Journal of Organometallic Chemistry, 281 (1985) C43—C46
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

INTRAMOLECULAR EXCHANGE IN TERTIARY PHOSPHINE DERIVATIVES OF DODECACARBONYLTRIOSMIUM

ANTONY J. DEEMING, SUSAN DONOVAN-MTUNZI and SHARIFF E. KABIR

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (Great Britain)

(Received October 16th, 1984)

Summary

Intramolecular tertiary phosphine exchange mechanisms in the compounds 1,2-[$Os_3(CO)_{10}(PMe_2Ph)_2$] and 1,2,3-[$Os_3(CO)_9\{P(OMe)_3\}L_2$] (L = PMe_2Ph or PPh_3) have been studied by ^{31}P and ^{13}C NMR methods. The ^{13}CO NMR results rule out a mechanism involving bridging carbonyl forms in favour of one involving axial—equatorial CO exchange at the same rate as phosphine exchange.

Dodecacarbonyltriosmium undergoes axial—equatorial CO exchange by an intramolecular pathway giving each ligand access to every ligand site [1]. Intermediates of C_{2v} symmetry like the solid-state structure of [$Fe_3(CO)_{12}$] are possible and this mechanism (A) (Fig. 1) has been used to interpret CO site exchange in [$Os_3(CO)_{11}(PEt_3)$] and 1,2-[$Os_3(CO)_{10}(PEt_3)_2$] [2] and in 1,1-[$Os_3(CO)_{10}(PMe_2Ph)_2$] [3].

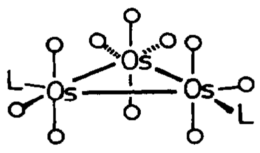
We have recently observed that 1,1-[$Os_3(CO)_{10}$(*cis*-butadiene)] reacts with PMe_2Ph to give a separable mixture containing 1,1-[$Os_3(CO)_{10}(PMe_2Ph)_2$] and 1,2-[$Os_3(CO)_{10}(PMe_2Ph)_2$], the latter existing in solution as two interconverting isomers **1** and **2** [3]. At −80°C the major isomer **1** gives two equal intensity $^{31}P\{^1H\}$ NMR singlets (δ 1.10 and 6.77 ppm)* while the minor isomer **2** gives a singlet (δ 4.41 ppm). As the temperature is raised coalescence gives a singlet at δ 3.9 ppm above 80°C. The interchange of the PMe_2Ph ligands within **1** does not occur primarily by the interconversion of **1** and **2** since line-shape analysis has given the rate of PMe_2Ph exchange within isomer **1** as 20 times faster than the interconversion between **1** and **2**.

Two mechanisms for PMe_2Ph exchange within isomer **1** might be considered. We originally considered mechanism B requiring an intermediate with three

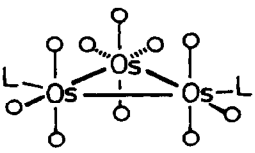
---

* $^{31}P\{^1H\}$ NMR shifts are given relative to 85% H_3PO_4.

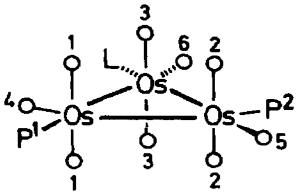
0022-328X/85/$03.30



(1)



(2)



(3)

L = P(OMe)$_3$
P = PPh$_3$ or PMe$_2$Ph

bridging CO ligands to be very attractive. A similar process involving the equilibrium between forms with and without bridging CO has been invoked to explain the dynamic behaviour of $[Os_3(CO)_{10}(\mu\text{-}1,2\text{-diazine})]$ (1,2-diazine = pyridazine) [4]. The proposed intermediate form with three bridging CO ligands is observed as the ground state structure in the analogous ruthenium compound [5]. An alternative mechanism C requires simultaneous turnstile rotations at the two substituted osmium atoms (such as shown in Fig. 1) to be faster than a rotation at a single osmium atom which would lead to isomer 2. Whereas mechanism C leads to axial—equatorial CO exchange, mechanism B does not. However,

