Triosmium Clusters with 2-Pyridylphosphines as Ligands†

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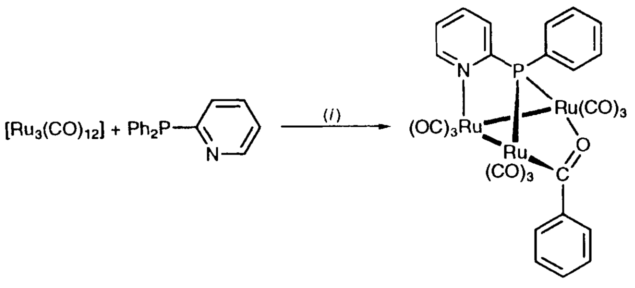
Room-temperature reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with the tertiary phosphines (L), diphenyl(2-pyridyl)phosphine, phenyldi(2-pyridyl)phosphine, and tri(2-pyridyl)phosphine, led to clusters of the type $[Os_3(CO)_{11}L]$ **1**, $[Os_3(CO)_{10}L_2]$ **2**, and $[Os_3(CO)_{10}(\mu\text{-L})]$ **3** which is the major product in each case. Clusters **1** and **2** have ligands L co-ordinated through the phosphorus atom alone, whereas **3** contain diaxially co-ordinated bridging ligands through one P and one pyridyl substituent. Two isomers of **3** [L = $PPh(2\text{-}C_5H_4N)_2$] are in rapid exchange in solution above room temperature and the clusters **3** [L = $PPh_2(2\text{-}C_5H_4N)$ or $P(2\text{-}C_5H_4N)_3$] gain a time-averaged plane of symmetry by a process which is the counterpart of this isomerisation; dynamic transfer of pyridine co-ordination between two metal atoms is proposed on ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR evidence. Protonation of **3** [L = $PPh_2(2\text{-}C_5H_4N)$] arrests this process. Thermal treatment of **3** [L = $PPh_2(2\text{-}C_5H_4N)$] led to a major product $[Os_3(\sigma\text{-Ph})\{\mu_3\text{-PPh}(2\text{-}C_5H_4N)\}(CO)_9]$ (60%) (crystal structure reported) which contains the five-electron donating phenyl(2-pyridyl)phosphido bridge and a terminal phenyl ligand. Minor products are the cluster $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-PPh}_2)(CO)_{10}]$ (6%) (crystal structure reported), $[Os_2(\mu\text{-}C_5H_4N)(\mu\text{-PPh}_2)(CO)_6]$ (trace), which is derived from the former, and $[Os_3(\mu\text{-PhCO})\{\mu_3\text{-PPh}(2\text{-}C_5H_4N)\}(CO)_9]$ (trace). These clusters are generated by cleavage of either phosphorus–phenyl or phosphorus–2-pyridyl bonds; cleavage of a bond within the five-membered ring forming the bridge is less favoured than that of an exocyclic substituent.

When catalysed by $[N(PPh_3)_2]CN$, the cluster $[Ru_3(CO)_{12}]$ reacts with diphenyl(2-pyridyl)phosphine in tetrahydrofuran to give the product $[Ru_3(\mu\text{-PhCO})\{\mu_3\text{-PPh}(2\text{-}C_5H_4N)\}(CO)_9]$, in which a phenyl group has migrated from a phosphorus atom to a CO ligand, almost certainly *via* a metal atom (Scheme 1).[1] Usually the use of catalysts {including $[N(PPh_3)_2]CN$, sodium–benzophenone and $[Fe_2(CO)_{6-x}(PPh_3)_x(SMe)_2]$ (x = 1 or 2)} with simple tertiary phosphines (L) leads to simple substitution products $[Ru_3(CO)_{12-x}L_x]$ (x = 1, 2 or 3)[2] and an intermediate of this kind, $[Ru_3(CO)_{11}\{PPh_2(2\text{-}C_5H_4N)\}]$, was observed using diphenyl(2-pyridyl)phosphine. However, this cluster is unstable and a P–C bond is broken spontaneously at room temperature. We have likewise studied the reactions of the cluster $[Ru_3(CO)_{12}]$ with other 2-pyridylphosphines, phenyldi(2-pyridyl)phosphine and tri(2-pyridyl)phosphine, using $[N(PPh_3)_2]Cl$ as catalyst. Metal-mediated P–C bond cleavage occurs at room temperature in these cases as well to give products in which either 2-pyridyl or phenyl groups have migrated (Schemes 2 and 3).[3] We have not isolated intermediates prior to P–C bond fission but speculated that these were of the type $[Ru_3(CO)_{10}(\mu\text{-L})]$ where L is a 2-pyridylphosphine co-ordinated through N and P atoms. This would account for the lack of 2-pyridyl migration from diphenyl(2-pyridyl)phosphine and approximately equal amounts of 2-pyridyl and phenyl migration from phenyldi(2-pyridyl)phosphine, if, as we suspected, cleavage within the ring formed by the ligand bridge is much less favourable than cleavage of exocyclic substituents.

To test these ideas we decided to synthesise the osmium analogues of the supposed ruthenium intermediates prior to P–C bond cleavage, which were expected to be more inert with osmium, and to establish their reactivity. We have studied the reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with all three 2-pyridylphosphines described above and now report the synthesis and fluxionality of three clusters of the type $[Os_3(CO)_{10}(\mu\text{-L})]$ where L is a tertiary phosphine containing one to three 2-pyridyl substituents and the thermal conversion of the cluster containing diphenyl(2-pyridyl)phosphine into P–C bond-cleaved products. Some of this work was communicated earlier.[4]



Scheme 1 (*i*) Tetrahydrofuran (thf), $[N(PPh_3)_2]CN$, 25 °C, 48 h

Results and Discussion

Reactions of $[Os_3(CO)_{10}(MeCN)_2]$ *with 2-Pyridylphosphines.*—Room-temperature reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with diphenyl(2-pyridyl)phosphine (L) leads to a mixture which was separated by TLC to give as the main product the cluster $[Os_3(CO)_{10}(\mu\text{-L})]$ **3a** (45%), isolated as orange crystals. Minor products were $[Os_3(CO)_{11}L]$ **1a** and $[Os_3(CO)_{10}L_2]$ **2a** (*ca.* 20% each), which were characterised analytically and spectroscopically as monodentate tertiary phosphine derivatives, closely resembling those containing simple monodentate tertiary phosphines (IR data, Table 1).[5] Cluster **3a** was shown to contain a co-ordinated 2-pyridyl group and a co-ordinated phosphorus atom; the co-ordination shift (from δ 8.72 for free L to δ 9.42 for **3a**) in the ^1H NMR spectrum for the hydrogen atom in the 6 position of the 2-pyridyl substituent (H^6) confirms that there is an Os–N bond (Table 2). There is essentially no shift of this signal on co-ordination for compounds **1a** and **2a** which have free 2-pyridyl substituents. Whereas the cluster $[Ru_3(CO)_{10}(\mu\text{-Ph}_2PCH_2PPh_2)]$ and related osmium compounds contain the ligand diequatorially

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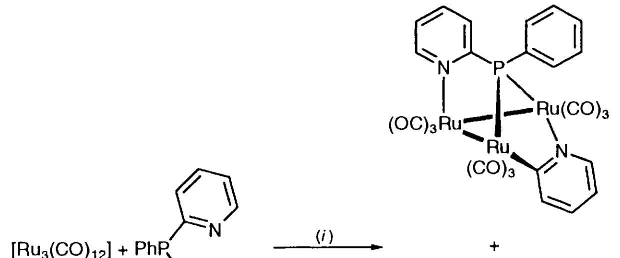
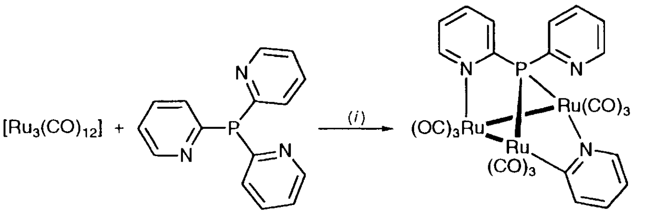
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 2 (*i*) thf, $[N(PPh_3)_2]Cl$, room temperature



Scheme 3 (*i*) thf, $[N(PPh_3)_2]Cl$, room temperature

co-ordinated,[6] the ligand L in **3a** is diaxially co-ordinated because of the much smaller distance between the donor atoms in L compared with that in dppm. The crystal structure of **3a**, reported in a communication,[4] confirms the geometry; it is consistent with the low-temperature NMR data which show that the phenyl substituents are inequivalent. The diequatorial form would have equivalent phenyl groups.

