Variable-temperature Carbon-13 Nuclear Magnetic Resonance Spectra of Phosphine-substituted Dodecarbonyl-*triangulo*-triosmium

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^{13}C N.m.r. spectra of the compounds [$Os_3(CO)_{12-n}(PEt_3)_n$] (n = 1 or 2) indicate that carbonyl exchange occurs selectively along one edge of the Os_3 triangle at low temperatures. The process involves only six of the 12 − n carbonyl groups in [$Os_3(CO)_{12-n}(PEt_3)_n$] (n = 1 or 2), and a mechanism involving a double carbonyl bridge is proposed.

A CARBON-13 n.m.r. study of isotopically enriched [$Os_3(CO)_{12}$] from *ca.* 70—180 °C showed that rapid intramolecular scrambling of the equatorial and axial carbonyl groups occurs.[1] At least three mechanisms may be proposed for this process, two involving the formation of CO bridges and the third a polytopal rearrangement about individual osmium atoms. It is not possible to differentiate between the mechanisms on the evidence at present available. We have now undertaken a variable-temperature ^{13}C n.m.r. study of some phosphine-substituted trinuclear osmium carbonyls in order to obtain further information about the mechanisms of carbonyl exchange in cluster compounds, although it must be borne in mind that the introduction of the phosphine may give rise to a different mechanism from that occurring in the parent carbonyls. There is evidence that the introduction of tertiary phosphines into polynuclear carbonyl clusters induces the formation of CO bridges.[2] It therefore seemed reasonable to suppose that phosphine-substituted derivatives [$Os_3(CO)_{12-n}(PEt_3)_n$] would more readily undergo CO scrambling by a CO migration process. This has been found to be the case. However, in addition, and more interestingly, we find that for the clusters [$Os_3(CO)_{12-n}(PEt_3)_n$] (n = 1 or 2) two distinct fluxional processes occur at different temperatures.

RESULTS AND DISCUSSION

At −60 °C the ^{13}C n.m.r. spectrum of the trisubstituted species [$Os_3(CO)_9(PEt_3)_3$] (in toluene) showed two ^{13}C carbonyl peaks at δ 199.4 and 186.4 p.p.m. (downfield from $SiMe_4$) with an intensity ratio of *ca.* 2 : 1. The lower-field peak was split, but this is not clearly resolved. Two peaks with intensity ratio 2 : 1 at δ 221.6 and 202.9 p.p.m. were also shown by the ruthenium analogue, but in this case a clear splitting into a doublet of 7 Hz was shown by the lower-field (higher-intensity) resonance. As tertiary-phosphine substituents are generally considered to only take up equatorial positions, the most reasonable structure in the compound is that shown in Figure 1, the splitting being associated with coupling between ^{31}P and the axial carbonyl ligands. This is supported by studies on the mono- and di-substituted compounds described below. The two carbonyl resonances in [$Os_3(CO)_9(PEt_3)_3$] broadened at 0 °C and coalesced completely at 20 °C indicating axial–equatorial exchange. In the ruthenium compound coalescence occurred at *ca.* 10—20 °C lower.

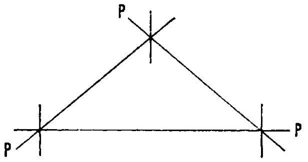

FIGURE 1 Orientation of phosphines in [$Os_3(CO)_9(PEt_3)_3$]

The disubstituted species [$Os_3(CO)_{10}(PEt_3)_2$] displayed seven carbonyl resonances at −60 °C, *viz.*: A, 197.1; B, 196.2; C, 187.8; D, 183.8; E, 180.9; F, 178.9; and G, 174.2 p.p.m. with an intensity ratio of *ca.* 2 : 2 : 2 : 1 : 1 : 1 : 1. Resonances A and B showed a small splitting of *ca.* 7 Hz indicating that these are due to the axial carbonyl groups adjacent to a phosphine. On increasing the temperature to −40 °C, the peaks A, C, D, and G began to broaden, and at −20 °C had nearly coalesced,

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[1] 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.

