Osmium(II) Complexes with the Hybrid Ligand 1-(Diphenylphosphino)-2-(2-pyridyl)ethane

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Osmium(II) forms with 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye) either mononuclear [OsX_2(ppye-*P,N*)$_2$] **1** or binuclear [(ppye-*P,N*)$_2$Os(μ-X)$_2$Os(ppye-*P,N*)$_2$][PF_6]$_2$ **2** (X = Cl or Br) derivatives, which have been characterized by UV/VIS, IR, and NMR spectroscopy. The six-co-ordinate **1** reacted with CO yielding either neutral [OsX_2(CO)(ppye-*P*)(ppye-*P,N*)] or cationic [OsX(CO)(ppye-*P,N*)$_2$]$^+$ depending on the nature of the solvent. The latter can also be prepared by reaction between **2** and CO in dichloromethane. All the carbonyl derivatives initially formed have the CO group *trans* to a P atom and can be thermally converted into the isomer having mutually *cis* P and CO groups. The binuclear complexes **2** dissociate in solution to give five-co-ordinate [OsX(ppye-*P,N*)$_2$]$^+$ or the solvento species [OsX(solv)(ppye-*P,N*)$_2$]$^+$ depending on the solvent. With MeCN also the disolvento species [Os(MeCN)$_2$(ppye-*P,N*)$_2$]$^{2+}$ is formed, which has been isolated in the solid state as the hexafluorophosphate salt. It undergoes substitution reactions with neutral ligands affording the monoacetonitrile complexes [Os(MeCN)L(ppye-*P,N*)$_2$]$^{2+}$ [L = P(OEt)$_3$, PMe_2Ph or pyridine]. Complexes **2** also react with the same ligands giving cationic derivatives of the type [OsX(L)(ppye-*P,N*)$_2$]$^+$.

This paper reports part of a study on the co-ordinating behaviour of 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye)[1] toward d^6 metal ions. Unsymmetrical compounds of this type, containing both P and hard donor atoms such as N[2] or O,[3] are of current interest with respect to the development of novel catalysts. The hard end of these potentially bidentate ligands can easily be displaced from the metal complex so that free co-ordination sites may be provided during the catalytic cycle, thus making possible the substrate binding. The versatile co-ordination behaviour of ppye has been recognized in the previously reported complexes of nickel,[1,4] palladium,[5] copper,[1] rhodium,[6] and iridium,[6,7] in which it acts either as a chelating bidentate or as a P-bound, unidentate ligand.

More recently we reported that ppye forms the six-co-ordinate ruthenium(II) complexes [RuX_2(ppye-*P,N*)$_2$] (X = Cl, Br or I).[8] As expected on the basis of the hemilabile character of ppye, these derivatives were found to undergo carbonylation in low-polarity solvents to give the neutral adducts [RuX_2(CO)(ppye-*P*)(ppye-*P,N*)] with concomitant dissociation of the pyridyl arm of one chelate ligand. In contrast, in polar solvents the cationic derivatives [RuX(CO)(ppye-*P,N*)$_2$]$^+$ are obtained. As substitution reactions in d^6 six-co-ordinate metal complexes occur *via* a dissociative mechanism,[9] these results indicate that [RuX_2(ppye-*P,N*)$_2$] can form five-co-ordinate unsaturated intermediates by rupture of either Ru–X or Ru–N bonds. This is noteworthy in view of the relevance of five-co-ordinate unsaturated complexes of Ru^{II} and in general of d^6 metal ions in homogeneous catalysis.[10] Since a similar situation can be predicted for osmium(II), we decided to study the co-ordinating behaviour of ppye toward this transition metal. It should be noted that the chemistry of osmium(II) diphosphine complexes is quite extensive, but complexes with unsymmetrical bidentate ligands containing both P and hard donor atoms are still relatively unexplored.[11,12]

