Fluxional Ligand Migrations in Triosmium Clusters containing 2-Pyridylphosphines

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The cluster $[Os_3(CO)_{10}(\mu\text{-}L)]$ (L = $Ph_2PC_5H_4N$) (X-ray structure reported), containing the diaxially coordinated 2-pyridyldiphenylphosphine bridge, undergoes rapid transfer of the pyridine between two metal atoms while the phosphorus atom remains firmly coordinated to the third.

The ligand 2-pyridyldiphenylphosphine ($Ph_2PC_5H_4N$, L) has been widely used to bridge metal centres and an extensive coordination and organometallic chemistry based on it has been developed.[1] It is generally reckoned to stabilize dinuclear compounds by being firmly attached to the metal atoms it bridges. We have now shown that the ligand L reacts with $[Os_3(CO)_{10}(MeCN)_2]$ in dichloromethane solution at room temperature to give orange crystals of the cluster $[Os_3(CO)_{10}(\mu\text{-}L)]$ **1** (45%) and yellow crystals of $[Os_3(CO)_{11}L]$ **2** (21%) which were separated by TLC on silica from other products including $[Os_3(CO)_{10}L_2]$. The ^1H NMR spectrum† shows that **2** contains the ligand L coordinated through the phosphorus atom only [6-H pyridyl resonance at δ 8.87 compared with δ 8.72 for the free ligand] and its IR spectrum† is very similar to that of $[Os_3(CO)_{11}(PPh_3)]$ indicating that they are isostructural.[2]

The cluster **1** is very interesting because of its crystal structure and fluxional behaviour in solution. Its single-crystal X-ray structure‡ (Fig. 1) establishes that the N and P atoms are both coordinated axially, consistent with the non-equivalence of the Ph groups as observed in the ^1H NMR spectra† between −20 and −90 °C, a result that is inconsistent with diequatorial coordination. This stereochemistry contrasts with that of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ and $[Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$), *e.g.* in which bridging dppm ligands are diequatorially coordinated.[3,4] Normally ligands bulkier than hydride[5] or acetontirile[6] are equatorially coordinated and we believe that the small span of L (N···P = 2.650 Å)[7] compared with that of dppm (P···P = 2.970 Å)[8] favours diaxial coordination. The N···P distance in **1** is 2.716 Å whereas the P···P distance in $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ is 3.127 Å.[3] These distances might be compared with the

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† *Spectroscopic data* for compound **1**: IR ν(CO)/cm^{-1} (cyclohexane): 2083s, 2032vs, 2017vs, 2004s, 1977s, 1969s, 1955m, 1938w; ^1H NMR (400 MHz, CD_2Cl_2, −60 °C): 2-pyridyl: δ 9.42 (6-H), 7.55 (4-H), 7.30 (5-H), 7.25 (3-H); phenyl: δ 7.50, 7.45, 7.09; (1,1,2,2-$C_2D_2Cl_4$, 80 °C): 2-pyridyl: 9.41 (6-H), 7.51 (4-H), 7.22 (5-H, 3-H); phenyl: δ 7.45, 7.33 (signals at δ 7.61 and 7.09 at 20 °C have coalesced); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 20 °C), δ 5.6 (s).

Compound **2**, IR ν(CO)/cm^{-1} (cyclohexane): 2108m, 2053s, 2042m, 2020vs, 1999m, 1987m, 1971m; ^1H NMR (400 MHz, $CDCl_3$, 20 °C): 2-pyridyl: δ 8.87 (6-H), 7.57 (5-H), 7.27 (4-H), 7.09 (3-H); phenyl: δ 7.40–7.50; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 20 °C): 4.2(s).

Compound **3**: IR ν(CO)/cm^{-1} (cyclohexane): 2083s, 2034vs, 2018vs, 2003m, 1977s, 1968s, 1952w, 1939w; ^1H NMR (400 MHz, CD_2Cl_2, −20 °C): *N*-bonded 2-pyridyl: δ 9.40 (6-H), 7.91 (3-H), 7.59 (4-H), 7.30 (5-H), *N*-non-bonded 2-pyridyl: δ 8.70, 8.59 (6-H), 8.03, 7.88 (5-H), 7.74, 7.39, 7.29, 7.19 (3-H, 4-H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 20 °C): δ 12.7(s).

