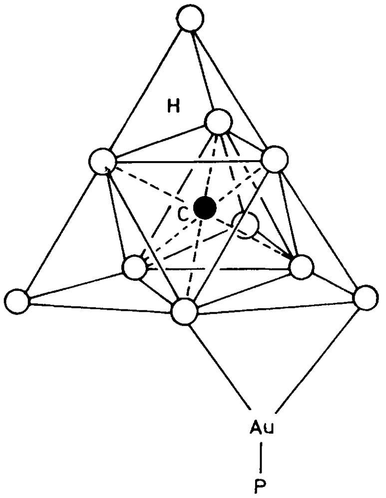

**Figure 7.** Proposed molecular structure of $[Os_{10}HC(CO)_{24}\{Au(PPh_3)\}]$ (**3**) in $CD_2Cl_2$

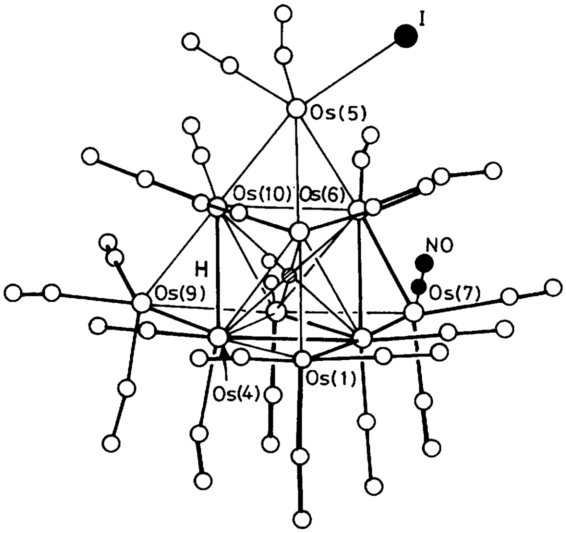

**Figure 8.** Structure of $[N(PPh_3)_2][Os_{10}HC(CO)_{22}(NO)I]$ (**4**)

compound (**1**), the largest observed couplings to $^{13}C$ were *ca.* 2 Hz. No change in the $^1H$ n.m.r. spectrum of (**2**) could be detected on cooling to $-80$ °C.

The neutral decaosmium cluster $[Os_{10}HC(CO)_{24}\{Au(PPh_3)\}]$ (**3**)[20,21] shows two sets of osmium satellites about the hydride peak ($\delta$ $-20.4$). The two $^1H-^{187}Os$ couplings of 15.4 and 26.2 Hz (Figure 6) were found to be in the ratio of 3:1, consistent with the hydride being in a tetrahedral environment. From $^1H$ and $^{31}P-\{^1H\}$ studies on (**3**) we conclude that the $Au(PPh_3)$ moiety is either $\mu$ or $\mu_3$ bridging as in $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$.[20,22] A molecular structure for (**3**) is proposed (Figure 7) in solution.

The decaosmium dianion $[N(PPh_3)_2]_2[Os_{10}C(CO)_{22}(NO)I]$[20] has been characterised by single-crystal *X*-ray crystallography, and found to consist of a tetracapped octahedron, with an interstitial octahedral carbide (Figure 8) and terminal nitrosyl and iodide ligands. Protonation of the dianion in $CH_2Cl_2$ produces $[Os_{10}HC(CO)_{22}(NO)I]^-$ (**4**) quantitatively, which has been characterised on the basis of $^1H$ n.m.r. studies. The $^1H$ n.m.r. spectrum of (**4**) shows two sets of osmium satellites about the hydride peak ($\delta$ $-17.5$), of 13.8 and 25.9 Hz, with the satellite intensities being in the ratio of 3:1. This is as expected for a hydride in a tetrahedral environment, as in (**1**) and (**3**). The satellite patterns of compounds (**1**)—(**4**) are all temperature independent.