The corresponding complexes $[Os_3(CO)_{10}(\mu\text{-L})]$ **3b** from phenyldi(2-pyridyl)phosphine and **3c** from tri(2-pyridyl)-phosphine were isolated similarly but in much lower yields (23 and 10% respectively) together with smaller amounts of **1b** and **1c**. It seems that the lower yields of **3b** and **3c** compared with that of **3a** are the result of these having non-co-ordinated 2-pyridyl substituents. The cluster $[Os_3(CO)_{10}(MeCN)_2]$ is known to react rapidly with pyridine and substituted pyridines by orthometallation[7] and we believe that intractable products were probably obtained by further reaction with the bis-(acetonitrile) cluster to give linked clusters which were not isolated by TLC. The three clusters **3a**, **3b** and **3c** are isostructural (very similar IR spectra around 2000 cm^{-1}) and all show variable-temperature NMR spectra; see next section.

Fluxionality of the Clusters $[Os_3(CO)_{10}(\mu\text{-L})]$ *where* L *is a Pyridylphosphine*.—Fig. 1 shows the ^1H NMR spectra for cluster **3a** recorded at different temperatures. The 2-pyridyl resonances (marked *) remain sharp, or fairly sharp, while there are coalescences of phenyl resonances. This is consistent with a dynamic process leading to phenyl exchange and a time-averaged plane of symmetry. The spectra for $[Os_3(CO)_{10}\{\mu\text{-}P(2\text{-}C_5H_4N)_3\}]$ **3c** are clearer and more revealing because exchange between the two non-co-ordinated 2-pyridyl groups occurs without exchange of these with the co-ordinated 2-pyridyl substituent (see spectra shown in ref. 4). This means that the process cannot involve monodentate P-bonded intermediates.

Table 1 Infrared data for clusters **1**–**8**

Compound	$\tilde{\nu}$(CO)*/cm^{-1}
1a $[Os_3(CO)_{11}\{PPh_2(C_5H_4N)\}]$	2108m, 2053s, 2042m, 2020vs, 1999m, 1987m, 1971m
1b $[Os_3(CO)_{11}\{PPh(C_5H_4N)_2\}]$	2107w, 2053s, 2040m, 2019vs, 1997m, 1987m, 1974w
1c $[Os_3(CO)_{11}\{P(C_5H_4N)_3\}]$	2107w, 2052s, 2039m, 2019vs, 1996m, 1987m, 1977m, 1967w
2a $[Os_3(CO)_{10}\{PPh_2(C_5H_4N)\}_2]$	2086m, 2031s, 2041vs, 1963m
3a $[Os_3(CO)_{10}\{\mu\text{-PPh}_2(C_5H_4N)\}]$	2083s, 2032vs, 2017vs, 2004s, 1977s, 1969s, 1955m, 1938w
3b $[Os_3(CO)_{10}\{\mu\text{-PPh}(C_5H_4N)_2\}]$	2083s, 2033vs, 2018vs, 2003m, 1978s, 1969s, 1952w, 1938w
3c $[Os_3(CO)_{10}\{\mu\text{-P}(C_5H_4N)_3\}]$	2083vs, 2034vs, 2018vs, 2003m, 1977s, 1968vs, 1952w, 1939w
4 $[Os_3H(CO)_{10}\{\mu\text{-PPh}_2(C_5H_4N)\}][PF_6]$	2133m, 2119m, 2087s, 2081s, 2071vs, 2054vs, 2046s, 2020s, 2016s, 1978w (br)
5 $[Os_3(\sigma\text{-Ph})\{\mu_3\text{-PPh}(C_5H_4N)\}(CO)_9]$	2080s, 2037vs, 2030s, 2002m, 1991m, 1975m, 1964w, 1940w
6 $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-PPh}_2)(CO)_{10}]$	2094m, 2054vs, 2042m, 2012vs, 2004s, 2001(sh), 1993w, 1976s, 1967m
7 $[Os_2(\mu\text{-}C_5H_4N)(\mu\text{-PPh}_2)(CO)_6]$	2072s, 2038vs, 2003s, 2002s, 1970s, 1958s
8 $[Os_3(\mu\text{-PhCO})\{\mu_3\text{-PPh}(C_5H_4N)\}(CO)_9]$	2075w, 2049vs, 2025s, 1992m, 1990 (sh), 1972m, 1949w

* Measured in cyclohexane solution except for cluster **4** which was in dichloromethane.

Three mechanisms, A–C, might therefore be considered (Scheme 4). Process B requires transfer of the tertiary phosphine co-ordination between two Os atoms. Intramolecular tertiary phosphine migration between metal atoms in a Pt_3 cluster has been established.[8] Presumably this mechanism requires a $\mu\text{-PR}_3$ intermediate and such systems have been characterised although they are extremely rare.[9] We can rule out this process in the present case because the Os–P bond remains intact throughout. Thus Fig. 2 shows that the $^{31}P\text{-}\{^1H\}$ NMR singlets recorded at −40 and 50 °C show clear ^{187}Os satellites [$J(^{187}Os^{31}P)$ = 165 Hz] which are not temperature dependent. Similar observations were used to deduce that tertiary phosphine migration does not occur in the fluxionality of $[Os_3(CO)_{10}(PEt_3)_2]$.[10] Process B would have given a high-temperature spectrum with $J(^{187}Os^{31}P)$ around 83 Hz while migration of the P atom over all three Os atoms, for example by processes A and B occurring together at similar rates, would give $J(^{187}O^{31}P)$ around 55 Hz at the high-temperature limit. In either case there would have been a collapse of the satellites at intermediate temperatures. These spectra are therefore consistent with either mechanism A or C.

The $^{13}C\text{-}\{^1H\}$ NMR spectra are more understandable in terms of mechanism A. Coalescence of nine of the ten carbonyl signals occurs to give a broad singlet at δ 183.5, while one CO signal, probably that of the CO *trans* to P (δ 184.2, *J* = 4.5 Hz) remains distinct. The coalescences occur at lower temperatures than those in the ^1H NMR spectra and therefore fast carbonyl exchanges not leading to ^1H NMR coalescence are occurring. A merry-go-round process in the metal plane as with other closely related diaxially substituted clusters,[11] possibly together with other processes in addition to A, would allow exchange of all except the CO *trans* to the P atom. It is difficult to envisage

Table 2 NMR data for clusters **1–8** and for the free phosphines[a]