Compound **4**: IR ν(CO)/cm^{-1} (cyclohexane): 2083s, 2033vs, 2018vs, 2003m, 1978s, 1969s, 1952w, 1938w; ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): two isomers: *N*-bonded 2-pyridyl: δ 9.49 and 9.37 (6-H); *N*-non-bonded 2-pyridyl: δ 8.72 and 8.67 (6-H); other resonances at δ 8.12, 8.03, 7.86, 7.81, 7.62, 7.51, 7.41, 7.35, 7.27, 7.19, 7.01; $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 20 °C): δ 11.0 (s) and 8.4 (s) (*ca.* 1 : 1 ratio).

‡ *Structure determination*: Nicolet R3v/m diffractometer, Mo-radiation (λ = 0.71073 Å), room temp. data corrected empirically for absorption. Orange crystal, $C_{27}H_{14}NO_{10}POs_3$, M = 1113.99 g mol^{-1}, size = 0.40 × 0.35 × 0.30 mm^3, monoclinic, $P2_1/n$, $a = 9.278(4)$, $b = 25.508(7)$, $c = 13.096(6)$ Å, $\beta = 107.31(4)°$, $U = 2959(2)$ Å^3, $Z = 4$, $D_c = 2.50$ g cm^{-3}, μ(Mo-Kα) = 129.7 cm^{-1}, $F(000) = 2024$. Direct methods, $R = 0.0556$, $R' = 0.0545$, where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$, after refinement 379 parameters using 4107 data with $I_o > 1.5\sigma(I_o)$ in the range $5 \leqslant 2\theta \leqslant 50°$. All non-H atoms were refined anisotropically with H-atoms included in idealised positions (C–H 0.96 Å, $U = 0.08$ Å^3). Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

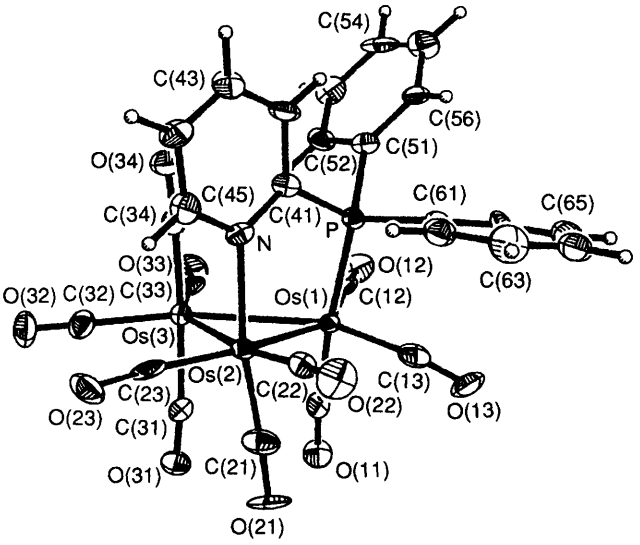


Fig. 1 Molecular structure of $[Os_3(CO)_{10}(\mu\text{-}Ph_2PC_5H_4N)]$, cluster **1**. Selected bond lengths (Å) and angles (°): Os(1)–Os(2), 2.827(2); Os(2)–Os(3), 2.872(2); Os(1)–Os(3), 2.929(2); Os(1)–P, 2.380(4); Os(2)–N, 2.22(1); P–C(41), 1.85(2); N–C(41), 1.32(2); Os(1)–C(11), 1.92(2); Os(2)–C(21), 1.87(2); Os(3)–C(31), 2.01(2); Os(3)–C(34), 1.94(2); av. Os–C (equatorial), 1.894; Os(1)–Os(2)–N, 93.2(4); Os(2)–Os(1)–P, 81.9(1); Os(1)–P–C(41), 117.3(5); Os(2)–N–C(41), 125(1); N–C(41)–P, 117(1).

