Carbon-13 Nuclear Magnetic Resonance Study of Complexes of the Type $[Os_3(CO)_{10}H(X)]$

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A variable-temperature ^{13}C n.m.r. spectroscopic study of complexes $[Os_3(CO)_{10}H(X)]$ (X = SEt, SPh, NBu^{n}H, OH, Cl, Br, I, CO_2Me, or CO_2CF_3) has, in some instances, given conclusive proof of a carbonyl-exchange process involving polytopal rearrangement in an $[Os(CO)_4]$ unit.

VARIABLE-TEMPERATURE ^{13}C n.m.r. spectroscopic studies on trinuclear osmium carbonyl clusters have indicated the number of independent fluxional processes that may occur. Thus restricted, or total, hydride exchange [1] or fluxional processes involving an organic moiety [1-3] will often result in increased symmetry in the cluster. Of more interest, however, are processes involving some form of carbonyl-site exchange, which can be considered to involve either the interconversion of terminal and edge-bridging carbonyls or polytopal rearrangements. Although considerable evidence has been collected to support both symmetric [2,4] and asymmetric [5] bridge-opening–bridge-closing mechanisms, as yet no definitive proof has been put forward for exchange involving $[Os(CO)_4]$ units occurring independently of carbonyl bridging. Thus in the case of the parent carbonyl $[Os_3(CO)_{12}]$, because of its very high symmetry, the rapid intramolecular scrambling of the equatorial and axial carbonyl groups can be adequately explained in terms of at least three exchange mechanisms, two involving the formation of carbonyl bridges and the third a polytopal rearrangement about individual osmium atoms.[6] This type of rotation has been postulated [7] to explain the observed spectrum of $[Ru_3(CO)_{10}(NO)_2]$

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[1] J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organometallic Chem.*, 1975, **97**, C16.

[2] E. G. Bryan, B. F. G. Johnson, and J. Lewis, unpublished work.

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[4] B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1974, 441.

[5] B. F. G. Johnson, J. Lewis, B. E. Reichert, and K. T. Schorpp, *J.C.S. Dalton*, 1976, 1403.

[6] A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1042.

[7] B. F. G. Johnson and J. Lewis, *Pure Appl. Chem.*, 1975, **44**, 43.

(three lines in the intensity ratio 2 : 2 : 1). However, recent observations have shown that the axial and equatorial carbonyls on the unique osmium atom have very similar chemical shifts which can, in fact, be resolved in different solvent systems (see Table). Further evidence to support this observation comes from the fact that for $[Ru_3(CO)_8(NO)_2(PPh_3)_2]$, where phosphine substitution occurs in the equatorial plane on the two similar ruthenium atoms,[8] the axial and equatorial carbonyls on the unique ruthenium atom remain resolvable up to 95 °C (see Table). Whilst investigating the variable-temperature ^{13}C n.m.r. spectroscopic properties of complexes of the type $[Os_3(CO)_{10}H(X)]$ (X = a three-electron donor) we have, in many instances, obtained evidence of a polytopal rearrangement involving an $[Os(CO)_4]$ unit.

Limiting ^{13}C n.m.r. data for complexes

Complex	δ/p.p.m.	Relative intensity	Assignment [a]	Coupling constants [b]
$[Os_3(CO)_{10}H(SEt)]$	180.0	1	A, B	
	179.8	1	A, B	
	176.3	2	D, E, F	
	173.7	2	C	
	170.4	2	D, E, F	
	169.5	2	D. E, F	10.4
$[Os_3(CO)_{10}H(SPh)]$	180.7	1	A, B	
	180.1	1	A, B	
	176.0	2	D, E, F	
	173.8	2	C	
	171.8	2	D, E, F	
	169.3	2	D, E, F	10.5
$[Os_3(CO)_{10}H(NBu^nH)]$	191.3	1	A, B	
	183.4	1	A, B	
	179.4	2	C, D, E, F	
	178.2	2	C, D, E, F	
	174.9	2	C, D, E, F	12.2
	172.8	2	C, D, E, F	
$[Os_3(CO)_{10}H(OH)]$	182.1	1	A, B	
	180.6	1	A, B	
	176.4	4	C, D, E, F	
	172.3	2	C, D, E, F	15.0
	169.6	2	C, D, E, F	
$[Os_3(CO)_{10}H(Cl)]$	183.8	1	A, B	
	183.3	1	A, B	
	177.5	2	D, E, F	
	176.9	2	C	
	172.9	2	D, E, F	
	172.5	2	D, E, F	10.0
$[Os_3(CO)_{10}H(Br)]$	185.4	1	A, B	
	184.8	1	A, B	
	178.1	2	D, E, F	
	177.1	2	C	
	173.3	2	D, E, F	
	172.3	2	D, E, F	11.7
$[Os_3(CO)_{10}H(I)]$	184.9	1	A, B	
	183.8	1	A, B	
	175.3	2	D, E, F	
	173.8	2	C	
	170.5	2	D, E, F	
	168.5	2	D, E, F	9.6
$[Os_3(CO)_{10}H(CO_2Me)]$	186.2	1	A, B	
	184.6	1	A, B	
	178.7	2	C	
	177.0	6	D, E, F	
$[Os_3(CO)_{10}H(CO_2CF_3)]$	185.0	1	A, B	
	183.4	1	A, B	
	177.1	2	D, E, F	
	176.1	2	C	
	175.8	2	D, E, F	
	175.3	2	D, E, F	
$[Ru_3(CO)_{10}(NO)_2]$	198.4	4		
	196.3	2		
	196.2	2		
	182.2	2		
$[Ru_3(CO)_8(NO)_2(PPh_3)_2]$	206.1	4		
	200.4	2		8.3
	197.7	2		$[J(^{13}C-^{31}P)]$

[a] Based on relative intensity and fluxional behaviour. [b] $J(^{13}C-^{1}H)$ in Hz unless otherwise stated.

