¹⁸⁷Os–¹H Coupling in Hydrido-osmium Clusters as an Aid to the Assignment of Molecular Structures

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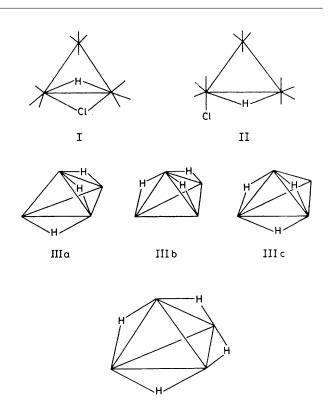
Proton n.m.r. spectra of hydrido-osmium species show low intensity satellites as a result of coupling to natural abundance ¹⁸⁷Os; a study of the coupling constants, and satellite intensities, observed in the ¹H n.m.r. spectra of hydrido-osmium clusters provides valuable information about molecular structures and fluxional processes and evidence is presented for the presence of a tetrahedral interstitial hydride in [HOs₁₀C(CO)₂₄]⁻.

In n.m.r. spectroscopy the characteristic splitting patterns arising from coupling to spin $\frac{1}{2}$ nuclei act as valuable diagnostic aids in organometallic chemistry. Coupling to nuclei such as ³¹P (100%), ¹⁹⁵Pt (33.7%), ¹⁰³Rh (100%), and ¹⁸³W (14.3%) has provided structural information.¹ Koridze *et al.*² have reported coupling to ¹⁸⁷Os in the ¹³C n.m.r. spectra of [¹⁸⁷Os₃(CO)₁₂] and [¹⁸⁷Os₃(CO)₁₂H]⁺, but the scarcity of isotopically pure ¹⁸⁷Os obviously limits the generality of labelling techniques. A few values of ¹J(¹⁸⁷Os₋⁻¹H) have been reported³ for mononuclear hydrido-osmium species, and here we report the use of high resolution ¹H n.m.r. spectroscopy to observe this coupling, at natural abundance of ¹⁸⁷Os ($I = \frac{1}{2}$, 1.6% natural abundance), in a range of osmium carbonyl clusters.[†]

The ¹H n.m.r. spectrum of $[Os_3H(CO)_{10}Cl]^4$ (1) shows a single satellite peak either side of the major hydride signal at δ –14.3 (Table 1). The measured coupling constant ¹J_{Os-H} was 36.6 Hz. No change in the satellite pattern occurred on cooling the sample. The cluster (1) possesses symmetrically bridging hydrido- and chloro-ligands (I) along one Os–Os edge and thus shows only one Os–H coupling with the two equivalent osmium atoms. Additional, small couplings in (1)–(4) in the range 0–15 Hz could be observed which are due to coupling with ¹³C in the carbonyl ligands, as found in related molecules.⁵

The compound $[Os_3H(CO)_{11}Cl]^6$ (2) shows two sets of

[†] All spectra were obtained using Bruker WH400 or WM250 instruments. An S: N ratio of approximately 500: 1 was sufficient to observe ¹J(¹⁸⁷Os-¹H) and accumulation times were typically 10 min.



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osmium satellites about the hydride peak at δ -16.1, and again no temperature dependence was observed. We interpret this as indicative of the hydride bridging two non-equivalent osmium atoms (II), confirming earlier proposals based on i.r. data and chemical reactivity.⁶ The anion $[Os_4H_3(CO)_{12}]^-$ (3) has been shown by solution i.r. and ¹H n.m.r. spectroscopy to exist as isomers of C_2 and C_{3v} symmetry.⁷ The C_2 isomer of (3) (and its Ru analogue⁸) has been characterized crystallographically,⁹ and the hydrides were found to occupy three edges of the tetrahedron in a 'Z' arrangement (IIIa). The ¹H n.m.r. spectrum indicates that this structure is maintained in solution and shows resonances at δ -16.2 (doublet) and δ -18.8 (triplet) in the intensity ratio 2:1. The low field resonance exhibits two ¹H-¹⁸⁷Os couplings whilst that to higher field shows only one. The C_{3v} isomer only shows one ¹H n.m.r. resonance, but two ¹H-¹⁸⁷Os couplings, indicating that the hydrides are bridging two non-equivalent osmium atoms. This is consistent with a structure with three hydrides bridging apical to basal edges of the tetrahedron (IIIb), and not one in which the hydrides bridge the basal edges (IIIc) as found for the Ru C_{3v} isomer.⁸

