

Scalar Coupling to Naturally Abundant ^{187}Os : A New Probe of the Fluxionality of Osmium Carbonyl Cluster Complexes

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Low intensity satellites resulting from coupling to natural abundance ^{187}Os have been observed in the ^{13}C and ^{31}P n.m.r. spectra of several osmium carbonyl cluster complexes; studying the magnitude of the couplings gives new insight into the fluxional behaviour of these polynuclear compounds.

Nuclear magnetic resonance studies have established that ligand migration processes in transition metal carbonyl cluster complexes may be localised at one or more metal atoms, or alternatively, delocalised over entire cluster units.¹⁻³ Frequently the presence of spin-spin coupling between metal and ligand atoms (e.g. $^1J(^{103}\text{Rh}-^{13}\text{C})$) greatly facilitates the differentiation of rearrangement pathways and the paradigm of $\text{Rh}_4(\text{CO})_{12}$ is now classic.⁴ Osmium has a naturally occurring spin $\frac{1}{2}$ isotope (^{187}Os , 1.64% abundant) and studies in this laboratory⁵ and by other groups⁶ have demonstrated how low-intensity satellites arising from coupling to ^{187}Os in the ^1H n.m.r. spectra of hydrido-osmium cluster compounds can be used in the assignment of molecular structure and fluxionality. Koridze and coworkers⁷ reported the first measurement of coupling constants $^1J(^{187}\text{Os}-^{13}\text{C})$ in the ^{13}C n.m.r. spectra of isotopically pure $[^{187}\text{Os}_3(\text{CO})_{12}]$. At 25 °C, both axial and equatorial carbonyl ligand sets give rise to doublet resonances, while at 150 °C coalescence to a binomial quartet is observed. Under conditions of rapid exchange $^1J(^{187}\text{Os}-^{13}\text{C}) = \frac{1}{3} \times \text{mean } ^1J(^{187}\text{Os}-^{13}\text{C})$ (slow exchange limit) indicating unambiguously that $\text{CO}_{\text{ax}}-\text{CO}_{\text{eq}}$ exchange in $[\text{Os}_3(\text{CO})_{12}]$ is both an intramolecular and internuclear process. We now report the first examples of coupling to naturally abundant ^{187}Os in the ^{13}C and ^{31}P n.m.r. spectra of several polynuclear osmium complexes and show that interpretation of the satellite spectra gives hitherto unobtainable information about the intramolecular dynamics of these clusters. Farrugia⁸ has independently observed ^{187}Os satellites in the ^{13}C n.m.r. spectra of Os_3Pt cluster complexes.

Recording the carbonyl region of the ^{13}C n.m.r. spectra of

^{13}C -enriched osmium cluster compounds at high signal-to-noise and restricted sweep width allows observation of low intensity ^{187}Os satellites about the major carbonyl resonances.[†] In general appropriate Gaussian apodization functions must be applied to the spectra as the ^{187}Os satellites

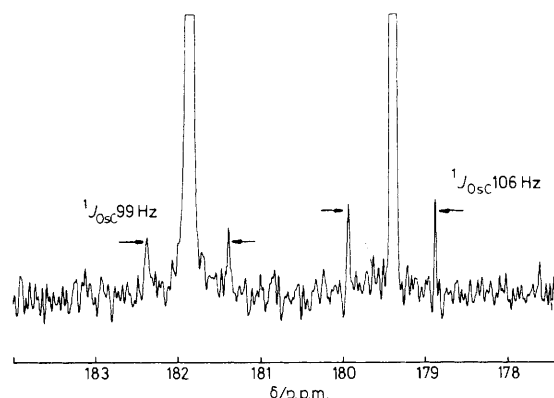
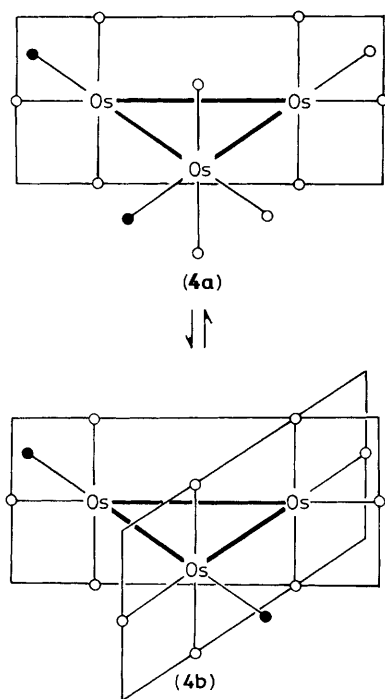


Figure 1. ^{13}C N.m.r. spectrum of $[\text{Os}_6(\text{CO})_{18}]$ (3) at 80 °C showing ^{187}Os satellites to lower-field carbonyl resonances.

[†] Spectra were obtained in CD_2Cl_2 (<25 °C) or $\text{CDCl}_2\text{CDCl}_2$ (>25 °C) solution in the presence of the shiftless relaxation agent $\text{Cr}(\text{acac})_3$ using 5 mm sample tubes with Bruker WM 400 or WM 250 instruments. All samples were prepared from enriched $[\text{Os}_3(\text{CO})_{12}]$ -(^{13}C , ca. 30%) and for limiting complex concentrations of ca. 25 mM, satellite spectra could be obtained after 5000–10 000 scans.