Compound	δ (^{1}H NMR)
1a[b]	C_5H_4N: 8.87 (H^6), 7.57 (H^4), 7.27 (H^5), 7.09 (H^3). PPh_2: 7.40–7.50
1b[c]	C_5H_4N: 8.86 (H^6), 7.65 (H^4), 7.33 (H^5), 7.25 (H^3). PPh: 7.41–7.50
1c[d]	C_5H_4N: 8.82 (H^6), 7.64 (H^4), 7.38 (H^3), 7.28 (H^5)
2[e]	C_5H_4N: 8.81 (H^6). Other broad signals 7.60–7.00
3a[f]	C_5H_4N: 9.42 (H^6), 7.55 (H^4), 7.30 (H^5), 7.25 (H^3). PPh_2: 7.50, 7.45, 7.09 at −60 °C C_5H_4N: 9.41 (H^6), 7.51 (H^4), 7.22 (H^5, H^3). PPh_2: 7.45, 7.33[g] at 80 °C
3b[h]	C_5H_4N (co-ordinated): 9.49 and 9.37 (H^6). C_5H_4N (non-co-ordinated): 8.72 and 8.67 (H^6). Other signals at δ 8.12, 8.03, 7.86, 7.81, 7.62, 7.51, 7.41, 7.35, 7.27, 7.19, 7.01
3c[i]	C_5H_4N (co-ordinated): 9.40 (H^6), 7.91 (H^3), 7.59 (H^4), 7.30 (H^5). C_5H_4N (non-co-ordinated): 8.70, 8.59 (H^6), 8.03, 7.88 (H^5), 7.74, 7.39, 7.29, 7.19 (H^3,H^4)
4[j]	Isomer **4a**: C_5H_4N, 9.60 (H^6); hydride, −13.95 (s) Isomer **4b**: C_5H_4N, 9.56 (H^6); hydride, −17.96 (d, J = 7.7) Isomer **4c**: C_5H_4N, 9.47 (H^6); hydride, −14.00 (d, J = 15.9) Other signals: 8.05–6.95
5[k]	C_5H_4N: 8.57 (H^6), 7.50 (H^4), 6.84 (H^5), 6.47 (H^3). OsPh: 7.81 (*ortho*), 7.28 (*meta*), 7.23 (*para*). PPh: 7.65 (*ortho*), 7.44 (*meta, para*)
6[l]	C_5H_4N: 8.69 (H^6), 7.86 (H^3), 7.21 (H^4), 6.78 (H^5). PPh_2: 7.88, 7.46, 7.41, 6.96, 6.55
7	C_5H_4N: 7.57 (H^6), 7.24[m] (H^3), 6.79 (H^4), 6.30 (H^5). PPh_2: 7.73 (*ortho*), 7.45 (*ortho*), 7.32 (*meta*), 7.28 (*para*), 7.02 (*para*), 6.96 (*meta*)
8	C_5H_4N: 8.67 (H^6), 7.37 (H^5), 6.94 (H^4), 6.12 (H^3). PhCO: 7.72 (*ortho*), 7.55 (*meta*), 7.47 (*para*). PPh: 7.66 (*ortho*), 7.42 (*para*), 7.33 (*meta*)
$PPh_2(2\text{-}C_5H_4N)$	C_5H_4N: 8.72 (H^6), 7.55 (H^4), 7.17 (H^5), 7.07 (H^3). PPh_2: 7.42–7.34
$PPh(2\text{-}C_5H_4N)_2$	C_5H_4N: 8.70 (H^6), 7.57 (H^4), 7.23 (H^3), 7.17 (H^5). PPh: 7.50, 7.37
$P(2\text{-}C_5H_4N)_3$	C_5H_4N: 8.69 (H^6), 7.59 (H^4), 7.37 (H^3), 7.19 (H^5)

[a] ^{1}H NMR in $CDCl_3$ at 20 °C at 400 MHz unless stated otherwise; ^{31}P-{^{1}H} NMR in $CDCl_3$ at 20 °C at 162 MHz unless stated otherwise; ^{13}C-{^{1}H} NMR in $CDCl_3$ at 20 °C at 100.6 MHz; J in Hz. [b] ^{31}P-{^{1}H} NMR: δ 4.2 (s). [c] ^{1}H NMR in CD_2Cl_2. ^{31}P-{^{1}H} NMR: δ 10.0 (s). [d] ^{31}P-{^{1}H} NMR: δ 12.1 (s). [e] ^{31}P-{^{1}H} NMR: major isomer (C_s) δ 3.8 and −0.6, minor isomer (C_{2v}) δ 2.5 (all broad singlets). [f] ^{1}H NMR in CD_2Cl_2 at −60 °C and in $CDCl_2CDCl_2$ at 80 °C. ^{31}P-{^{1}H} NMR in CD_2Cl_2: δ 5.6 (s). ^{13}C-{^{1}H} NMR (CD_2Cl_2, −85 °C): δ 191.7 (s), 187.6 (s), 187.2 (s), 186.3 (s), 185.1 (d), 183.8 (d), 183.6 (d), 178.9 (s), 178.7 (br, 2C). [g] Derived by coalescence of signals at δ 7.61 and 7.09 at 20 °C. [h] Two isomers; ^{1}H NMR in CD_2Cl_2. ^{31}P-{^{1}H} NMR in CD_2Cl_2: δ 11.0 (s) and 8.4 (s) (isomers in approximate ratio 1 : 1). [i] ^{1}H NMR in CD_2Cl_2 at −20 °C. ^{31}P-{^{1}H} NMR in CD_2Cl_2: δ 12.7 (s). [j] ^{31}P-{^{1}H} NMR: **4a**, δ 5.1 (s); **4b**, 1.1 (s); **4c** 3.2 (s). [k] ^{31}P-{^{1}H} NMR: δ 61.4 (s). ^{13}C-{^{1}H} NMR: CO signals, δ 209.2 (s, 2C), 186.4 (d, J = 58, 2C), 180.1 (s, 2C), 174.3 (d, J = 6 Hz, 1C), 171.7 (s, 2C). [l] ^{31}P-{^{1}H} NMR: δ −85.3 (s). [m] Probable δ, signal obscured.

