

Internuclear Exchange of Carbonyl Groups in $\text{Os}_3(\text{CO})_{12}$: Coupling Constants $J(^{187}\text{Os}-^{13}\text{C})$ in Trinuclear Osmium Carbonyls

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Summary The first measurement of nuclear spin-spin coupling constants $^1J(^{187}\text{Os}-^{13}\text{C})$ is reported for the complexes $^{187}\text{Os}_3(\text{CO})_{12}$ and $[^{187}\text{Os}_3\text{H}(\text{CO})_{12}]^+$; in the ^{13}C n.m.r. spectrum of $^{187}\text{Os}_3(\text{CO})_{12}$ at 150 °C, the averaged resonance is a 1:3:3:1 quadruplet, $J(^{187}\text{Os}-^{13}\text{C})$ 33 ± 1 Hz, which indicates that the intramolecular rearrangement occurs *via* an internuclear mechanism.

THE stereodynamic behaviour of $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) complexes and their derivatives has received especial attention.¹ The crystal structures of all three carbonyls are known; $\text{Fe}_3(\text{CO})_{12}$ has the least symmetrical (C_2) structure with two asymmetric bridging CO groups, whereas the ruthenium and osmium carbonyls have a symmetrical D_{3h} structure and contain only terminal carbonyls.² In solution $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ undergo a rapid rearrangement leading to scrambling of the carbonyl groups; even at -150 °C the ^{13}C n.m.r. spectrum of $\text{Fe}_3(\text{CO})_{12}$ contains a single resonance implying an extremely low exchange-process barrier. The complex $\text{Os}_3(\text{CO})_{12}$ in solution at room temperature is stereochemically rigid: its ^{13}C n.m.r. spectrum shows two resonances of equal intensity for the axial and equatorial CO groups, in accordance with the crystal structure. Upon heating the $\text{Os}_3(\text{CO})_{12}$ solution these signals broaden, coalesce and, at 150 °C, under conditions of rapid exchange, the spectrum consists of a narrow single line.³ It is supposed that the process of scrambling the CO groups in $\text{Fe}_3(\text{CO})_{12}$ includes, as an intermediate compound or intermediate state, a structure with non-bridging CO groups.⁴ As for $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$, their $\text{CO}_{\text{ax}} \rightleftharpoons \text{CO}_{\text{eq}}$ exchange may have either a local nature, *i.e.* take place at an individual metal atom, or an internuclear one, with the participation of bridging intermediates of different structures [one of them

is the structure found for $\text{Fe}_3(\text{CO})_{12}$ in the solid state]. It has been repeatedly noted, however, that it is impossible to choose between different mechanisms of carbonyl scrambling in such symmetrical molecules as $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$, although carbonyl exchange *via* bridged intermediates has been observed in phosphine-substituted derivatives of $\text{Os}_3(\text{CO})_{12}$.⁵

In the present communication we show that the $\text{CO}_{\text{ax}} \rightleftharpoons \text{CO}_{\text{eq}}$ exchange in $\text{Os}_3(\text{CO})_{12}$ is an internuclear process. This follows from the results of ^{13}C n.m.r. studies of the complex $^{187}\text{Os}_3(\text{CO})_{12}$ enriched with a metal isotope with 1/2 nuclear spin (^{187}Os , natural abundance 1.64%). A sample of ^{187}Os (99.8%) was oxidized in osmium tetroxide and the product was carbonylated by the usual method.⁶ The product, $^{187}\text{Os}_3(\text{CO})_{12}$, after enrichment with ^{13}C (up to *ca.* 60%) by heating with excess of ^{13}CO in toluene, was investigated by ^{13}C n.m.r. spectroscopy at 25 and 150 °C [in C_6D_6 and $\text{C}_6\text{H}_5\text{CD}_3$ solutions in the presence of $\text{Cr}(\text{acac})_3$ ($\text{Hacac} = \text{acetylacetonate}$)]. The spectrum obtained at 25 °C showed two doublets at δ 182.3 and 170.4 p.p.m., with $^1J(^{187}\text{Os}-^{13}\text{C})$ 90 ± 2 and 115 ± 2 Hz, respectively (Table). On the basis of arguments derived from a consideration of the spectrum of the hydride complex $[^{187}\text{Os}_3\text{H}(\text{CO})_{12}]^+$ (see below), the signal with the lower value of $J(^{187}\text{Os}-^{13}\text{C})$ has been assigned to the carbons of the axial carbonyl groups. At 150 °C the spectrum of the complex $^{187}\text{Os}_3(\text{CO})_{12}$ contains a 1:3:3:1 quadruplet with $J(^{187}\text{Os}-^{13}\text{C})$ 33 ± 1 Hz at δ 176.4 p.p.m. (Figure). The value of the averaged coupling constant observed under conditions of rapid exchange makes up one third of the mean $^1J(^{187}\text{Os}-^{13}\text{C})$ value for carbon atoms of the axial and equatorial groups. This value and the signal multiplicity show unambiguously that, first, the exchange process is intramolecular, and secondly, under conditions of rapid exchange all CO groups have access to the three osmium atoms (internuclear process).