Results and Discussion

The osmium(II) complexes *trans,cis,cis*-[OsX_2(ppye-*P,N*)$_2$] (X = Cl **1a** or Br **1b**)† and [(ppye-*P,N*)$_2$Os(μ-X)$_2$Os(ppye-*P,N*)$_2$][PF_6]$_2$ (X = Cl **2a** or Br **2b**) can be prepared by ligand exchange between [$OsX_2(PPh_3)_3$] and ppye. The yellow-orange (**1a**) or orange-red (**1b**) diamagnetic compounds are obtained in good yield by refluxing the appropriate precursor and ppye in 1:2 molar ratio in toluene. When the reaction is carried out in boiling ethanol in the presence of an excess of NH_4PF_6 the yellow (**2a**) or yellow-green (**2b**) dihalide-bridged dimers are quantitatively formed. The structure of **1a**, **1b** and **2a**, **2b** have been established by a combination of $^{31}P-\{^1H\}$ NMR, IR and UV/VIS spectroscopy (Tables 1 and 2).

The presence of chelating ppye ligands is supported by the IR spectra in Nujol mull and in dichloromethane solution, which exhibit pyridine-ring stretching vibrations in the range 1604–1607 cm^{-1}, shifted to higher frequencies with respect to the free compound (1589 cm^{-1}).[1,4–8] The visible spectra of **1a**, **1b** in Nujol mull and in dichloromethane solution are similar, thus indicating that the complexes probably have the same structure in the solid state and in solution. The conductivity of the complexes is negligible, also in aged solutions. Moreover the far-infrared spectrum of **1a** exhibits a single Os–Cl stretching at 299 cm^{-1}, which can be assigned to terminal chlorine atoms in mutually *trans* positions. We assume that complexes **1a**, **1b** possess a structure like that of the *trans,cis,cis*-[RuX_2(ppye-*P,N*)$_2$] analogues.[8] The same geometry has been assigned to related [$OsBr_2L_2$] species (L = ether phosphine ligand).[12]

The room-temperature $^{31}P-\{^1H\}$ NMR spectra of complexes **1a**, **1b** in freshly prepared dichloromethane solutions exhibit rather broad singlets, the width and chemical shift of which are strongly dependent on sample concentration. By lowering the sample concentration from 0.2 to 10^{-3} mol dm^{-3} (CD_2Cl_2, 293 K), the half-width of the $^{31}P-\{^1H\}$ signal of **1a** increases from 51 to *ca.* 500 Hz and the chemical shift changes from δ −29.0 to −34.0. A progressive narrowing of the signal is observed on lowering the temperature and at 183 K, the lowest available temperature, $w_{\frac{1}{2}}$ is 6 Hz in the case of a 0.2 mol dm^{-3} solution. The signals of **1b** are broader when compared to **1a**

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† Throughout this paper the *cis* and *trans* notation refers to the pairs of X, P (ppye) or N (ppye) atoms.