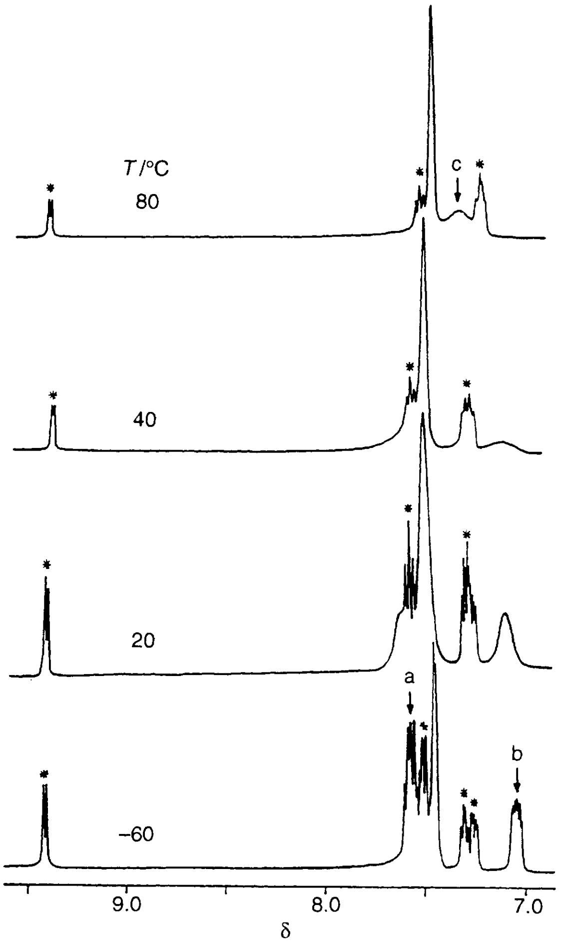


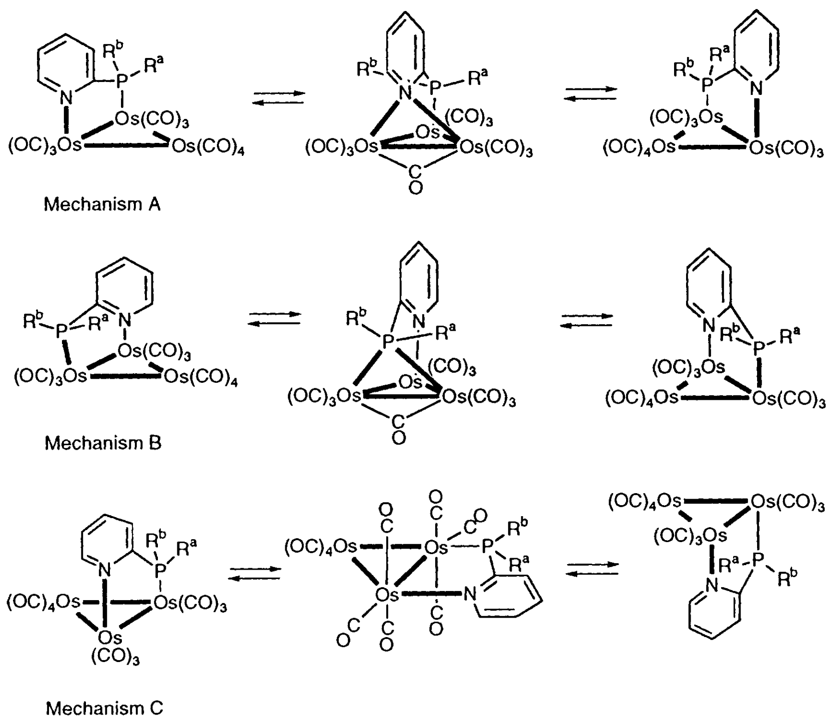
Fig. 1 Proton NMR spectrum of $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$ **3a** at different temperatures. *ortho*-Hydrogen signals for the non-equivalent phenyl groups, marked a and b, coalesce at about 60 °C to give signal c. Spectra at 20 and −60 °C are for CD_2Cl_2 solutions and the others are for CD_2ClCD_2Cl solutions. The asterisk indicates 2-pyridyl signals

process C occurring rapidly and without exchanging just one carbonyl ligand. In spite of this evidence we cannot claim to have eliminated mechanism C as a possibility.

Protonation of the Cluster $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$.—Protonation of tertiary phosphine triosmium clusters has been shown to occur preferentially at Os–Os edges that are the most substituted by the phosphorus ligands.[12] In general this will mean that 1,2-disubstituted clusters will have the hydride on the 1,2 edge. The cluster $[Os_3(CO)_{10}(\mu\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$) is exceptional in this respect since it is protonated on one of the other edges and the hydride ^{1}H NMR signal is a doublet.[13] We have argued that this is because this tight diequatorial bridge does not allow the necessary movement of the equatorial ligands away from the diphosphine-bridged Os–Os bond to allow the hydride to be located on this edge. Other diphosphines such as $Ph_2PCH_2CH_2PPh_2$ (dppe) are more flexible and the hydride can be incorporated on the most basic, most substituted edge.[14] Such geometric arguments do not apply to diaxially bridged trinuclear clusters since the hydrides are expected to be incorporated equatorially, so that the bridging ligand would not interfere geometrically. We anticipated therefore that protonation would occur most favourably between the substituted osmium atoms and that this would lock the ligand bridge along this edge and suppress the fluxionality described above for the neutral compound.

Treatment of $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$ **3a** in dichloromethane with a five-fold excess of CF_3CO_2H leads to complete protonation and the product $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}][PF_6]$ **4** was isolated after work-up with ammonium hexafluorophosphate. Cluster **4** gave a rather complex IR spectrum around 2000 cm^{-1} (Table 1) and its NMR spectra (Table 2) are consistent with a mixture of three isomers. Three ^{1}H NMR hydride signals at δ −13.95 (s), −17.96 (d, $^2J_{PH}$ = 7.7), and −14.00 (d, $^2J_{PH}$ = 15.9 Hz) and three corresponding H^6 doublets at δ 9.60, 9.56 and 9.47 are in an approximate intensity ratio 1:2:4. The ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectra could also be interpreted in terms of three isomers in this intensity ratio, although the latter spectrum was understandably very complex.

We believe that the isomers of complex **4** result from



Scheme 4

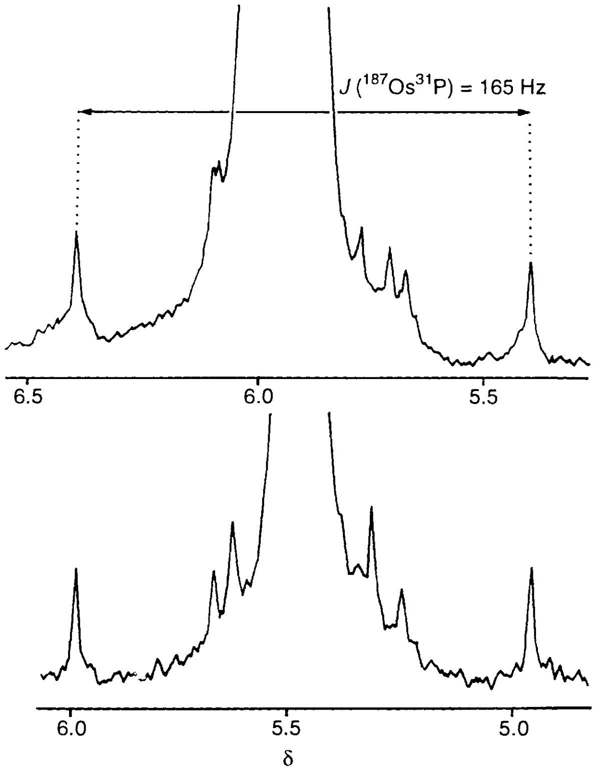


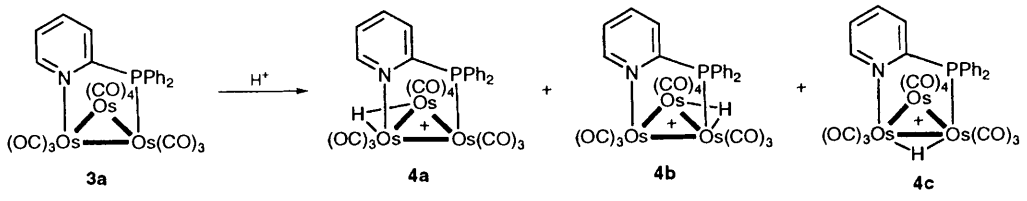
Fig. 2 Expanded $^{31}P-\{^1H\}$ NMR singlets for cluster **3a** ($CDCl_3$ solution) showing that the ^{187}Os satellites and the associated $J(^{187}Os^{31}P)$ values do not change significantly between −40 (above) and 50 °C

protonation at each of the three non-equivalent edges of the cluster **3a**. The minor isomer **4a** in Scheme 5 gives a hydride singlet (no ^{31}P coupling) while the others, **4b** and **4c**, give doublets and, although we cannot assign spectra to a particular isomer it is suggested that the major isomer has the hydride across the same edge as the ligand, diphenyl(2-pyridyl)phosphine. Certainly protonation has suppressed fluxionality since each isomer gives sharp signals at room temperature. Ligand mobility leading to coalescences as in the neutral compounds **3** would require the hydride to migrate as well as the other μ ligand. Clearly this involves a higher energy barrier and is undetected.