Table 1. ^{13}C N.m.r. spectroscopic data for osmium complexes (1)–(6).

Complex	$T/^\circ\text{C}$	δ	Intensity	Assignment	$^1J(^{187}\text{Os}-^{13}\text{C})/\text{Hz}$
$[\text{Os}_3(\text{CO})_{12}]$ (1) ⁷	25	182.3	6	CO_{ax}	90 ± 2
		170.4	6	CO_{eq}	115 ± 2
		176.4	12		33 ± 1
$[\text{HOs}_3(\text{CO})_{12}]^+$ (2) ⁷	25	177.6	2	D	85 ± 1
		171.1	4	A	84 ± 1
		166.7	2	E	121 ± 2
		161.4	2	B	120 ± 2
		160.8	2	C	116 ± 2
$[\text{Os}_6(\text{CO})_{18}]$ (3)	80	181.9	6	B	99 ± 1
		179.4	6	A	106 ± 1
		175.0	6	C	not observed
$[\text{Os}_3(\text{CO})_{10}(\text{PEt}_3)_2]$ (4a)	-65	195.5	2	A	84 ± 1
		194.7	2	B	86 ± 1
		186.3	2	C	88 ± 1
		181.0	1	D	122 ± 1
		179.0	1	E	119 ± 1
		177.5	1	F	123 ± 1
		172.8	1	G	118 ± 1
		186.3	10		32 ± 1
(4a)/(4b)	110	186.3	10		32 ± 1
$[\text{Os}_3(\text{CO})_9(\mu_3-\eta^2-\eta^2-\text{C}_6\text{H}_6)]$ (5)	20	175.86	6	CO_{eq}	117 ± 1
		175.82	3	CO_{ax}	117 ± 1
$[\text{Os}_5\text{C}(\text{CO})_{15}]$ (6)	50	172.4	3	$\text{CO}_{\text{apical}}$	not observed
		171.0	12	CO_{basal}	119 ± 1

**Figure 2.** Interconversion of isomers of $[\text{Os}_3(\text{CO})_{10}(\text{PEt}_3)_2]$ (4): $\circ = \text{CO}$, $\bullet = \text{PEt}_3$. Carbonyl exchange can occur in the planes illustrated through the merry-go-round mechanism.

typically lie beneath the broad wings of the intense central resonances. Occasionally one or both satellites of a particular resonance are obscured by adjacent signals. To avoid spurious assignment of trace impurities, then, it is prudent to make satellite assignments only when both lines symmetrically disposed about the central resonance are observed.

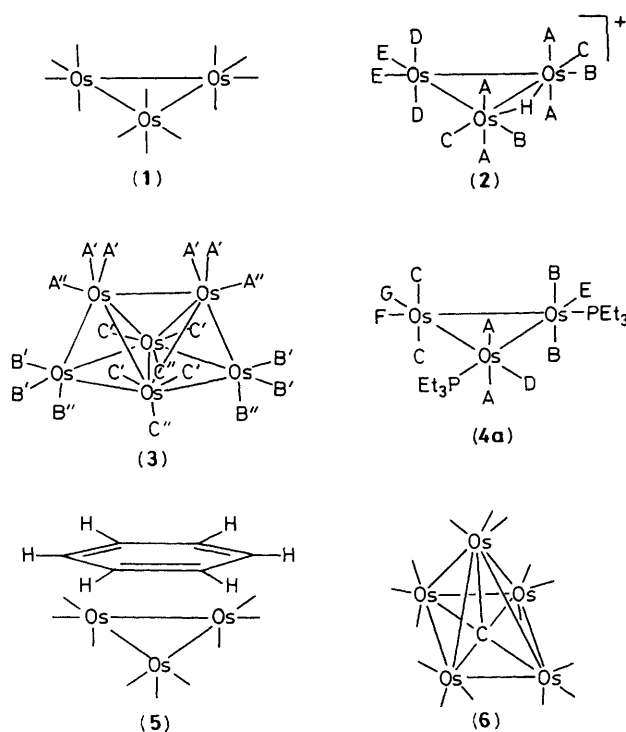
Table 2. $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectroscopic data for $[\text{Os}_3(\text{CO})_{10}(\text{PEt}_3)_2]$ (4).

Isomer	$T/^\circ\text{C}$	δ^a	$^1J(^{187}\text{Os}-^{31}\text{P})/\text{Hz}$
(4a)	-30	44.3	208 ± 2
		38.0	202 ± 2
(4b)	-30	41.3	192 ± 2
(4a)/(4b)	110	41.2	206 ± 2

^a Referenced to external $\text{P}(\text{OMe})_3$.