Table 1 Selected IR and $^{31}P-\{^1H\}$ NMR data

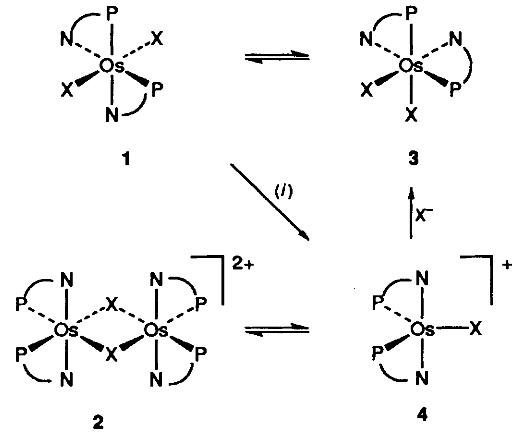
	IR[a]/cm^{-1}		$^{31}P-\{^1H\}$ NMR (ppye)[b]	
Complex	ν_{max}	ν(py CN)	δ	^2J(P–P′)/Hz
1a	299[c]	1604	−32.4(s)[d]	
1b		1604	−34.4 (s)[d]	
2a	283[c]	1607	−18.9 (s)	
2b		1606	−20.9 (s)	
3a[e]			−19.7 (d), −27.5 (d)	16.7
3b[e]			−21.5 (d), −33.8 (d)	16.1
4a[e]			2.5 (s)	
4b[e]			1.4 (s)	
5a	302,[c] 1944[f]	1602, 1587	−14.2 (d), −19.7 (d)	21.6
5b	1947[f]	1601, 1587	−17.6 (d), −21.9 (d)	21.9
6a	306,[c] 1919[f]	1602, 1587	−4.3, −5.1[g]	302.2
6b	1924[f]	1601, 1586	−5.8, −9.1[g]	298.6
7a	1971[f]	1608	−14.5 (d), −18.7 (d)	15.9
7b	1968[f]	1607	−17.4, −17.6[g]	14.5
8a	1918[f]	1607	2.1 (s)	
8b	1918[f]	1607	−1.2 (s)	
9a[e]			−22.8, −25.6[h]	8.8
10a[e]			−3.7 (d)[i]	
11a		1609	−25.0 (dd), −27.2 (dd)[j]	9.6
12a[e]			−15.4 (d), −20.5 (d)	14.8
13a[e]			−9.1 (d), −16.1 (d)	17.2
13b[e]			−9.1 (d), −17.8 (d)	16.7
14	2285, 2320[k]	1609	−12.1 (s)	
15[e]			−20.1 (dd), −26.1 (dd)[l]	16.1
16[e]			−6.9 (d)[m]	
17[e]			−25.9, −26.1[n]	13.9
18[e]			≈ −14 (br), ≈ −20 (br)	

[a] Nujol mull. [b] In CH_2Cl_2 solution at 293 K, unless otherwise stated. Multiplicity given in parentheses: s = singlet, d = doublet, dd = doublet of doublets, t = triplet. [c] ν(Os–Cl). [d] At 193 K. [e] Complex not isolated in the solid state. [f] ν(CO). [g] AB spin system. [h] AB part of an ABX spin system. Additional parameters from computer simulation: δ(P*) 68.9, $^2J(P_A-P^*) = 28.5$, $^2J(P_B-P^*) = 431.1$. Hz [P* = $P(OEt)_3$]. Positive *trans*-^2J(P–P) and negative *cis*-^2J(P–P) have been assumed for all simulations. [i] δ(P*) 57.7(t), $^2J(P-P^*) = 27.6$ Hz [P* = $P(OEt)_3$]. [j] AM part of an AMX spin system. Additional parameters: δ(P*) −39.5, $^2J(P_A-P^*) = 16.9$, $^2J(P_B-P^*) = 280.2$ Hz (P* = PMe_2Ph). [k] ν(CN). [l] AM part of an AMX spin system. Additional parameters: δ(P*) 65.7, $^2J(P_A-P^*) = 35.8$, $^2J(P_B-P^*) = 394.7$ Hz [P* = $P(OEt)_3$]. [m] δ(P*) 62.5 (t), $^2J(P-P^*) = 29.0$ Hz [P* = $P(OEt)_3$]. [n] AB part of an ABC spin system; additional parameters from computer simulation: δ(P*) 38.7, $^2J(P_A-P^*) = 19.7$, $^2J(P_B-P^*) = 248.0$ Hz (P* = PMe_2Ph).

Table 2 The UV/VIS data for complexes **1a**, **1b** and **2a**, **2b**

Complex	Medium	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1} for solution)
1a	CH_2Cl_2	500 (sh), 440 (6700)
	Toluene	495 (sh), 440 (4300)
	Nujol mull	500 (sh), 435
1b[a]	CH_2Cl_2	520 (sh), 445 (3500)
	Nujol mull	520, 450
2a[b]	CH_2Cl_2	570 (200), 370 (11 000)
	Nujol mull	490 (sh), 410
2b[b]	CH_2Cl_2	565 (200), 370 (sh)
	Nujol mull	500 (sh), 410

[a] Insoluble in toluene. [b] In 10^{-3} mol dm^{-3} solution the predominant species is **4** (see text); ε calculated assuming quantitative dissociation.