Addition of protons to anionic clusters to yield hydrido clusters leaves the cluster electron count unaffected, yet this process is sometimes accompanied by structural changes. For example $[Os_{10}C(CO)_{24}]^{2-}$ and (**1**) have tetracapped octahedral arrangements of metal atoms as predicted by Wades rules.[21] The dianion $[Os_8(CO)_{22}]^{2-}$ has a bicapped octahedral structure, and the hydride monoanion $[Os_8H(CO)_{22}]^-$ a fused tetrahedral structure,[23] with a structural change having occurred on addition of a proton to $[Os_8(CO)_{22}]^{2-}$. The hydride in $[Os_8H(CO)_{22}]^-$ was characterised both by single-crystal *X*-ray crystallography and by $^1H$ n.m.r. spectroscopy in $CD_2Cl_2$ at r.t. The monoanion $[Os_8H(CO)_{22}]^-$ exhibits one $^{187}Os-^1H$ coupling of 34 Hz, consistent with the hydride bridging an edge.[24] Attempts have been made to investigate dihydrido systems such as $[Os_{10}H_2C(CO)_{24}]$ (**5**) by magic angle spinning $^1H$ n.m.r. spectroscopy,[25] but these have proved to be unsuccessful possibly due to its longer nuclear relaxation time than the species under study here.

*Multi-hydrido Systems.*—The isolation and characterisation of many large hydrido clusters is hampered by their acidity. The clusters $[Ni_{38}Pt_6H_{(6-n)}(CO)_{48}]^{n-}$ ($n = 3$—$6$)[26] and $[Rh_{12}H_2(\mu_3\text{-}CO)(\mu\text{-}CO)_9(CO)_{13}]$[27] exist in solution as equilibrium mixtures of anions. Ready deprotonation of these species occurs on dissolution in basic solvents such as acetone or acetonitrile.

The interstitial co-ordination of hydride atoms has been inferred in the compounds $[Ni_9Pt_3H_{4-n}(CO)_{21}]^{n-}$ ($n$ = 2—4),[28] from $^1H$ and $^{195}Pt$ n.m.r. and $X$-ray data. In solution, hydride migration was considered to involve fast migration from trigonal-prismatic sites to the tetrahedral sites.

The presence of $^{187}Os$ satellites has recently been used in multihydrido clusters for the assignment of molecular structures and solution dynamics.[15,18]

The dianion $[N(PPh_3)_2]_2[Os_{10}H_4(CO)_{24}]$ (**6**) was recently reported[29] as having a core structure very similar to that of the dianion $[Os_{10}C(CO)_{24}]^{2-}$ (a tetracapped octahedron). Single-crystal $X$-ray analysis of (**6**) revealed polyhedral expansion in three of the four tetrahedral sites (mean tetrahedral bond lengths for the capping tetrahedron 2.839, 2.389, 2.829, and 2.809 ± 0.002 Å) and expansion of the octahedral site (mean octahedral Os–Os bond length 2.857 Å) which is enlarged with respect to the empty '$Os_6$' cavity in $[Os_8(CO)_{22}]^{2-}$ (2.831 Å).[30] It was concluded that the hydrides were interstitial, three in the tetrahedral sites and one in the octahedral site.