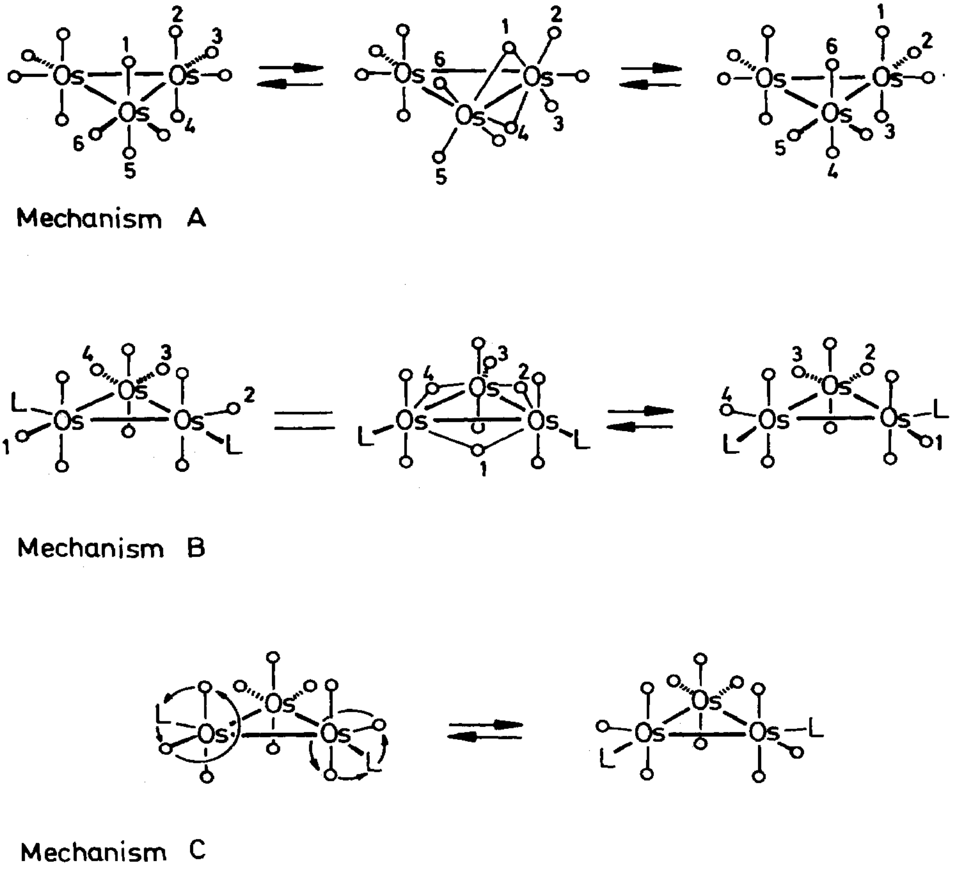


Fig. 1. Possible mechanisms for site exchange in $[Os_3(CO)_{12}]$ and substituted derivatives.

there is no way to distinguish mechanisms B and C on this basis for the phosphine compounds because there is an even faster process of type A which leads to the exchange of the six axial and equatorial CO ligands in the one vertical plane not blocked by a tertiary phosphine ligand.

To distinguish mechanisms of type B and C we considered molecules for which processes of type A are not possible. The tri-substituted compounds 1,2,3-$[Os_3(CO)_9L_3]$ are suitable because each of the three planes in which mechanism A could operate contains a ligand L which cannot bridge and hence this process is prevented. The exchange of axial and equatorial CO ligands in $[Os_3(CO)_9(PEt_3)_3]$ only gives coalescence of ^{13}C NMR signals between 0 and 20°C, presumably via a turnstile mechanism [2], so that in principle low temperature processes related to B or C might be detectable. The cluster 1,2,3-$[Os_3(CO)_9\{P(OMe)_3\}(PPh_3)_2]$, compound **3**, formed by treating $[Os_3(CO)_{11}\{P(OMe)_3\}]$ with an excess of PPh_3, gives three $^{31}P\{^1H\}$ NMR singlets at −30°C (δ 98.5 for $P(OMe)_3$ and −3.93 and −5.43 ppm for PPh_3). The PPh_3 signals coalesce as shown in Fig. 2. If the process leading to this exchange in **3** corresponded to mechanism B there would be specific CO exchange of CO^4 with CO^6 and of CO^1 with CO^2 at the same rate as exchange of P^1 with P^2 and presumably at a different rate from axial—equatorial CO exchange by another mechanism. However, we observe that all six ^{13}CO signals, three axial (δ 196.5, 195.6, and