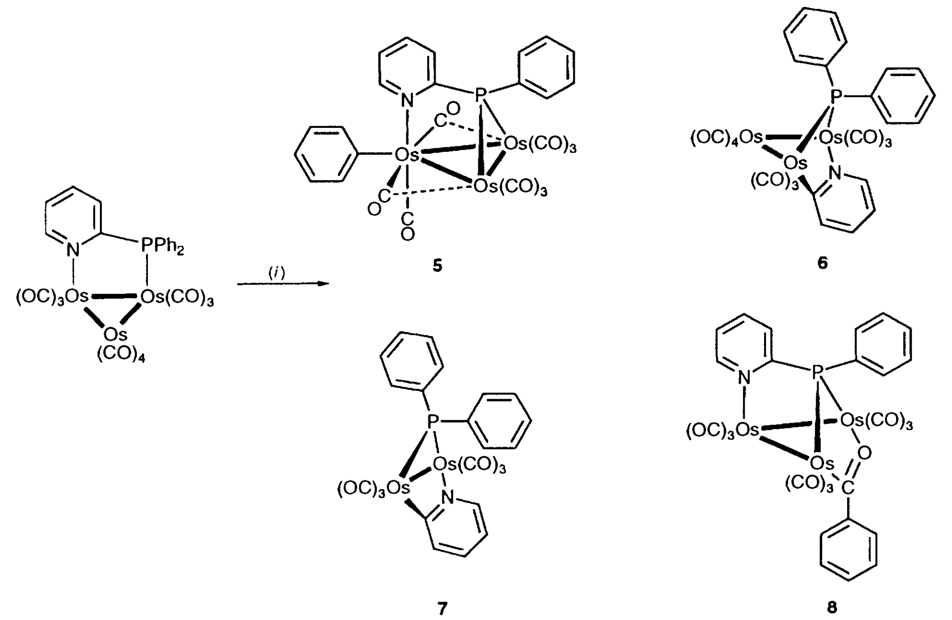
Thermolysis of the Cluster $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$ **3a**.—Refluxing heptane solutions of cluster **3a** gave complete conversion over 4 h into several products: a decarbonylation product **5** (60%), two isomers of the starting cluster, **6** (6%) and **8** (trace), and a dinuclear compound **7** (trace) (Scheme 6). The dinuclear compound **7** was separately shown to be formed from cluster **6** together with $[Os_3(CO)_{12}]$. The latter is presumably generated by clustering of the $Os(CO)_4$ fragments displaced during the conversion of **6** into **7**.

The cluster **5** was shown by ^1H NMR, in particular, but also by $^{31}P-\{^1H\}$ and $^{13}C-\{^1H\}$ NMR spectroscopy, and ultimately by single-crystal X-ray analysis, to be derived by loss of CO and by phenyl-group transfer from P to Os atoms. The ^1H NMR spectrum shows that there is a 2-pyridyl and two phenyl groups, one of which shows no coupling to phosphorus and therefore there must have been a P–C bond fission to that substituent. The reaction of $[Ru_3(CO)_{12}]$ with this ligand, catalysed by $[N(PPh_3)_2]CN$ (see Introduction and Scheme 1) gives the μ-PhCO complex, $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$, but the spectra for **5** do not correspond to the osmium analogue of this. Decarbonylation has occurred so that **5** is a Ph rather than PhCO complex. If the phenyl ligand were a σ,η^2 three-electron-donating bridge, the cluster could be structurally very similar to that of the ruthenium PhCO cluster with two Os–Os bonds. Alternatively the phenyl ligand might be an σ one-electron donating bridge and the cluster would have three Os–Os bonds. However, the IR spectrum around 2000 cm^{-1} was sufficiently different from those of compounds of that basic structure to suggest that neither of these was correct.

The crystal structure showed that the Ph group was not bridging and was bonded to the osmium atom not bonded to phosphorus (Fig. 3). Selected bond lengths and angles are in Table 3. Consistent with the phenyl being a one-electron donor,



Scheme 5



Scheme 6 (*i*) Heptane, 98 °C, 4 h

there are three metal–metal bonds [Os(1)–Os(2) 2.791(1), Os(1)–Os(3) 2.946(1) and Os(2)–Os(3) 2.957(1) Å], the shortest edge being that bridged by the phosphido group of the μ_3-phenyl(2-pyridyl)phosphido bridge. This μ_3 ligand is co-ordinated as expected and as in related triruthenium complexes: $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$,[1] $[Ru_3(\mu\text{-}I)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ and related compounds.[15,16] Aryl groups in clusters have previously been found to bridge through one carbon atom (μ,σ one-electron donor[17,18] or μ,σ three-electron donor[19]) or through two carbon atoms (μ,η^2 three-electron donor); a substituted phenyl of this kind[20] and one bridging transition and main-group metal atoms[21] have been identified (Fig. 4, **A**–**C** respectively). Sometimes the structural difference between these forms is small and precise identification without accurate X-ray structural data is questionable. Fluxionality involving phenyl motions is to be expected but does not seem to have been identified at this stage. Simple terminal co-ordination of phenyl in clusters as in **5** is not common, although a triruthenium example has been reported recently.[18] The phenyl ligand in **5** is equatorially co-ordinated and the only way to fit in three carbonyl ligands and the axial pyridine of the μ_3 bridge is to have two carbonyls equatorial and mutually *trans*. The incorporation of C(32)O(32) and C(33)O(33) in this way means that they must approach Os(1) and Os(2) and as a consequence they are semi-bridging. Fig. 3 shows that the Os–C–O groups are non-linear and 'open' bonds are shown for the long contacts [Os(1)–C(32) 2.95(1) and Os(2)–C(33) 2.74(1) Å] in the bridges. Another example of a cluster containing *trans* equatorial CO ligands is $[Os_3(\mu\text{-}H)(\mu_3\text{-}CF_3CCHCF_3)(CO)_{10}]$[22] and this situation is a consequence of trying to support ten terminal ligands in a trimetallic cluster containing a μ_3 ligand. One metal atom, Os(3), is seven-co-ordinate and approximately pentagonal bipyramidal in geometry.

The other fully characterised product is cluster **6**, derived by isomerisation with cleavage of a phosphorus–pyridyl bond, that is a bond in the ligand bridge of cluster **3a**. The yield of this compound is low (6%). The ^1H NMR spectrum shows that the 2-pyridyl group is not coupled to ^{31}P and therefore has cleaved from the PPh_2 group. The compound was finally shown to be $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_{10}]$, isomeric with the starting cluster **3a**, by single-crystal X-ray analysis (Fig. 5). Selected bond lengths and angles are in Table 4. The cluster has 50 electrons and therefore two Os–Os bonds [Os(1)–Os(3) 2.940(2) and Os(2)–Os(3) 2.925(2) Å]. The ligand-bridged Os atoms are not bonded [Os(1)···Os(2) 3.630(2) Å]. The cluster is therefore of the well known type $[Os_3(\mu\text{-}X)(\mu\text{-}Y)(CO)_{10}]$ where X and Y are three-electron donors. The phenyl groups are approximately perpendicular and this leads to an over 0.4 ppm chemical shift between the *ortho* H atoms of these rings. Apart from the different Os–Os distances, the cluster relates quite closely to the 48-electron clusters $[Os_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}]$.[23,24]

Cluster **6** is presumably formed by cleavage of the phosphorus-2-pyridyl bond of cluster **3a** but this is much less favourable than P–Ph cleavage. The dinuclear compound $[Os_2(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_6]$ **7** was shown separately to be derived from cluster **6**. The $Os(CO)_4$ group displaced in this transformation leads to $[Os_3(CO)_{12}]$.

The final product characterised, cluster **8**, was also obtained in trace amounts and shown by elemental analysis and mass spectrometry to be another isomer of **3a**. There is some doubt about the structure of this compound. The ^1H NMR spectrum reveals phosphorus-31 coupling in the 2-pyridyl substituent but not in one of the two phenyl groups. Thus the ligand has cleaved into Ph and $PPh(2\text{-}C_5H_4N)$ components. Since the compound contains ten carbonyl groups we believe that it must be [Os3-