The $^1H$ n.m.r. spectrum of compound (**6**) in $CH_2Cl_2$ at r.t. revealed the presence of one sharp resonance at δ −16.48; no $^{187}Os-^1H$ satellites could be detected, due to the signal being too broad. It is considered that at room temperature the activation energy barrier for (**6**) is very low, so it is fluxional with hydrides 'jumping' from octahedral to tetrahedral sites. Such a process has been suggested for $[Rh_{13}H_2(CO)_{24}]^{3-}$ in solution.[31,32] Alternatively one could consider the movement of interstitial hydrides to the surface of the cluster in *solution*. Polyhedral rearrangements in cluster units are well documented,[33] although in (**6**) this mechanism seems to be unlikely. On cooling a solution of compound (**6**) to 193 K in $CD_2Cl_2$, the resonance at δ −16.48 gradually broadens and slowly disappears, with the appearance of two new signals at δ −14.70 and −19.08 in the ratio of 1:1 (signal width at half-height 12 Hz); the signals are still too broad to observe $^{187}Os-^1H$ satellites. It is possible that at low temperature there are only two types of hydride environment, with one of the three protons migrating into the central octahedron. This would produce a species with two hydrides in the central octahedron and two in tetrahedral sites. An alternative mechanism is for two hydrogen atoms to migrate to the cluster surface with two remaining interstitial. Rapid migration of protons in both the octahedral and tetrahedral interstitial sites occurs in (**6**) at r.t. where it is completely fluxional; on cooling an alternative mechanism must be invoked as in Figure 9.[34]

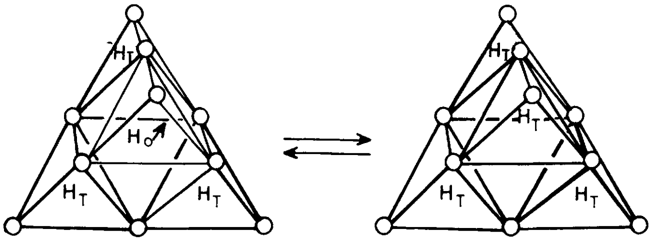

**Figure 9.** Proposed hydride 'flipping' mechanism in $[N(PPh_3)_2]_2$-$[Os_{10}H_4(CO)_{24}]$ (**6**)

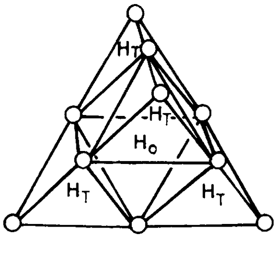

**Figure 10.** Proposed molecular structure of $[N(PPh_3)_2][Os_{10}H_5$-$(CO)_{24}]$ (**7**) in $CD_2Cl_2$

Protonation of compound (**5**) in $CH_2Cl_2$ yields the monoanion $[Os_{10}H_5(CO)_{24}]^-$ (**7**)[29,34] previously characterised only by i.r. spectroscopy. The clusters $[Os_{10}C(CO)_{24}]^{2-}$, (**1**), and (**6**) were found to have identical metal-core structures by single-crystal $X$-ray crystallography. It seems likely that the fifth hydrogen atom is in the remaining empty tetrahedral site in (**7**). The $^1H$ n.m.r. spectrum of (**7**) is in accord with this hypothesis, with two broad signals at δ −15.9 and −16.2 in the intensity ratio of 4:1. The spectrum remains unaltered on cooling to −80 °C. Due to the broad linewidths of the two signals no $^{187}Os-^1H$ satellites could be observed. In *solution* it seems that all of the five interstitial sites could be filled (Figure 10).

Finally, we report $^1H$ n.m.r. results on the monoanion $[Os_{10}H_4(CO)_{24}X]^-$ (**8**)[29] (X = I, Br, or Cl). The room-temperature $^1H$ n.m.r. spectrum of (**8**; X = I) in $CD_2Cl_2$ revealed the presence of two signals at δ −16.05 and −17.14 in a ratio of 3:1; the spectrum obtained for (**8**) was also temperature independent. The corresponding carbido derivative $[Os_{10}C(CO)_{24}I]^-$ [35] has the iodine atom bridging an $Os_4$ butterfly but with one osmium cap opened. There is no further reaction of (**8**) with halogen (X = Cl, Br, or I) as would be expected if three of the hydrogen atoms are in tetrahedral sites. As for (**6**) and (**7**), no $^{187}Os-^1H$ satellites are observed for compound (**8**), due to the broad nature of the two peaks. We propose that in solution in (**8**) three hydrogen atoms are in tetrahedral sites, one is in the octahedral cavity, and the halogen atoms bridges an $Os_4$ butterfly (Figure 11), as for $[Os_{10}C$-$(CO)_{24}I]^-$.