[2] K. J. Kavel and J. R. Norton, *J. Amer. Chem. Soc.*, 1974, **96**, 6812.

while the other resonances were virtually unaffected, *i.e.* two pairs of axial carbonyls, one adjacent to a phosphine and the other not, and two equatorial carbonyls are exchanging.* The only possible structure consistent with the low-temperature limit is as shown in Figure 2(*a*), where the assignments proposed are based on the observed exchange process. (Relative assignments within the pairs D and G and E and F are arbitrary; however, they are not relevant to the following argument.) It seems likely that the exchange occurs *via* an intermediate with two carbonyls bridging an edge. *X*-Ray structures of $[Fe_3(CO)_{12}]$ [3,4] and $[Fe_3(CO)_{11}(PPh_3)]$ [5] have shown that on the metal atoms adjoining the bridging edge one carbonyl (or the phosphine) is *trans* to the other metal–metal bond and hence occupies a position virtually unchanged from that in an unbridged form. If it is assumed that a phosphine is relatively non-mobile (as compared with a carbonyl) and remains in its position on formation of the bridged intermediate in $[Os_3(CO)_{10}(PEt_3)_2]$, a bridge can only be formed along one edge using the axial groups A and C and subsequent cyclic permutation as shown in Figure 2 will involve only A, C, D, and G, all of which lie in a plane not including a phosphine, in the exchange process. A similar exchange cannot take place in the planes B, C, F, P (Figure 3) and A, B, E, P since even if the phosphine were sufficiently mobile to adopt the altered position in the initial bridged intermediate it would be unable to move to the axial position in the subsequent step.

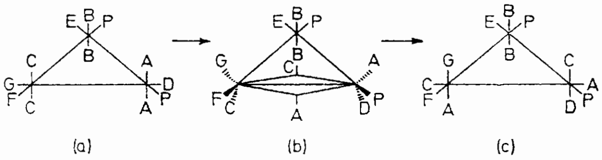

FIGURE 2 Proposed mechanism of carbonyl exchange in $[Os_3(CO)_{10}(PEt_3)_2]$

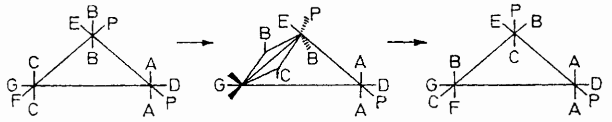

FIGURE 3 Illustration of the necessity for a phosphine to migrate to an axial position if exchange is to occur in the plane B,C,F,P. This exchange is not observed

The spectrum of $[Os_3(CO)_{11}(PEt_3)]$ at −60 °C showed eight resonances, *viz.*: A, 194.1; C, 186.3; B, 184.4; H, 178.1; D, 176.8; E, 173.8; F, 172.8; and G, 170.4 p.p.m. with an intensity ratio of 2 : 2 : 2 : 1 : 1 : 1 : 1. Only A showed a splitting due to $^{31}P-^{13}C$ coupling of *ca.* 6 Hz. The assignment of the peaks was made to correspond with the positions in Figure 2(*a*) with the carbonyl H replacing the phosphine adjacent to B and E. Again assignments within the groups D and G and E, F, and H are arbitrary but do not affect the proposed mechanism. On increasing the temperature to −20 °C the peaks A, C, D, and G broadened and began to coalesce at 0 °C. As $[Os_3(CO)_{12}]$ does not show axial–equatorial coalescence until 70 °C,[1] it appears that the labilizing influence of a phosphine on an osmium atom is required for the adjacent carbonyls to form a bridging intermediate and to undergo exchange at low temperature. When this requirement is added to that of a non-mobile phosphine as in the mechanism proposed for $[Os_3(CO)_{10}(PEt_3)_2]$, the only possible exchange process *via* a bridged intermediate is that shown in Figure 2, which causes the carbonyls A, C, D, and G to exchange as observed.

In both the mono- and di-substituted species complete coalescence of all the carbonyl resonances to give a single peak occurred at *ca.* 40 °C, indicating total scrambling of all positions. This process appears to involve a breakdown in the rigidity of the phosphine, as indicated by the ^{31}P n.m.r. spectrum of $[Os_3(CO)_{10}(PEt_3)_2]$. At −60 °C this showed two peaks at δ −127 and −134 p.p.m. (δ given as downfield of P_4O_6) which coalesced at *ca.* 30—40 °C.

EXPERIMENTAL

The compounds $[Os_3(CO)_{12-n}(PEt_3)_n]$ and $[Ru_3(CO)_9(PEt_3)_3]$ were prepared by the published methods [6,7] using ^{13}C-enriched samples of $[M_3(CO)_{12}]$.

^{13}C N.m.r. spectra of the 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 relaxation agent, using toluene as the reference. Chemical shifts were subsequently converted into the $SiMe_4$ scale. ^{31}P Chemical shifts were obtained in the absence of the chromium complex using a capillary containing P_4O_6 as the external reference. The spectra were recorded on a Varian XL-100 spectrometer operating in the Fourier-transform mode, using 12-mm sample tubes. $[^2H_8]$Toluene was added to all solutions for the deuterium lock.

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* It appears that the coalescence is to a single peak, but as the remainder of the spectrum broadens and begins to coalesce above 0° C, a sharp singlet for the coalescence of peaks A, C, D, and G is not attained.

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