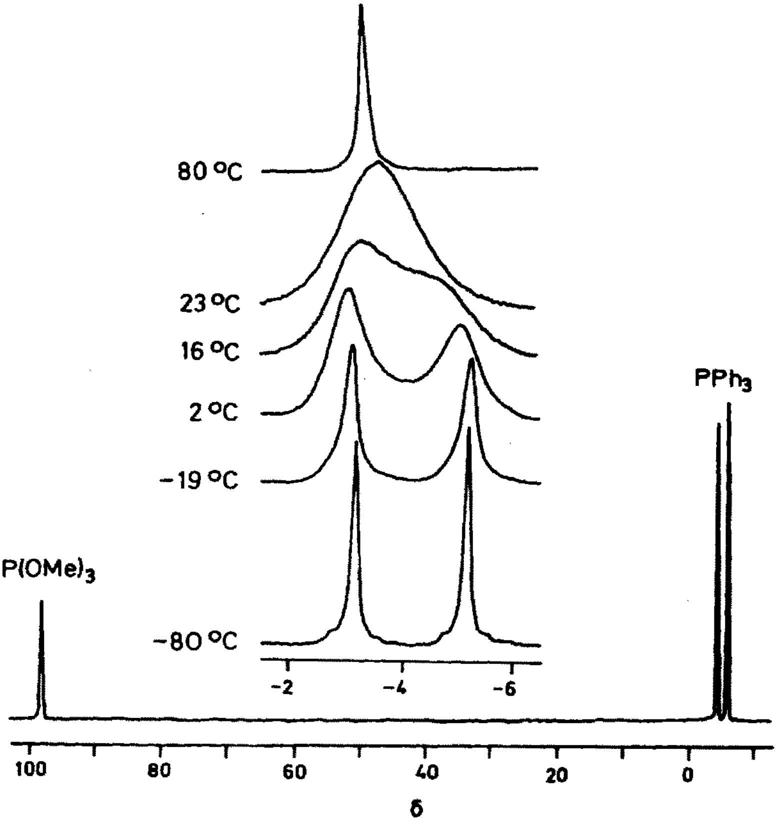


Fig. 2. $^{31}P\{^1H\}$ NMR spectra for 1,2,3-$[Os_3(CO)_9\{P(OMe)_3\}(PPh_3)_2]$, compound 3, in toluene with expanded spectra shown for the PPh_3 resonances at different temperatures.

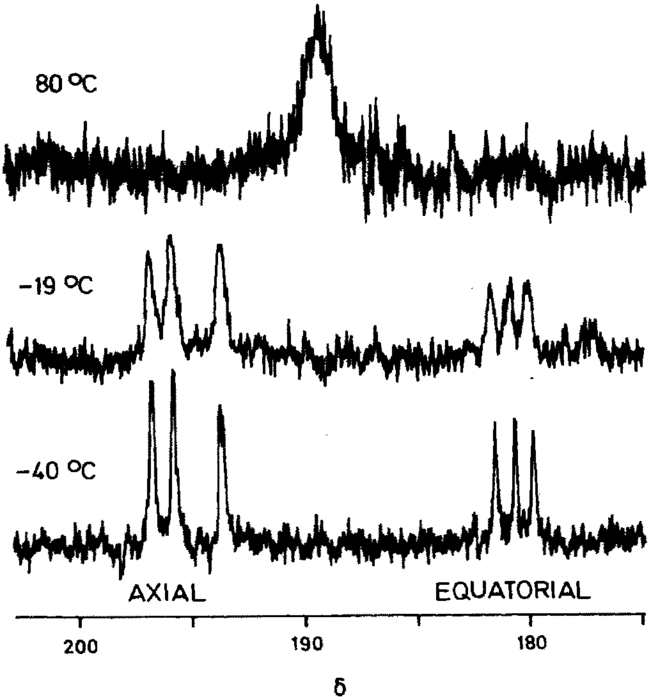


Fig. 3. Natural abundance $^{13}C\{^1H\}$ NMR spectra for compound 3 in toluene in the presence of 0.05 mol dm $^{-3}$ $[Cr(acac)_3]$.

193.5 ppm; doublets) and three equatorial (δ 181.3, 180.4, and 179.5 ppm; singlets), all broaden at the same temperature and coalesce to give a single resonance (δ 189.4 ppm) at 80°C (Fig. 3). Similar observations were made on $[Os_3(CO)_9\{P(OMe)_3\}(PMe_2Ph)_2]$. Thus the lowest energy process involves axial—equatorial site-exchange and we can clearly rule out a mechanism corresponding to B. Furthermore the CO exchange rate is the same at each osmium atom which points to turnstile rotations at the different osmium atoms being coupled as in compound 1 if C also operates in that case. A reorientation of the metal triangle within a ligand polyhedron of the type discussed for $[Fe_3(CO)_{11}(PR_3)]$ etc. [6] would presumably have to occur without transfer of tertiary phosphines between metal atoms and it is difficult to see how this in itself could account for these exchanges.

Acknowledgements. We thank the Association of Commonwealth Universities for a Scholarship (to S.E.K.), the S.E.R.C. for financial support, and Johnson—Matthey Limited for a generous loan of osmium tetraoxide.

References

1 A.A. Koridze, O.A. Kizas, N.M. Astakhova, P.V. Petrovskii and Yu.K. Grishin, J. Chem. Soc., Chem. Commun., (1981) 853.
2 B.F.G. Johnson, J. Lewis, B.E. Reichert and K.T. Schorpp, J. Chem. Soc., Dalton Trans., (1976) 1403.
3 A.J. Deeming, S. Donovan-Mtunzi, S.E. Kabir and P.J. Manning, J. Chem. Soc., Dalton Trans., in press.
4 F.A. Cotton, B.E. Hanson and J.D. Jamerson, J. Am. Chem. Soc., 99 (1977) 6588.
5 F.A. Cotton and B.E. Hanson, Inorg. Chem., 16 (1977) 2820.
6 R.E. Benfield, P.D. Gavens, B.F.G. Johnson, M.J. Mays, S. Aime, L. Milone and D. Osella, J. Chem. Soc., Dalton Trans., (1981) 1535 and ref. therein.