## Experimental

All solvents were distilled prior to use, and the chemical manipulations performed under dry $N_2$ using Schlenk techniques. Infrared spectra were recorded in $CH_2Cl_2$ on a Perkin-Elmer PE983 spectrometer. Fast-atom bombardment mass spectroscopy (f.a.b.m.s.) was performed on a N.E.I. MS12 spectrometer using tris(perfluoroheptyl-*s*-triazine) as calibrant. The instrument was run in negative-ion mode with a glycerol matrix. Microanalyses were performed in the University Chemical Laboratory, Cambridge. The following compounds were prepared by established procedures: $[PPh_3Me][Os_{11}HC$-$(CO)_{27}]$,[19] $[N(PPh_3)_2]_2[Os_{10}C(CO)_{22}(NO)I]$,[20] $[Os_{10}HC$-

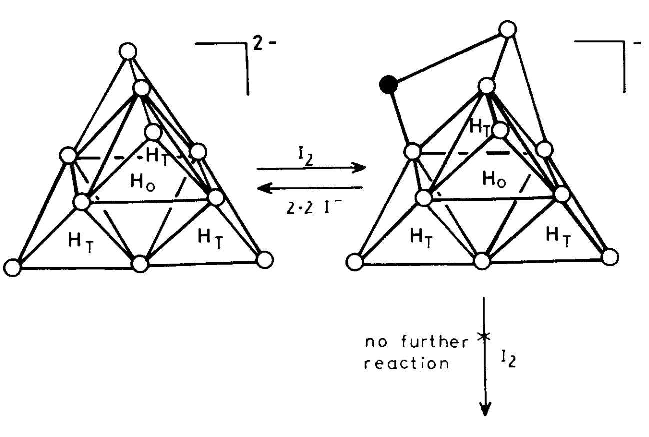

**Figure 11.** Proposed molecular structure of $[N(PPh_3)_2][Os_{10}H_4$-$(CO)_{24}I]$ (**8**)

$(CO)_{24}\{Au(PPh_3)\}]$,[21] and $[N(PPh_3)_2]_2[Os_{10}H_4C(CO)_{24}]$.[29,34]

The $^1H$ and $^{13}C$ n.m.r. spectra were recorded on Bruker WM 250 and WH 400 spectrometers, using $CD_2Cl_2$ or $CDCl_3$ as internal lock signals over a range of temperatures. Typical $^1H$ n.m.r. accumulation conditions were: $[N(PPh_3)_2][Os_{10}HC(CO)_{24}]$ (20 mg, 0.0064 mmol) (400 MHz) in $CD_2Cl_2$ (2 $cm^3$) at 19 °C; number of pulses, 800; sweep width, 120 Hz; acquisition time, 5.43 s; $[PPh_3Me][Os_{11}HC(CO)_{27}]$ (25 mg, 0.0079 mmol) (400 MHz) in $CD_2Cl_2$ at 18 °C; number of pulses, 760; sweep width, 600 Hz; acquisition time 13.65 s. Typical $^{13}C$ n.m.r. accumulation conditions were: $[N(PPh_3)_2][Os_{10}H^{13}C(^{13}CO)_{24}]$ (40 mg, 0.0128 mmol) (250 MHz) in $CDCl_3$ (4 $cm^3$) at 22 °C; number of pulses, 5 700; sweep width, 41 666.6 Hz; acquisition time; 0.19 s.