The anion $[HOs_{10}C(CO)_{24}]^-$ (4) has recently been characterized crystallographically¹⁰ and shown to consist of an octahedral core of osmium atoms with an interstitial carbide, and four of the faces capped by Os(CO)₃ groups (IV) (Figure 1). Although the hydride was not located in the solid state structure, it was proposed, on the basis of the carbonyl packing and Os–Os bond lengths, that it occupied a tetrahedral interstitial site. The ¹H n.m.r. spectrum of (4) (Figure 1) exhibits two ¹H–¹⁸⁷Os couplings of 15.9 and 26.6 Hz, with the satellite intensities being in a ratio of 3:1, entirely as expected for a hydride in a tetrahedral environment. The possibility of smaller couplings with ¹³C in either the carbide or carbonyls was eliminated by recording the ¹H n.m.r. spectrum of an enriched (*ca.* 16% ¹³C) sample (Figure 1). The largest observed coupling to ¹³C was *ca.* 2 Hz, and this was confirmed by observing the fully proton-coupled ¹³C n.m.r. spectrum. The ¹³C n.m.r. spectrum of the ¹³C-labelled sample demonstrated that all of the carbonyls and 'the carbide (δ 409 p.p.m.) had been enriched. No change in the ¹H or ¹³C n.m.r. spectra could be detected on cooling to -80 °C.

Although the satellite patterns of compounds (1)—(4) were temperature independent, we have found that $^{187}\text{Os}^{-1}\text{H}$ couplings may also be of use in the investigation of fluxional processes. Thus, $[\text{Os}_4\text{H}_4(\text{CO})_{12}]^7$ (5) exhibits a single set of

Table 1. ¹ H N.m.	r. data for	the hydrido-osmium	clusters (1)	(5).
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(1) (2) (3a) (3b) (4) (5)	Complex $\begin{bmatrix} Os_3H(CO)_{10}CI \\ [Os_3H(CO)_{11}CI \\ K[Os_4H_3(CO)_{12}]^b(C_2) \end{bmatrix}$ $K[Os_4H_3(CO)_{12}]^b(C_3)$ $PPN[HOs_{10}C(CO)_{24}]$ $[Os_4H(CO)_{12}]^b(C_3)$	Chemical shift $(\delta)^a$ - 14.3 - 16.1 - 16.2 (int. 2) - 18.8 (int. 1) - 16.7 - 15.3 - 20.4	¹ <i>J</i> (¹⁸⁷ Os ⁻¹ H) /Hz 36.6 38.1, 27.3 31.5, 28.0° 29.5 30.9, 28.8 26.6, 15.9 ^d 14.4
(5)	$[Os_4 H_4 (CO)_{12}]$	20.4 20.4 ^e	14.4 30.5

^a Measured at 400 MHz and 25 °C unless otherwise stated. ^b -30 °C. ^c J_{H-H} 1.0 Hz. ^d J_{C-H} 2.0 Hz. ^e -105 °C.

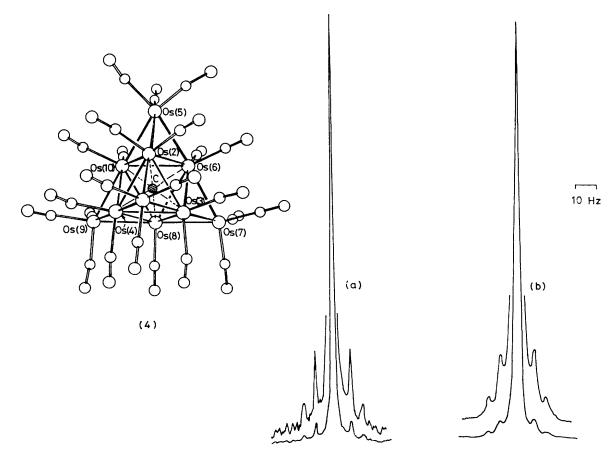


Figure 1. The structure of $[HOs_{10}C(CO)_{24}]^-$ (4) and its ¹H n.m.r. spectra with (a) ¹³C at natural abundance and (b) ¹³C enriched to *ca*. 16%.

satellites with ${}^{1}J_{H-Os}$ 14.4 Hz at room temperature, whereas the limiting low temperature spectrum (-105 °C, 400 MHz) reveals a coupling constant of 30.5 Hz (double the room temperature value, within experimental error). These results are consistent with migration of the hydride ligands over all six Os-Os edges at room temperature, but a static structure at -105 °C with only four edges bridged (V) as found in the solid state structure.¹¹ Solid state ¹H n.m.r. studies¹² had indicated that the hydride ligands in [Ru₄H₄(CO)₁₂] are mobile, but those in [Os₄H₄(CO)₁₂] are static up to 300 K. Presumably dynamic behaviour of (5) is facilitated in solution by removal of crystal packing constraints.

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