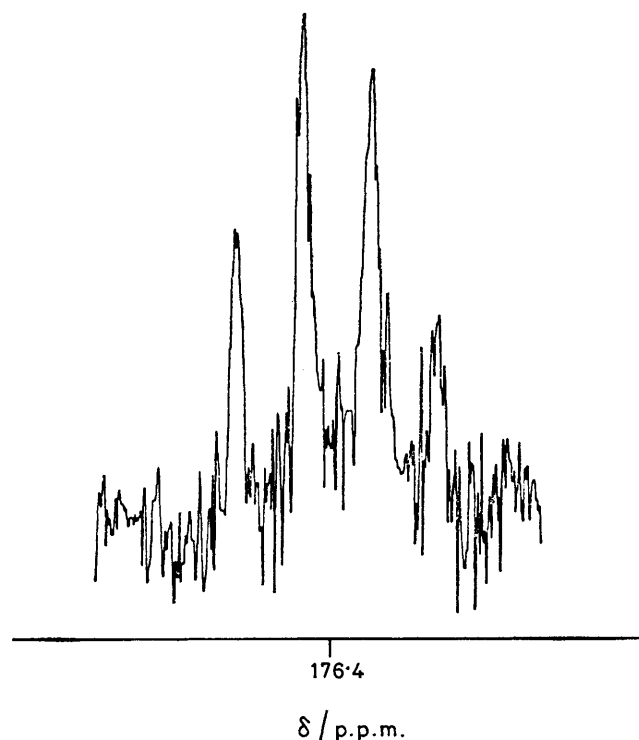
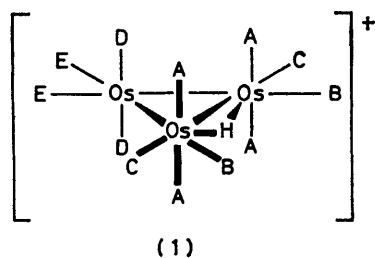


FIGURE. ^{13}C N.m.r. spectrum of $^{187}\text{Os}_3(\text{CO})_{12}$ at 150°C .

We also investigated a cationic hydrido-complex formed upon dissolution of dodecacarbonyltriosmium in concentrated sulphuric acid.⁷ The ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum of a sample with ^{187}Os in natural abundance showed five resonances of relative intensity 1:2:1:1:1 at δ 177.6, 177.1, 166.7, 161.4, and 160.8 p.p.m. (with respect to external SiMe_4), respectively (Table). In the uncoupled ^{13}C spectrum the resonance of maximum intensity is observed as a broadened singlet, and the two high-field resonances appear as doublets with $^2J(^{13}\text{C}-^1\text{H})$ 3.7 and 6.6 Hz, respectively. These results indicate unambiguously that the hydrogen atom is bridging and lies in the Os_3 plane, *i.e.* the complex $[\text{Os}_3\text{H}(\text{CO})_{12}]^+$ has structure (1). The measurement of $^1J(^{187}\text{Os}-^{13}\text{C})$ constants for complex (1) made it possible to assign the resonances of the axial and equatorial groups. The assignments of the B and C resonances are only tentative; we assume that the $^2J(^{13}\text{C}-^1\text{H})$ value should be greater for the ligand in the C position.

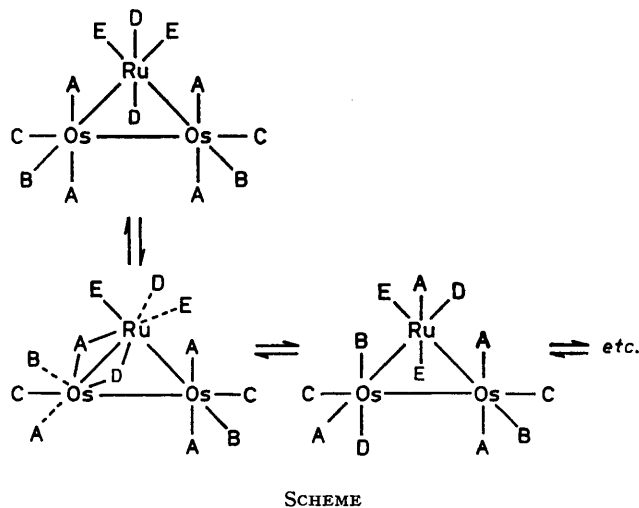


Thus, investigation of complex $^{187}\text{Os}(\text{CO})_{12}$ established that carbonyl scrambling in the osmium cluster results from an internuclear exchange process. The results obtained do not allow us to choose between different mechanisms of internuclear exchange. It is of interest, however, that in the mixed cluster $\text{RuOs}_2(\text{CO})_{12}$ one of the identified processes is

TABLE. ^{13}C N.m.r. spectroscopic data for osmium complexes at 25°C .

Complex	$\delta/\text{p.p.m.}$	Relative intensity	Assignment	Spin-spin splitting constants/Hz	
				$^1J(^{187}\text{Os}-^{13}\text{C})$	$^2J(^{13}\text{C}-^1\text{H})$
$^{187}\text{Os}(\text{CO})_{12}$	182.3	1	CO_{ax}	90 ± 2	
	170.4	1	CO_{eq}	115 ± 2	
$[\text{Os}_3\text{H}(\text{CO})_{12}]^+$ (1)	177.6	1	D	85 ± 1	
	171.1	2	A	84 ± 1	broadened peak
	166.7	1	E	121 ± 2	
	161.4	1	B	120 ± 2	3.3
	160.8	1	C	116 ± 2	6.6

two-centre exchange.⁸ Thus, in the ^{13}C n.m.r. spectrum of this complex at 145°C , a single resonance is observed at δ 183.9 p.p.m. which broadens upon cooling, coalesces at *ca.* 70°C , and at 30°C the spectrum contains two signals of relative intensity 5:1 at δ 186.4 and 170.6 p.p.m., respectively. The process observed at 30°C can be explained by the Scheme, according to which the exchange occurs *via*



formation of species with two bridging CO groups only between ruthenium and osmium atoms. As a result of this process 10 carbonyl groups take part in the intramolecular exchange, while two CO groups *trans* to the Os-Os bond do

not take part in the exchange. A referee suggested that our results might also be explained in terms of migration of the metal plane within the ligand polyhedron.⁹ At present, however, we cannot give preference to either inter-nuclear mechanism; this will be the subject of our full paper.

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