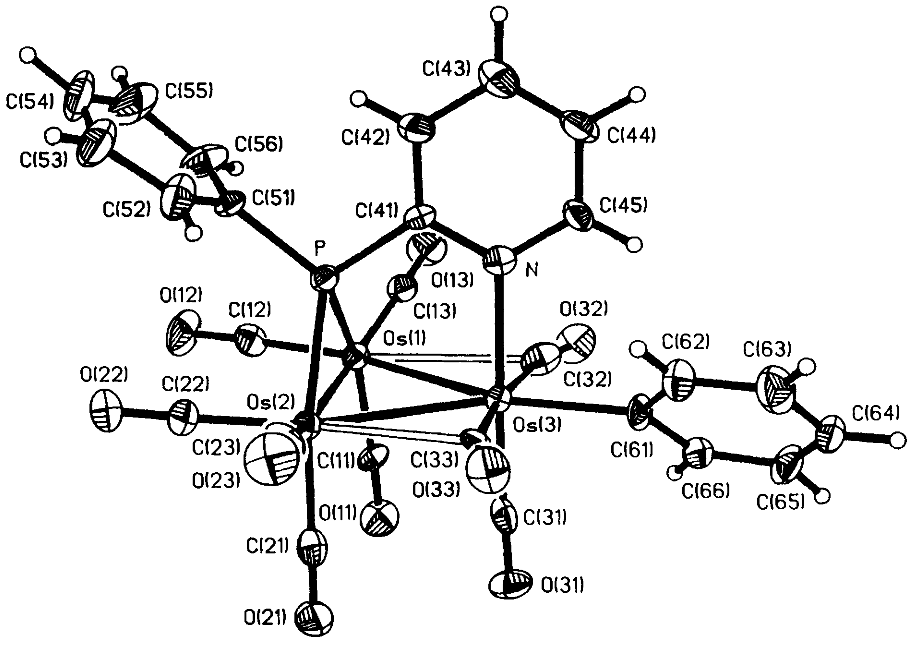


Fig. 3 Molecular structure of the cluster $[Os_3(\sigma\text{-}Ph)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **5**

Table 3 Selected bond lengths (Å) and angles (°) for $[Os_3(\sigma\text{-}Ph)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **5**

Os(1)–Os(2)	2.791(1)	Os(3)–C(32)	2.01(1)
Os(1)–Os(3)	2.946(1)	Os(3)–C(33)	1.97(1)
Os(2)–Os(3)	2.957(1)	Os(1)–C(32)	2.95(1)
Os(1)–P	2.344(3)	Os(2)–C(33)	2.74(1)
Os(2)–P	2.338(4)	P–C(51)	1.84(2)
Os(3)–N	2.22(1)	P–C(41)	1.81(1)
Os(3)–C(61)	2.17(2)		
Os(1)–Os(2)–Os(3)	61.6(1)	Os(1)–P–C(41)	113.8(4)
Os(1)–Os(3)–Os(2)	56.4(1)	Os(2)–P–C(41)	120.6(5)
Os(2)–Os(1)–Os(3)	62.0(1)	P–C(41)–N	113.1(7)
Os(2)–Os(3)–C(61)	146.9(3)	C(41)–N–Os(3)	120.2(7)
Os(1)–Os(3)–C(61)	156.7(3)	N–Os(3)–C(61)	90.5(5)
Os(1)–Os(2)–P	53.5(1)	C(61)–Os(3)–C(31)	87.6(6)
Os(2)–Os(1)–P	53.3(1)	C(61)–Os(3)–C(32)	86.7(6)
Os(3)–Os(2)–P	73.9(1)	C(61)–Os(3)–C(33)	83.2(5)
Os(3)–Os(1)–P	74.1(1)	Os(3)–C(32)–O(32)	168(2)
Os(1)–Os(3)–N	86.3(3)	Os(3)–C(33)–O(33)	162(1)
Os(2)–Os(3)–N	93.9(3)	C(32)–Os(3)–C(33)	169.8(6)
Os(1)–P–Os(2)	73.2(1)		

Table 4 Selected bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_{10}]$ **6**

Os(1)···Os(2)	3.630(2)	Os(1)–N(1)	2.15(1)
Os(1)–Os(3)	2.940(2)	Os(2)–C(41)	2.18(1)
Os(2)–Os(3)	2.925(2)	P–C(51)	1.88(2)
Os(1)–P	2.417(5)	P–C(61)	1.84(2)
Os(2)–P	2.426(5)		
Os(1)–Os(2)–Os(3)	52.0(1)	P–Os(1)–N(1)	83.3(4)
Os(1)–Os(3)–Os(2)	76.5(1)	P–Os(2)–C(41)	82.3(4)
Os(2)–Os(1)–Os(3)	51.6(1)	Os(1)–N(1)–C(41)	120(1)
Os(3)–Os(1)–P	81.0(1)	Os(2)–C(41)–N(1)	122(1)
Os(3)–Os(2)–P	81.2(1)	Os(1)–P–C(51)	117.0(5)
Os(1)–P–Os(2)	97.1(2)	Os(1)–P–C(61)	113.8(6)
Os(3)–Os(1)–N(1)	89.1(4)	Os(2)–P–C(51)	112.0(5)
Os(3)–Os(2)–C(41)	87.7(4)	Os(2)–P–C(61)	120.9(6)

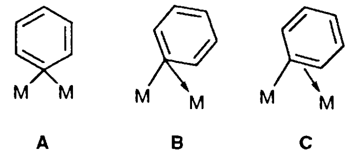


Fig. 4 Modes of phenyl bridging

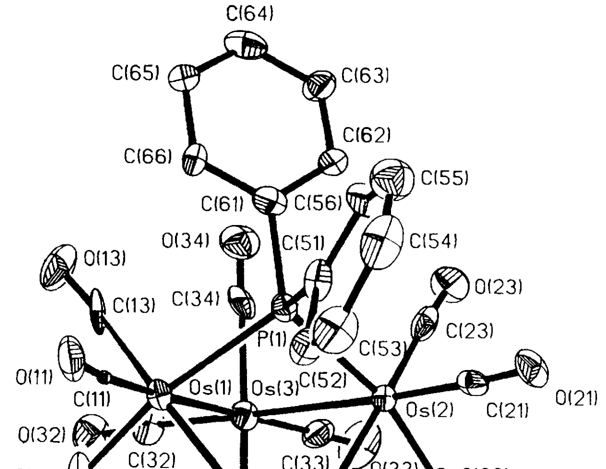


Fig. 5 Molecular structure of the cluster $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_{10}]$ **6**

$(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ and the IR spectrum around 2000 cm^{-1} is quite similar to that of the corresponding ruthenium complex.[1] However, there are significant differences in some of the NMR shifts which may mean that the complexes of Os and Ru are not isostructural. Until we obtain more than trace quantities and can grow good single crystals this point will remain unsettled.

Certainly there seems to be a distinct difference between the reactions of $[Os_3(CO)_{12}]$ and of $[Ru_3(CO)_{12}]$ with diphenyl(2-pyridyl)phosphine. The major, indeed only, ruthenium product is $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh_2(2\text{-}C_5H_4N)\}(CO)_9]$ whereas this is a very minor product from osmium, the major product being $[Os_3(\sigma\text{-}Ph)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **5**. Probably both are formed *via* the product of phenyl transfer, $[M_3Ph\{\mu_3\text{-}PPh_2(2\text{-}C_5H_4N)\}(CO)_{10}]$, which decarbonylates when M = Os but undergoes phenyl transfer to CO when M = Ru. We would expect carbonyl insertion to be more favourable for ruthenium than osmium.

Experimental

The 2-pyridyl compounds, $PPh_2(2\text{-}C_5H_4N)$[25] and $P(2\text{-}C_5H_4N)_3$,[26] were synthesised essentially as reported previously, while $PPh(2\text{-}C_5H_4N)_2$ was prepared in a similar way to $P(2\text{-}C_5H_4N)_3$, using $PPhCl_2$ instead of PCl_3 as starting material.

