

osmium satellites about the hydride peak at $\delta -16.1$, 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 $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ (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 $\delta -16.2$ (doublet) and $\delta -18.8$ (triplet) in the intensity ratio 2:1. The low field resonance exhibits two $^1\text{H}-^{187}\text{Os}$ couplings whilst that to higher field shows only one. The C_{3v} isomer only shows one ^1H n.m.r. resonance, but two $^1\text{H}-^{187}\text{Os}$ 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 $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ (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 $\text{Os}(\text{CO})_3$ 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 $^1\text{H}-^{187}\text{Os}$ 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 ^{13}C in either the carbide or carbonyls was eliminated by recording the ^1H n.m.r. spectrum of an enriched (*ca.* 16% ^{13}C) sample (Figure 1). The largest observed coupling to ^{13}C was *ca.* 2 Hz, and this was confirmed by observing the fully proton-coupled ^{13}C n.m.r. spectrum. The ^{13}C n.m.r. spectrum of the ^{13}C -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 ^{13}C 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, $[\text{Os}_4\text{H}_4(\text{CO})_{12}]^-$ (5) exhibits a single set of

Table 1. ^1H N.m.r. data for the hydrido-osmium clusters (1)–(5).

Complex	Chemical shift (δ) ^a	$^1J(^{187}\text{Os}-^1\text{H})$ /Hz
(1) $[\text{Os}_3\text{H}(\text{CO})_{10}\text{Cl}]$	-14.3	36.6
(2) $[\text{Os}_3\text{H}(\text{CO})_{11}\text{Cl}]$	-16.1	38.1, 27.3
(3a) $\text{K}[\text{Os}_4\text{H}_3(\text{CO})_{12}]^{\text{b}}(C_2)$	-16.2 (int. 2)	31.5, 28.0 ^c
	-18.8 (int. 1)	29.5
(3b) $\text{K}[\text{Os}_4\text{H}_3(\text{CO})_{12}]^{\text{b}}(C_3)$	-16.7	30.9, 28.8
(4) $\text{PPN}[\text{HOs}_{10}\text{C}(\text{CO})_{24}]$	-15.3	26.6, 15.9 ^d
(5) $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$	-20.4	14.4
	-20.4 ^e	30.5

^a Measured at 400 MHz and 25 $^\circ\text{C}$ unless otherwise stated.

^b -30°C . ^c $J_{\text{H}-\text{H}}$ 1.0 Hz. ^d $J_{\text{C}-\text{H}}$ 2.0 Hz. ^e -105°C .

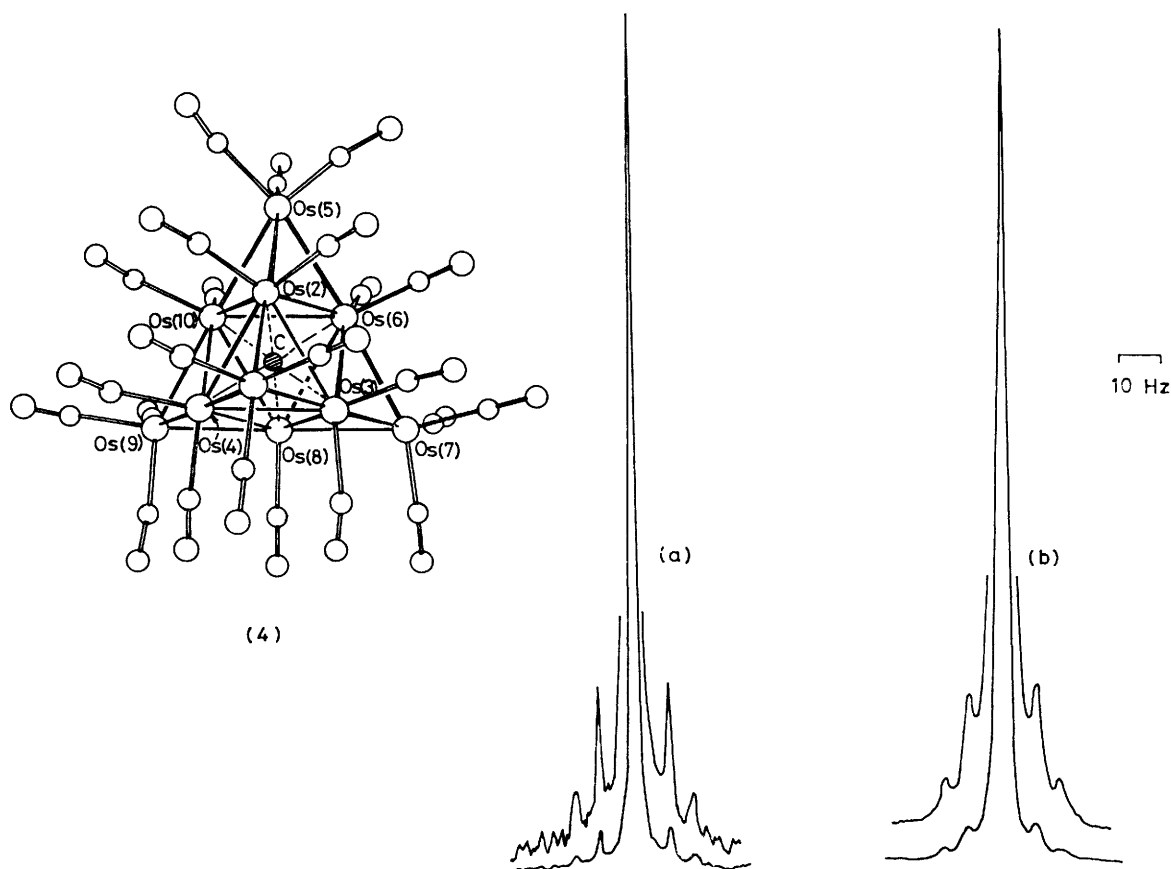


Figure 1. The structure of $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ (4) and its ^1H n.m.r. spectra with (a) ^{13}C at natural abundance and (b) ^{13}C enriched to *ca.* 16%.

satellites with $^1J_{\text{H-Os}}$ 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 $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ are mobile, but those in $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$ 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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