Scheme 1 $\overset{\frown}{P\ N}$ = ppye, X = Cl or Br; in dichloromethane, unless otherwise stated. (*i*) In EtOH at 50 °C

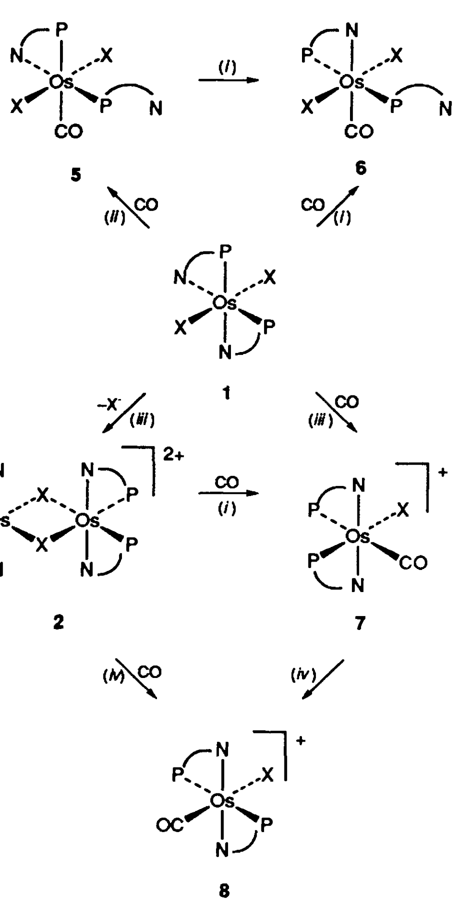
at the same concentration and temperature: for a 0.2 mol dm^{-3} solution $w_{\frac{1}{2}}$ = 430 Hz at 293 K (δ −33.6) and 58 Hz at 193 K (δ −34.4). Such a spectral pattern indicates that a dynamic process occurs in solution, the rate of which is slowed on cooling. As the spectral patterns are not affected by addition of an excess of the appropriate halide ion, we suggest that this process may involve dissociation of the pyridine arm of the ppye ligand. The low-temperature $^{13}C-\{^1H\}$ NMR spectra of **1a**, **1b** in dichloromethane solution show two pairs of equivalent phenyl rings, in agreement with structure **1** (see Scheme 1). All the aromatic carbon resonances are singlets, probably due to a fortuitous cancellation of the $^{13}C-^{31}P$ coupling constants [$^nJ(P-C) + {}^{n+2}J(P-C) = 0$],[13] and therefore do not provide any structural information.

On standing in chlorocarbon solvents complexes **1a**, **1b** partially isomerize to the all-*cis* derivatives *cis,cis,cis*-[$OsCl_2$(ppye-*P*,*N*)$_2$] (X = Cl **3a** or Br **3b**), as shown by the appearance in the ^{31}P NMR spectra of two sharp doublets with a ^2J(P–P′) of about 17 Hz, typical of phosphorus atoms in mutually *cis* positions. The features of the NMR resonances suggest that the ring-opening/ring-closing mechanism is not operative in isomers **3a**, **3b**. Attempts to obtain these complexes in pure form were unsuccessful. A comparison with the ^{31}P chemical shifts of **1a**, **1b** suggest that the high-field (δ −27 to −34, Table 1) should be assigned to the P atom *trans* to the pyridyl group. It should also be noted that the ^{31}P co-ordination chemical shifts ($\delta_{complex} - \delta_{free\ ligand}$) of the osmium(II) complexes with ppye ($\delta_{free\ ligand} = -14.9$) reported in this paper are unusually low or negative when compared with those of the analogous ruthenium(II) derivatives.[8] A similar effect has been observed for the six-co-ordinate complexes of osmium(II) with ditertiary phosphines.[14]

Finally, the dihalide derivatives **1a**, **1b** are almost insoluble in polar solvents such as ethanol at room temperature, but at 50 °C they slowly dissolve with formation of the five-co-ordinate cations $[OsX(ppye\text{-}P,N)_2]^+$ **4** which dimerize to the slightly soluble **2a**, **2b**. In more co-ordinating solvents such as MeCN or $MeNO_2$ (solv), solvates of the type $[OsX(solv)(ppye\text{-}P,N)_2]^+$ are formed, as indicated by the $^{31}P\text{-}\{^1H\}$ NMR spectra showing AX patterns (see below).