Reactions of $[Os_3(CO)_{10}(MeCN)_2]$.—*With diphenyl*(2-*pyridyl*)*phosphine*. A solution of the bis(acetonitrile) cluster (0.309 g, 0.331 mmol) and $PPh_2(2\text{-}C_5H_4N)$ (0.0933 g, 0.354 mmol, 1.07 mol per mol Os_3) in degassed dichloromethane (50 cm^3) was stirred under nitrogen for 2 d. Removal of the solvent under reduced pressure and TLC [SiO_2; eluent light petroleum (b.p. 30–40 °C)–dichloromethane (5:3 v/v)] gave four bands. The major orange band gave $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$ **3a** as an orange solid (0.166 g, 45%) (Found: C, 29.05; H, 1.45; N, 1.2. $C_{27}H_{14}NO_{10}Os_3P$ requires C, 29.1; H, 1.25; N, 1.25%). A yellow band gave the cluster $[Os_3(CO)_{11}\{PPh_2(2\text{-}C_5H_4N)\}]$ **1a** as a yellow solid (0.078 g, 21%) (Found: C, 29.65; H, 1.35; N, 1.2. $C_{28}H_{14}NO_{11}Os_3P$ requires C, 29.45; H, 1.25; N, 1.25%) and an orange-yellow band gave an analytically impure sample of $[Os_3(CO)_{10}\{PPh_2(2\text{-}C_5H_4N)\}_2]$ **2a** as an orange solid (0.070 g, *ca*. 20%) which was characterised spectroscopically. A fourth very minor band was not characterised.

With phenyldi(2-*pyridyl*)*phosphine*. A solution of the cluster $[Os_3(CO)_{10}(MeCN)_2]$ (0.338 g, 0.362 mmol) and the tertiary phosphine (0.100 g, 0.378 mmol, 1.05 mol per mol Os_3) in degassed dichloromethane (30 cm^3) was stirred under nitrogen for 3 d. After removal of the solvent under reduced pressure, the residue was separated by TLC [SiO_2; eluent light petroleum (b.p. 30–40 °C)–dichloromethane (5:3 v/v)] into three bands which yielded the compound $[Os_3(CO)_{10}\{\mu\text{-}PPh(2\text{-}C_5H_4N)_2\}]$ **3b** as an orange solid (0.091 g, 23%) (Found: C, 28.0; H, 1.25; N, 2.3. $C_{26}H_{13}N_2O_{10}Os_3P$ requires C, 28.0; H, 1.2; N, 2.5%) and $[Os_3(CO)_{11}\{PPh(2\text{-}C_5H_4N)_2\}]$ **1b** as a yellow solid (0.025 g, 6%) (Found: C, 28.2; H, 1.3; N, 2.2. $C_{27}H_{13}N_2O_{11}Os_3P$ requires C, 28.35; H, 1.15; N, 2.45%). A third minor band was not characterised but this did appear to be cluster **2b**.

With tri(2-*pyridyl*)*phosphine*. A similar treatment and work-up to the above gave the compound $[Os_3(CO)_{10}\{\mu\text{-}P(2\text{-}C_5H_4N)_3\}]$ **3c** as an orange solid (10%) (Found: C, 26.15; H, 1.0; N, 3.55. $C_{25}H_{12}N_3O_{10}Os_3P$ requires C, 26.9; H, 1.1; N, 3.75%) and the cluster $[Os_3(CO)_{11}\{P(2\text{-}C_5H_4N)_3\}]$ **1c** as a yellow solid (5%) (Found: C, 27.65; H, 1.25; N, 3.45. $C_{26}H_{12}N_3O_{11}Os_3P$ requires C, 27.3; H, 1.05; N, 3.65%).

Protonation of the Cluster $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$.—Trifluoroacetic acid (0.030 cm^3, 0.389 mmol, 5.1 mol per mol Os_3) was added to a dichloromethane (10 cm^3) solution of the triosmium cluster and the solution was stirred at room temperature for 1 h. After removal of the solvent under reduced pressure, the residue was dissolved in methanol (1 cm^3) and a methanolic solution (0.8 cm^3) of NH_4PF_6 (0.0342 g, 0.210 mmol, 2.7 mol per mol Os_3) was added. The addition of water gave a yellow precipitate which was filtered off and dried. Recrystallisation from dichloromethane (0.5 cm^3) by addition of diethyl ether (10 cm^3) gave $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}][PF_6]$ **4** as a yellow solid (0.0758 g, 78%) (Found: C, 25.15; H, 1.6; N, 1.0. $C_{27}H_{15}F_6NO_{10}Os_3P_2$ requires C, 25.75; H, 1.2; N, 1.1%). The compound was characterised spectroscopically as a mixture of three isomers.

Thermolysis of the Cluster $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$ **3a**.—A suspension of the triosmium cluster (0.170 g, 0.153 mmol) in heptane (40 cm^3) was refluxed under nitrogen for *ca*. 4 h. The orange solution was evaporated to dryness under reduced pressure and TLC [SiO_2; eluent light petroleum (b.p. 30–40 °C)–dichloromethane (1:7 v/v)] gave seven bands. The main band gave $[Os_3(\sigma\text{-}Ph)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **5** as a yellow solid (0.100 g, 60%) (Found: C, 28.8; H, 1.4; N, 1.3. $C_{26}H_{14}NO_9Os_3P$ requires C, 28.75; H, 1.3; N, 1.3%). Two pale yellow bands yielded a very pale yellow solid (< 0.002 g) which was identified as $[Os_2(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_6]$ **7** spectroscopically (mass, IR and NMR spectra) but not analytically and the cluster $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_{10}]$ **6** as pale yellow crystals (0.011 g, 6%) after two recrystallisations from dichloromethane–hexane (Found: C, 28.7; H, 1.0; N, 1.0. $C_{27}H_{14}NO_{10}Os_3P$ requires C, 29.1; H, 1.25; N, 1.25%). An orange band gave a trace amount of $[Os_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **8** as a yellow solid (Found: C, 29.0; H, 1.55; N, 1.1. $C_{27}H_{14}NO_{10}Os_3P$ requires C, 29.1; H, 1.25; N, 1.25%). The fifth band contained unreacted starting material (0.010 g) and the remaining two bands gave very small amounts of uncharacterised materials.

Thermolysis of the Cluster $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_{10}]$ **6**.—A suspension of cluster **6** (0.008 g, 0.0072 mmol) in nonane (3 cm^3) was refluxed under nitrogen for 1.5 h. Removal of the solvent under reduced pressure and TLC [SiO_2; eluent light petroleum (b.p. 30–40 °C)–dichloromethane (1:7 v/v)] gave two main bands yielding $[Os_3(CO)_{12}]$ as a yellow solid (identified by IR spectroscopy) and $[Os_2(\mu\text{-}C_5H_4N)(\mu\text{-}PPh_2)(CO)_6]$ **7** as a pale yellow solid. The yields of these compounds were not determined accurately but they appear to be the only metal carbonyl products.

Structure Determinations.—*Crystal data for cluster* **5**. $C_{26}H_{14}NO_9Os_3P$, yellow crystal, 0.40 × 0.27 × 0.11 mm^3, M = 1085.98, triclinic, space group $P\bar{1}$, a = 10.593(3), b = 13.350(3), c = 13.373(4) Å, α = 110.53(2), β = 98.00(2), γ = 108.93(2)°, U = 1605.6(7) $Å^3$, Z = 2, $F(000)$ = 984, D_c = 2.25 g cm^{-3}.

Data collection. The unit cell was determined from 34 orientation reflections ($10 \leqslant 2\theta \leqslant 28°$). 5931 Data, 5605 unique, collected at 20 °C on a Nicolet R3v/m diffractometer (Mo-Kα radiation; λ = 0.710 73 Å), ω–2θ scan mode, *hkl* range 0, −16, −16 to 13, 16, 16, ($5 \leqslant 2\theta \leqslant 50°$), corrections for Lorentz and polarisation effects and for small variations in intensity based on three standard reflections, empirical absorption correction (ψ-scan method), μ(Mo-Kα) = 119.6 cm^{-1}, maximum, minimum transmission factors = 0.96, 0.35.

Structure solution and refinement. Direct methods solution, 361 parameters in model, 4718 data with $I_o > 2\sigma(I_o)$, R = 0.0424 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ = 0.0471, $w = 1/[\sigma^2(F_o) + 0.002\,04F_o^2]$. All non-H atoms were refined anisotropically and H atoms were included in the model in idealised positions (C–H 0.96 Å, U_{iso} = 0.08 $Å^3$). The largest shift-to-error ratio in the final refinement was 0.001 and the largest peak in the final Fourier difference map was 1.92 e $Å^{-3}$. Table 5 lists the fractional atomic coordinates for cluster **5**.