Previous ^{13}C n.m.r. studies of the hexaosmium carbonyl cluster $[\text{Os}_6(\text{CO})_{18}]$ (3) have indicated that the bicapped tetrahedral geometry of the solid state is maintained in solution and that CO site exchange occurs readily over the temperature range -123 to $+100^\circ\text{C}$ in a localised fashion about individual osmium atoms.⁹ Three equal intensity singlets are observed in the high temperature limiting spectrum at this temperature. Values for $^1J(^{187}\text{Os}-^{13}\text{C})$ of 99 ± 1 and 106 ± 1 Hz (Table 1) for (3) should be compared with $^1J(^{187}\text{Os}-^{13}\text{C}_{\text{ax}})$ and $^1J(^{187}\text{Os}-^{13}\text{C}_{\text{eq}})$ in the slow exchange spectrum of $[\text{Os}_3(\text{CO})_{12}]$ (1),⁷ and are entirely consistent with carbonyl scrambling *via* independent migration processes localised at the three distinct types of osmium atom in (3).

Facile internuclear carbonyl exchange may be observed within ligand sets defining a common plane by the so-called merry-go-round process.² Synchronous motion of six CO ligands about a metal triangle or metal-metal edge permit three- and two-metal site exchange, respectively, *via* bridging CO intermediates. The structure and dynamic behaviour of $[\text{Os}_3(\text{CO})_{10}(\text{PEt}_3)_2]$ (4) has been investigated in solution by ^{13}C and ^{31}P n.m.r. spectroscopy.¹⁰ The observations are consistent with a ground state C_s geometry (4a) (see Figure 2) in which the phosphine ligands occupy non-equivalent equatorial sites of two osmium atoms. Cyclic permutation of the six



coplanar carbonyl ligands is a low energy process leading to two-centre exchange, while total carbonyl scrambling occurs at high temperatures. Deeming *et al*¹¹ recently reported that the 1,2-isomer of the related complex $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]$ exists as two rapidly interconverting isomers of C_s and C_{2v} symmetry. On reinvestigation we found completely analogous behaviour for (4): three lines in the low temperature $^{31}\text{P}\{^1\text{H}\}$ spectrum can be assigned to the non-equivalent phosphorus nuclei of the major C_s isomer (4a) and the equivalent nuclei of the minor C_{2v} isomer (4b) [(4a): (4b) ~ 7:1]. A single peak is seen in the fast exchange limit (Table 2) consistent with interconversion of isomers (4a) and (4b) and equilibration of the non-equivalent phosphines in (4a). Coupling constants $^1J(^{187}\text{Os}-^{31}\text{P})$ ca. 200 Hz measured from ^{187}Os satellites in the $^{31}\text{P}\{^1\text{H}\}$ spectra under conditions of both slow and fast exchange imply that isomer interconversion does not occur through internuclear phosphine migration. The alternative localised 'turnstile' exchange mechanism is more reasonable as phosphine ligands show little tendency to bridge bond in ground state cluster structures.

^{187}Os satellites are also observed in the low temperature ^{13}C n.m.r. spectrum for each resonance of the major isomer (4a) and about the single peak in the fast exchange limit. For rapid exchange $^1J(^{187}\text{Os}-^{13}\text{C}) = 32 \pm 1 \text{ Hz} = \frac{1}{3}$ mean $^1J(^{187}\text{Os}-^{13}\text{C})$ (slow exchange limit), indicating that all CO groups have access to the three osmium atoms via intramolecular rearrangement. We propose that total CO scrambling in (4) is achieved by merry-go-round processes operating in two intersecting planes in the C_{2v} isomer (4b) (see Figure 2).

The dynamic behaviour of highly symmetric osmium cluster compounds can be probed effectively through ^{187}Os satellite spectra. The arene-triosmium complex $[\text{Os}_3(\text{CO})_9(\mu_3-\eta^2-\eta^2-\eta^2-\text{C}_6\text{H}_6)]$ (5) has C_{3v} symmetry¹² and distinct resonances for the equatorial and axial carbonyl ligands are observed in the ^{13}C n.m.r. spectrum at room temperature. Stereochemical rigidity of the equatorial carbonyl belt may be established from the magnitude of $^1J(^{187}\text{Os}-^{13}\text{C})$ in (5) (Table 1). In the absence of spin-spin coupling, n.m.r. experiments would not distinguish between rigidity and in-plane carbonyl exchange via the merry-go-round mechanism. Similar arguments against the occurrence of 'hidden' exchange processes for the square-pyramidal carbido cluster $\text{Os}_5\text{C}(\text{CO})_{15}$ (6)¹³ follow from interpretation of ^{187}Os satellites in the ^{13}C n.m.r. spectrum at 50 °C. The data are consistent, however, with localised carbonyl interchange at individual basal and apical metal atoms.

We are currently extending these studies of coupling to naturally abundant ^{187}Os with a view to establishing guidelines for carbonyl resonance assignment and for the determination of osmium cluster structures *in solution*. It is already apparent that relationships exist between the magnitude of $^1J(^{187}\text{Os}-^{13}\text{C})$ and (i) the type of carbonyl environment (*e.g.* equatorial *vs.* *trans*-diaxial CO), and (ii) the metal atom co-ordination number [*e.g.* in $[\text{Os}_6(\text{CO})_{18}]$ (3)].¹⁴

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