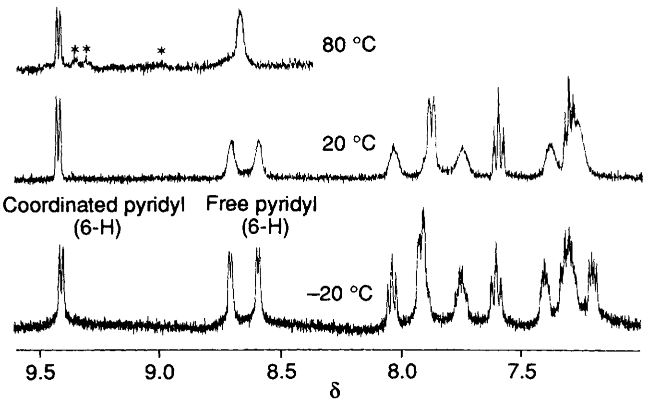
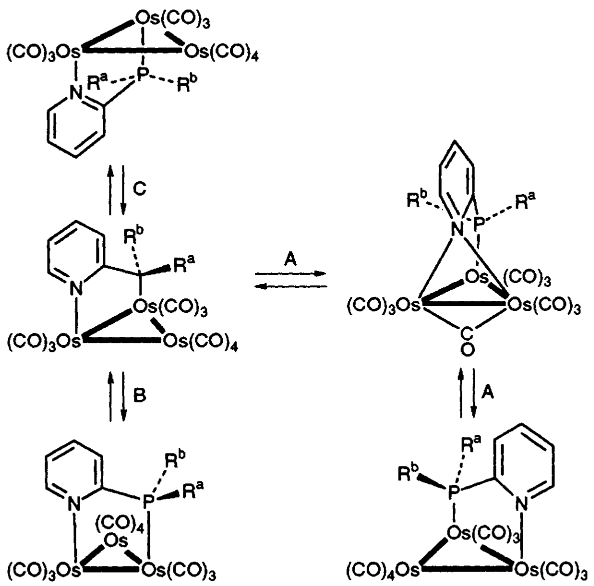


Fig. 2 400 MHz ^1H NMR spectra of the cluster $[Os_3(CO)_{10}\{\mu\text{-}P(C_5H_4N)_3\}]$ recorded in CD_2Cl_2 (−20 and 20 °C) or in 1,1,2,2-$C_2D_2Cl_4$ (80 °C). Signals for the 6-H protons of the pyridyl rings are indicated for the free and coordinated groups; * indicates peaks for decomposition products at 80 °C.

shortest axial–axial C···C distances (av = 2.875 Å) and the shortest equatorial–equatorial distances (av = 3.424 Å) in $[Os_3(CO)_{12}]$ (calculated from data given in ref. 5). Dppm is a more flexible ligand and has been found to span metal–metal distances from 2.1 to 4.4 Å,[9] while $Ph_2PC_5H_4N$ has never been found associated with a metal–metal distance greater than about 2.9 Å.

The ^1H and $^{13}C\{^1H\}$ NMR spectra† of **1** are temperature dependent. At 20 °C sharp 2-pyridyl ^1H NMR resonances are observed while the phenyl resonances are very broad (linewidths up to 30 Hz). Lower temperatures lead to better resolution whereas higher temperatures lead to coalescence of peaks at δ 7.61 and 7.09 to a new broad resonance at δ 7.33. We have not been able to assign these phenyl signals with confidence but the observed changes are consistent with dynamic exchange of the two non-equivalent phenyl groups leading to a time-averaged plane of symmetry.



Scheme 1 Possible mechanisms for R^a–R^b exchange in compounds **1**, **3** and **4**

The corresponding tri(2-pyridyl)phosphine complex $[Os_3(CO)_{10}\{\mu\text{-}P(C_5H_4N)_3\}]$ **3**, prepared similarly, gives more easily interpreted ^1H NMR spectra. At −20 °C there are three sharp sets of 2-pyridyl resonances [6-H resonances: δ 8.70 and 8.59 for the non-coordinated groups and δ 9.40 for the coordinated group] (Fig. 2). The pairwise coalescence of the non-coordinated 2-pyridyl resonances without the coordinated 2-pyridyl resonances changing very much shows that the exchange process does not involve the formation of monodentate *P*-bonded tri(2-pyridyl)phosphine which would lead to the mutual exchange of all three groups. Therefore we propose that R^a exchanges with R^b while the N and P atoms remain coordinated (Scheme 1). Processes A, B and C could account for the coalescences but we feel that process C is less likely than the others. Process A corresponds to a classical CO rearrangement process but with the pyridine and a CO ligand migrating *via* bridging positions instead of two CO ligands. However, a phosphine migration is an alternative and has been observed in triplatinum systems.[10]