*Preparations.*—$[N(PPh_3)_2]_2[Os_{10}{}^{13}C(^{13}CO)_{24}]$. **CAUTION**: The Carius tube must be oven dried at 75 °C for 5 h before use, and $[Os_3(CO)_{10}(NCMe)_2]$ should be left under vacuum for 2 h. The oven must be allowed to cool overnight to ensure crystallisation of the product in the tube, and to avoid tube implosion. Precautions against implosion should also be taken before opening the Carius tube. Thus the tube should be opened behind a safety shield at the neck by an operator wearing a facemask.

Solid $[Os_3(CO)_{10}(NCMe)_2]$ (2.0 g, 2.12 mmol) was placed into a two-necked flask (250 $cm^3$) containing freeze-thaw-degassed $CH_2Cl_2$ (60 $cm^3$). The flask was attached to a $^{13}CO$ gas-exchange line and $^{13}CO$ gas slowly saturated the solution by freeze-thawing the flask (three or four times) with liquid $N_2$ over a period of 24 h. The solution was stirred during the gas-exchange reaction and after *ca.* 10 h the solution gradually became more yellow, with precipitation of $[Os_3(^{13}CO)_{12}]$. Any remaining $^{13}CO$ in the reaction vessel was removed using the gas-exchange line. When this process was repeated at least once more, enrichment of *ca.* 35% ($^{13}C$) could be obtained for the $[Os_3(CO)_{12}]$. The enriched $[Os_3(CO)_{12}]$ was then converted into $[Os_3(^{13}CO)_{10}(NCMe)_2]$ using the literature procedure,[36] to yield 1.80 g of enriched $[Os_3(^{13}CO)_{10}(NCMe)_2]$.

Solid $[Os_3(^{13}CO)_{10}(NCMe)_2]$ (1.0 g, 1.06 mmol) was placed in a Carius tube (180 $cm^3$) and evacuated to $10^{-3}$ Torr (0.133 Pa) for 1 h. The tube was then sealed under vacuum, and placed on its side (ensuring a uniform distribution of the solid along the length of the tube) and inserted into a steel liner (in case of potential implosion at elevated temperature). The tube was placed in an oven and heated at 280 °C for 72 h.

The dark brown solid was extracted from the Carius tube after opening (using the procedure outlined above) with 15-$cm^3$ portions of acetone (in the atmosphere), until the tube was clean. The resulting solution (*ca.* 150 $cm^3$) was refluxed in the presence of an excess of $[N(PPh_3)_2]Cl$ (1.5 g, 2.63 mmol) in MeOH (40 $cm^3$) for 24 h. The solution was then reduced in volume leading to precipitation of $[Os_4H_4(^{13}CO)_{12}]$ (11 mg, 2%], filtered, and then adsorbed onto silica. The brown solid was then separated by column chromatography (70 × 6 cm); initially the eluant was 100% hexane to remove any unreacted '$Os_3$' clusters (3 mg, 0.5%), then 100% dichloromethane to separate yellow $[Os_4H_4(^{13}CO)_{12}]$ (15 mg, 3%) leaving a black band at the top of the column. The eluant was then changed to acetone–hexane (60:40), giving first a red band of $[N(PPh_3)_2]_2[Os_{10}{}^{13}C(^{13}CO)_{24}]$ which was closely followed by a dark brown band of $[N(PPh_3)_2]_2[Os_{11}{}^{13}C(^{13}CO)_{27}]$. The two bands were collected together, leaving osmium metal adsorbed on the silica. The solvent was then removed under reduced pressure, and the black residue redissolved in acetone (20 $cm^3$) and layered with MeOH (8 $cm^3$). Slow evaporation at 0 °C initially produced dark red crystals of $[N(PPh_3)_2]_2[Os_{10}{}^{13}C(^{13}CO)_{24}]$ which were collected by filtration, and dried under vacuum for 2 h (yield 877 mg, 76%) (Found: C, 31.6; H, 1.70; N, 0.75. Calc. for $C_{72}{}^{13}C_{25}H_{60}N_2O_{24}Os_{10}P_4$: C, 31.8; H, 1.65; N, 0.75%). I.r.: ν(CO) 2 033s, 2 028s (sh), 1 986s, and 1 979s (sh) $cm^{-1}$. $^{13}C$ n.m.r. ($CD_2Cl_2$ at r.t.): δ +178.2 (12 C, s), +189.9 (12 C, s), and +406.0 p.p.m. (1 C, s).