Crystal data for cluster **6**. $C_{27}H_{14}NO_{10}Os_3P$, pale yellow crystal, 0.30 × 0.25 × 0.11 mm^3, M = 1113.99, monoclinic, space group $P2_1/c$, a = 12.974(7), b = 9.721(3), c = 23.097(8) Å, β = 90.89(4)°, U = 2913(2) $Å^3$, Z = 4, $F(000)$ = 2024, D_c = 2.54 g cm^{-3}.

Data collection. Unit cell determined from 20 orientation reflections ($10 \leqslant 2\theta \leqslant 21°$). 6361 Data, 5022 unique, collected as for cluster **5**. ω Scan mode, *hkl* range 0, 0, −28 to 16, 12, 28 ($5 \leqslant 2\theta \leqslant 50°$). Corrections made as for **5**; μ(Mo-Kα) = 131.9 cm^{-1}, maximum, minimum transmission factors = 0.90, 0.29.

Structure solution and refinement. Direct methods solution,

Table 5 Fractional atomic coordinates (× 10^4) for $[Os_3(\sigma\text{-Ph})\{\mu_3\text{-PPh}(2\text{-}C_5H_4N)\}(CO)_9]$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	2 849(1)	7 137(1)	427(1)	C(65)	8 248(17)	6 145(13)	3 061(13)
Os(2)	2 493(1)	7 843(1)	2 557(1)	C(66)	7 111(14)	6 249(12)	2 600(12)
Os(3)	4 956(1)	7 321(1)	2 247(1)	C(11)	1 949(13)	5 464(9)	−37(8)
P	3 681(3)	9 059(2)	1 791(2)	O(11)	1 376(11)	4 501(8)	−263(8)
N	6 197(10)	9 076(8)	2 364(7)	C(12)	1 309(13)	7 221(11)	−338(11)
C(41)	5 556(12)	9 793(9)	2 269(8)	O(12)	289(12)	7 278(10)	−784(10)
C(42)	6 284(14)	10 912(11)	2 389(11)	C(13)	3 703(14)	7 144(10)	−722(10)
C(43)	7 740(15)	11 327(14)	2 547(13)	O(13)	4 181(12)	7 150(10)	−1 467(8)
C(44)	8 358(14)	10 565(12)	2 603(11)	C(21)	1 437(14)	6 279(12)	2 392(10)
C(45)	7 594(12)	9 464(11)	2 509(10)	O(21)	795(11)	5 350(8)	2 281(9)
C(51)	3 114(13)	10 175(9)	1 640(11)	C(22)	887(15)	8 082(12)	2 177(12)
C(52)	2 913(16)	10 917(12)	2 568(14)	O(22)	−121(11)	8 228(10)	1 890(10)
C(53)	2 380(19)	11 731(14)	2 493(18)	C(23)	2 747(14)	8 729(11)	4 076(10)
C(54)	2 147(19)	11 815(16)	1 504(18)	O(23)	2 903(13)	9 230(9)	5 024(8)
C(55)	2 359(21)	11 098(16)	578(16)	C(31)	3 969(13)	5 790(11)	2 097(10)
C(56)	2 773(18)	10 216(12)	634(12)	O(31)	3 429(11)	4 859(7)	1 997(8)
C(61)	6 831(13)	7 231(12)	3 018(10)	C(32)	5 390(16)	6 703(12)	797(10)
C(62)	7 818(15)	8 163(13)	3 998(12)	O(32)	5 790(12)	6 320(9)	96(7)
C(63)	9 017(17)	8 123(16)	4 535(13)	C(33)	4 859(12)	7 951(10)	3 794(10)
C(64)	9 214(16)	7 060(14)	4 006(13)	O(33)	5 118(11)	8 273(9)	4 756(7)

Table 6 Fractional atomic coordinates (× 10^4) for $[Os_3(\mu\text{-}C_5H_4N)(\mu\text{-PPh}_2)(CO)_{10}]$ **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	8 045(1)	1 596(1)	3 720(1)	C(65)	5 850(16)	1 782(20)	6 832(8)
Os(2)	7 283(1)	5 155(1)	8 936(1)	C(66)	6 127(13)	1 789(16)	7 451(7)
Os(3)	9 172(1)	4 115(1)	8 417(1)	C(11)	7 249(10)	52(12)	8 918(5)
P	6 595(4)	3 074(4)	8 495(2)	O(11)	6 718(13)	−848(14)	9 001(5)
N(1)	7 853(13)	2 397(15)	9 580(6)	C(12)	9 343(19)	809(21)	8 951(12)
C(41A)	7 853(13)	2 397(15)	9 580(6)	O(12)	10 142(14)	388(18)	9 122(8)
C(41)	7 584(13)	3 762(15)	9 661(6)	C(13)	8 292(16)	1 055(18)	7 933(9)
N(1A)	7 584(13)	3 762(15)	9 661(6)	O(13)	8 457(14)	662(17)	7 485(7)
C(42)	7 474(16)	4 233(21)	10 213(6)	C(21)	5 987(16)	5 584(16)	9 273(7)
C(43)	7 709(19)	3 417(25)	10 694(7)	O(21)	5 186(11)	5 884(15)	9 447(5)
C(44)	7 985(18)	2 055(19)	10 622(8)	C(22)	8 075(17)	6 564(19)	9 436(8)
C(45)	8 065(17)	1 596(20)	10 062(7)	O(22)	8 516(12)	7 446(15)	9 546(6)
C(51)	5 316(15)	2 577(16)	8 805(7)	C(23)	7 190(16)	6 398(21)	8 277(9)
C(52)	5 270(19)	1 951(18)	9 373(8)	O(23)	7 122(13)	7 166(14)	7 910(6)
C(53)	4 335(18)	1 591(22)	9 626(9)	C(31)	9 670(16)	3 911(19)	9 198(8)
C(54)	3 440(18)	1 923(22)	9 310(11)	O(31)	9 989(14)	3 811(18)	9 677(6)
C(55)	3 444(20)	2 498(23)	8 783(9)	C(32)	10 288(16)	3 097(21)	8 131(10)
C(56)	4 358(13)	2 913(20)	8 529(8)	O(32)	11 010(14)	2 495(19)	7 976(7)
C(61)	6 196(15)	3 043(20)	7 727(7)	C(33)	9 669(18)	6 004(23)	8 356(8)
C(62)	5 918(16)	4 269(19)	7 422(7)	O(33)	9 931(16)	7 090(17)	8 340(8)
C(63)	5 630(18)	4 198(19)	6 845(7)	C(34)	8 542(15)	4 138(20)	7 630(10)
C(64)	5 600(18)	2 941(23)	6 565(8)	O(34)	8 236(12)	4 187(17)	7 179(7)

359 parameters in model, 3745 data with $I_o > 1.5\sigma(I_o)$, $R = 0.0601$ and $R' = 0.0547$ where $w = 1/[\sigma^2(F_o) + 0.000\,437F_o^2]$. All non-H atoms were refined anisotropically, except for C(11), C(55), and the atoms of the 2-C_5H_4N ring bonded to osmium atoms. The 2-pyridyl ligand was considered to be disordered with 50% population in the two possible orientations. Atoms N(1) and C(41A) were refined with identical coordinates and likewise the pair C(41) and N(1A). Isotropic thermal parameters for N(1) and N(1A) were refined but fixed as equal and likewise those for atoms C(41) and C(41A). The H atoms were included in the model in idealised positions as for cluster **5**. The largest shift-to-error ratio in the final refinement was 0.017 and the largest peak in the final Fourier difference map was 3.00 e Å^{-3}. Table 6 lists the fractional atomic coordinates for cluster **6**.

All calculations were carried out using a MicroVax II computer running SHELXTL-PLUS.[27]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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