We examined ^{13}C NMR spectra of cluster **1**, hoping to discriminate between these processes. A set of ten ^{13}C carbonyl resonances consistent with the static structure is observed for a CD_2Cl_2 solution at −85 °C but there are fast processes leading to CO exchange which prevent our specifically identifying the CO exchanges corresponding to R^a–R^b exchange. At room temperature nine of the ten resonances have coalesced to a broad resonance at δ 183.5 while that for the CO ligand *trans* to the PPh_2 group remains as a doublet [δ 184.2 (d, J = 4.5 Hz)]. We suggest that process A together with other processes including a merry-go-round process in the M_3 plane over all three metal atoms as identified for $[M_3(CO)_{10}(\mu\text{-}1,2\text{-diazine})]$ (M = Ru or Os),[11,12] also containing diaxially coordinated ligands, would lead to just the one CO ligand not exchanging. Process B or C could not account for this observation. Final confirmation that the P-atom remains bonded to the same Os atom throughout came from the observation of sharp ^{187}Os satellites[13,14] to the $^{31}P\{^1H\}$ NMR singlet [$J(^{187}Os^{31}P)$ 165 Hz] at temperatures from −40 °C up to 50 °C. Any process involving the migration of the P-atom between the Os sites would have led to the collapse of the ^{187}Os satellites. Only process A, or the very unlikely process C, would be consistent with the observed $^{31}P\{^1H\}$ NMR spectra.

The corresponding cluster $[Os_3(CO)_{10}\{\mu\text{-}PhP(C_5H_4N)_2\}]$ **4** from di(2-pyridyl)phenylphosphine shows two isomers both in the ^{1}H and ^{31}P NMR spectra as expected but a rapid equilibrium between them at room temperature leads to broad resonances. This is completely consistent with what we have concluded for the clusters **1** and **3**.

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References

1 C. G. Arena, E. Rotondo, F. Faraone, M. Lanfranchi and A. Tiripicchio, *Organometallics*, 1991, **10**, 3877; S. Lo Schiavo, E. Rotondo, G. Bruno and F. Faraone, *Organometallics*, 1991, **10**, 1613; E. Rotondo, S. Lo Schiavo, G. Bruno, C. G. Arena, R. Gobetto and F. Faraone, *Inorg. Chem.*, 1989, **28**, 2944; J. L. Roustan, N. Ansari and F. R. Ahmed, *Inorg. Chem. Acta*, 1987, **129**, L11; Z.-Z. Zhang, H.-K. Wang, H.-G. Wang and R.-J. Wang, *J. Organomet. Chem.*, 1986, **314**, 357; T. J. Barder, F. A. Cotton, G. L. Powell, S. M. Tetrick and R. A. Walton, *J. Am. Chem. Soc.*, 1984, **106**, 1323; J. P. Farr, M. M. Olmstead, N. M. Rutherford, F. E. Wood and A. L. Balch, *Organometallics*, 1983, **2**, 1758; J. P. Farr, M. M. Olmstead, F. E. Wood and A. L. Balch, *J. Am. Chem. Soc.*, 1983, **105**, 792.

2 M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Rieger and M. L. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 442; B. F. G. Johnson, J. Lewis and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.

3 A. W. Coleman, D. F. Jones, P. H. Dixneuf, C. Brisson, J.-J. Bonnet and G. Lavigne, *Inorg. Chem.*, 1984, **23**, 952.

4 S. Cartwright, J. A. Clucas, R. H. Dawson, D. F. Foster, M. M. Harding and A. K. Smith, *J. Organomet. Chem.*, 1986, **302**, 403.

5 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.

6 P. A. Dawson, B. F. G. Johnson, J. Lewis, J. Puga, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1982, 233.

7 Calculated from data given by J.-P. Charland, J.-L. Roustan and N. Ansari, *Acta Crystallogr., Sect. C*, 1989, **45**, 680.

8 Calculated from data given by H. Schmidbaur, G. Reber, A. Schier, F. E. Wagner and G. Müller, *Inorg. Chim. Acta*, 1988, **147**, 143.

9 A. L. Balch, R. R. Guimerans, J. Linehan and F. E. Wood, *Inorg. Chem.*, 1985, **24**, 2021.

10 A. M. Bradford, G. Douglas, L. Manojlović-Muir, K. W. Muir and R. J. Puddephatt, *Organometallics*, 1990, **9**, 409.

11 F. A. Cotton, B. E. Hanson and J. D. Jamerson, *J. Am. Chem. Soc.*, 1977, **99**, 6588.

12 F. A. Cotton and B. E. Hanson, *Inorg. Chem.*, 1977, **16**, 2820.

13 M. A. Gallop, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1987, 1831.

14 R. Benn, H. Brenneke, E. Joussen, H. Lehmkuhl and F. López Ortiz, *Organometallics*, 1990, **9**, 756.