$[N(PPh_3)_2][Os_{10}H^{13}C(^{13}CO)_{24}]$ (**1**). The salt $[N(PPh_3)_2]_2[Os_{10}{}^{13}C(^{13}CO)_{24}]$ (40 mg, 0.0110 mmol) was dissolved in $CH_2Cl_2$ (15 $cm^3$) and a solution of $CF_3CO_2H$ (one drop) in $CH_2Cl_2$ (5 $cm^3$) added to the reaction mixture over *ca.* 5 min. The reaction was monitored by i.r. spectroscopy and found to be complete after 10 min with a change in solution colour from red-brown to orange-brown. The solution was then filtered through a Celite plug (1 × 1 cm) to remove any excess of acid. Microcrystals of $[N(PPh_3)_2][Os_{10}H^{13}C(^{13}CO)_{24}]$ (**1**) were obtained by slow evaporation of the $CH_2Cl_2$ solution under nitrogen at r.t. (yield, 36 mg, 94%) (Found: C, 23.40; H, 1.10; N, 0.45. Calc. for $C_{36}{}^{13}C_{25}H_{31}NO_{24}Os_{10}P_2$: C, 23.25; H, 1.00; N, 0.45%). Proton n.m.r. (see Table).

$[N(PPh_3)_2][Os_{10}HC(CO)_{22}(NO)I]$ (**4**). The salt $[N(PPh_3)_2]_2[Os_{10}C(CO)_{22}(NO)I]$ (40 mg, 0.0110 mmol) was dissolved in $CH_2Cl_2$ (15 $cm^3$) and a solution of $CF_3CO_2H$ (one drop) in $CH_2Cl_2$ (5 $cm^3$) added to the reaction mixture over *ca.* 5 min. The reaction was monitored by i.r. spectroscopy and was complete after 10 min with a change in colour from red to orange-brown. The solution was filtered through a Celite plug (1 × 1 cm) to remove any excess of acid present. Removal of the solvent from the reaction solution and crystallisation of the residue from $CH_2Cl_2$–hexane at r.t. yielded black microcrystals of $[N(PPh_3)_2][Os_{10}HC(CO)_{22}(NO)I]$ (**4**) (yield 33 mg, 89%) (Found: C, 22.15; H, 1.30; N, 0.90. Calc. for $C_{59}H_{31}IN_2O_{23}Os_{10}P_2$: C, 21.85; H, 0.95; N, 0.85%). I.r.: ν(CO) 2 096w, 2 069m, 2 053vs, 2 019s, and 2 002m $cm^{-1}$. Proton n.m.r. (see Table).

$[Os_{10}H_2C(CO)_{24}]$ (**5**). The salt $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (40 mg, 0.0110 mmol) was dissolved in $CH_3CN$ (5 $cm^3$) and excess of $HBF_4$ (six drops) in $CH_3CN$ (1 $cm^3$) added over 10 min. The solution was stirred for 45 min, initially forming the monoanion $[Os_{10}HC(CO)_{24}]^-$, but on prolonged stirring $[Os_{10}H_2C(CO)_{24}]$ (**5**) precipitated in quantitative yield as an insoluble black-brown powder. The solid was collected on a fritted filter, washed with cold $CH_3CN$ (3 × 5 $cm^3$), and dried *in vacuo* for 1 h (Found: C, 11.65; H, 0.20. Calc. for $C_{25}H_2O_{24}Os_{10}$: C, 11.50; H, 0.10%). I.r.: ν(CO) 2 110w, 2 068s br, 2 039s (sh), 2 025s, 1 990m (sh), 1 960m (sh), and 1 910w (sh) $cm^{-1}$ (KBr disc).