RESULTS AND DISCUSSION

The variable-temperature ^{13}C n.m.r. spectra between −90 and 70 °C of complexes $[Os_3(CO)_{10}H(X)]$ (1; X = SEt, SPh, NBu^nH, OH, Cl, Br, I, CO_2Me, or CO_2CF_3), which are recorded in the Table, are fully consistent,

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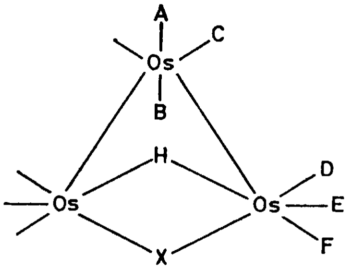
[8] J. P. Collman and J. R. Norton, *Inorg. Chem.*, 1973, **12**, 476.

allowing for accidental degeneracies, with the expected geometry. Thus for (1; X = SEt, SPh, NBu^nH, Cl, Br, I, or CO_2CF_3) six signals of relative intensity 1 : 1 : 2 : 2 : 2 : 2 are observed. However, the static structure cannot persist in solution as several of these complexes, notably $[Os_3(CO)_{10}H(NBu^nH)]$, are diastereotopic and no evidence for the existence of isomers could be established even at −90 °C.

In a number of cases, above 70 °C (X = SEt, SPh, Cl, Br, I, CO_2Me, or CO_2CF_3), considerable broadening of the two signals of relative intensity one, which must be assigned to carbonyls A and B, and one of the signals of intensity two occurs.* The assignment of the signal of intensity two is not simple, but, as no fluxional process has ever been proposed, or can be simply rationalized, which involves the two axial carbonyls on the unique osmium atom and just one of D, E, or F on the other two osmium atoms, it must arise from the equatorial carbonyls on the unique osmium atom. Thus the broadening observed in the spectra of the above complexes at >70 °C can be attributed to rotation of carbonyls about the unique osmium atom. It should be noted that, on the n.m.r. time scale, no exchange occurs either between osmium atoms by carbonyl bridging or by rotation of the carbonyls on the two similar osmium atoms even though such a polytopal rearrangement, involving $Os(CO)_3$ units, is known to be ready.[9]



(1)

There is then a direct analogy between complexes of this type and mononuclear disubstituted octahedral carbonyls such as $[Os(CO)_4(SiMe_3)_2]$.[10] These complexes have also been shown to exhibit stereochemical non-rigidity by an intramolecular isomerization process even though the barrier to intramolecular rearrangement in most octahedral complexes is very high.[11] Common exchange mechanisms used to explain the non-rigidity of mononuclear complexes of the type $[ML_4L'_2]$ cannot be used to rationalize the exchange occurring in this case. Thus, considering the size and nature of the substituents in $[Os_3(CO)_{10}H(X)]$, it seems unlikely that either a trigonal-twist mechanism, traversing a trigonal-prismatic intermediate,[11] or migration across a carbonyl carbon atom *via* a pseudo-five-co-ordinate acyl-type intermediate,[12] can occur. It has been previously proposed [6] that, for $[Os_3(CO)_{12}]$, axial–equatorial site exchange could occur *via* an increase in the OC–Os–CO equatorial angle to 180° and a decrease in the OC–Os–CO axial angle to 120° followed by rotation of the $[Os(CO)_4]$ unit by 90°. We now believe that a simpler exchange process could occur *via* a twist mechanism involving a square-based-pyramidal intermediate. A discussion of the other possible exchange mechanisms in five-co-ordinate complexes [11,13] does not seem justified at the present time.

EXPERIMENTAL

The following complexes were prepared by the literature methods: $[Os_3(CO)_{10}H(SR)]$ (R = Et or Ph),[14] $[Os_3(CO)_{10}H(OH)]$,[2] $[Os_3(CO)_{10}H(Y)]$ (Y = Cl, Br, or I),[2] $[Os_3(CO)_{10}H(NBu^nH)]$,[2] and $[Os_3(CO)_{10}H(CO_2CR_3)]$ (R = H or F).[2]

Carbon-13 n.m.r. spectra of isotopically enriched samples were obtained for toluene solutions which contained *ca.* 0.05 mol dm^{-3} tris(pentane-2,4-dionato)chromium(III) as a shiftless relaxation agent, using toluene as reference. Chemical shifts were subsequently converted into the $SiMe_4$ scale. The spectra were recorded on a Varian Associates XL-100 spectrometer operating in the Fourier-transform mode at 100 MHz using an internal deuterium lock.

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* This broadening increases with increasing temperature up to 95 °C, the highest temperature studied, and in fact when X = CO_2Me and CO_2CF_3 coalescence is reached at 90 °C.

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