$[N(PPh_3)_2][Os_{10}H_5(CO)_{24}]$ (**7**). The salt $[N(PPh_3)_2]_2[Os_{10}H_4(CO)_{24}]$ (**6**) (40 mg, 0.0110 mmol) was dissolved in $CH_2Cl_2$ (15 $cm^3$) and a solution of $CF_3CO_2H$ (one drop) in $CH_2Cl_2$ (5 $cm^3$) added slowly to the reaction mixture over 5 min. The reaction was monitored by i.r. spectroscopy and was complete after 10 min with a change in colour from red-brown to orange-brown. The reaction mixture was then filtered through a Celite plug (1 × 1 cm) to remove excess of acid. Black crystals of $[N(PPh_3)_2][Os_{10}H_5(CO)_{24}]$ (**7**) were obtained by slow evaporation of the solvent under $N_2$ (yield 36 mg, 94%) (Found: C, 23.10; H, 1.20; N, 0.40. Calc. for $C_{60}H_{35}NO_{24}Os_{10}P_2$: C, 22.95; H, 1.10; N, 0.45%). I.r.: ν(CO) 2 093w, 2 058vs, 2 052vs (sh), 2 016s (sh), and 2 010s $cm^{-1}$. Proton n.m.r. (see Table). F.a.b.m.s.: *m/z* 2 597 corresponding to $[Os_{10}H_5(CO)_{24}]$ for $^{192}Os$.

$[N(PPh_3)_2][Os_{10}H_4(CO)_{24}X]$ (**8**) (X = Cl, Br, *or* I). A general preparation for the iodo derivative is given.

The salt $[N(PPh_3)_2]_2[Os_{10}H_4(CO)_{24}]$ (40 mg, 0.0110 mmol) was dissolved in $CH_2Cl_2$ (15 $cm^3$) and a solution of $I_2$ (6 mg, 0.00242 mmol) in $CH_2Cl_2$ (5 $cm^3$) was added slowly to the reaction mixture over 25 min. The reaction was monitored by i.r. spectroscopy and was complete after 40 min with a change in colour from red-brown to orange-brown. The reaction mixture was then reduced in volume to *ca.* 5 $cm^3$ and chromatographed on silica plates with dichloromethane–hexane (1:3), to yield one red band ($R_f$ 0.5). Black crystals of $[N(PPh_3)_2][Os_{10}H_4(CO)_{24}I]$ were obtained by slow evaporation of the solvent under $N_2$ (yield 30 mg, 90%) (Found: C, 22.45; H, 1.35; N, 1.15. Calc. for $C_{60}H_{34}INO_{24}Os_{10}P_2$: C, 22.10; H, 1.05; N, 0.85%). If a solution of (**8**) in $CH_2Cl_2$ is stirred with 2.2 equivalents of $[N(PPh_3)_2]Cl$ the dianion (**6**) is slowly regenerated over *ca.* 15 min. Similar yields were obtained for the chloro and bromo derivatives.

I.r.: ν(CO) (X = I) 2 095w, 2 073m, 2 061s, 2 053s, 2 018s; (X = Br) 2 096w, 2 074m, 2 063s, 2 055s, 2 020s; (X = Cl) 2 098w, 2 076m, 2 065s, 2 059s, and 2 024s $cm^{-1}$. Proton n.m.r. (see Table). F.a.b.m.s.: (X = I) $m/z$ = 2 725 corresponding to $[Os_{10}H_4(CO)_{24}I]$: (X = Br) $m/z$ = 2 676 corresponding to $[Os_{10}H_4(CO)_{24}Br]$: (X = Cl) $m/z$ = 2 632 corresponding to $[Os_{10}H_4(CO)_{24}Cl]$ for $^{192}Os$.

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