Complexes **2a**, **2b**, which have similar solid-state electronic spectra, probably possess the same stereochemistry as that of the ruthenium analogues $[(ppye\text{-}P,N)_2Ru(\mu\text{-}X)_2Ru(ppye\text{-}P,N)_2][PF_6]_2$ for which the dihalide-bridged structure has been assessed by X-ray analysis.[8] Consistent with this structure, the far-infrared spectrum of **2a** shows a single absorption at 283 cm^{-1} which can be assigned to the Os–Cl–Os stretching vibration.

As for the ruthenium(II) analogues, the solution behaviour of complexes **2a**, **2b** depends on the nature of the solvent. In dichloromethane solution **2a**, **2b** dissociate to give the five-co-ordinate species $[OsX(ppye\text{-}P,N)_2]^+$ (X = Cl **4a** or Br **4b**) the presence of which is inferred from NMR data (Scheme 1). The room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectra show, in addition to a singlet at *ca.* δ −19 attributable to the binuclear species, a singlet in the δ 1–3 region: the latter can be assigned to the five-co-ordinate species **4a**, **4b**, for which a trigonal-bipyramidal structure is proposed, as for the related $[RuX(ppye\text{-}P,N)_2]^+$.[8] The intensity ratio between the two signals was found to be dependent both on sample concentration and temperature. At room temperature in a 10^{-3} mol dm^{-3} solution the bromo-derivative **2b** is quantitatively converted into **4b**, while **2a** is *ca.* 25% dissociated. In more concentrated solutions (10^{-1} mol dm^{-3}) the dissociation of **2a** is almost negligible, while it is about 60% for **2b**. The equilibrium shifts toward the dimeric species upon cooling. For 10^{-1} mol dm^{-3} solutions the signal due to the five-co-ordinate cation **4a** disappears at temperatures below 273 K, while about 5% of **4b** is still present in the spectrum of **2b** at 213 K. The presence of the five-co-ordinate cation **4b** in dilute solutions of **2b** is also supported by the appearance in the UV/VIS spectrum of a band at 565 nm, which is not detected in the solid state. This band disappears upon addition of an excess of Br$^-$ ion and the $^{31}P\text{-}\{^1H\}$ NMR data indicate that a mixture of **1b** and **3b** is formed.



Scheme 2 (*i*) In dichloromethane at room temperature (r.t.); (*ii*) in dichloromethane at −20 °C (X = Cl) or at r.t. (X = Br); (*iii*) in EtOH at 50 °C; (*iv*) in boiling 2-methoxyethanol

Carbon Monoxide Derivatives.—We have investigated the carbonylation reaction of complexes **1a**, **1b** and **2a**, **2b** in different solvents by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, and the results are summarized in Scheme 2. In low-polarity solvents such as CH_2Cl_2, **1a**, **1b** react with CO to give the kinetic products *trans,cis*-$[OsX_2(CO)(ppye\text{-}P)(ppye\text{-}P,N)]$ (X = Cl **5a** or Br **5b**) which are then converted into the more stable *trans,trans*-$[OsX_2(CO)(ppye\text{-}P)(ppye\text{-}P,N)]$ (X = Cl **6a** or Br **6b**). At room temperature the carbonylation of **1a** is slow and the isomerization of **5a** into **6a** occurs at comparable rate. However, we succeeded in isolating pure **5a** in the solid state by treating **1a** and CO at lower temperature (253 K). The carbonylation of **1b** is faster: **5b** is quantitatively formed within 20 min in dichloromethane at room temperature and its conversion into **6b** is achieved within 6 h. The isomerization of **5** into **6** occurs also under an argon atmosphere. The IR spectra of **5a**, **5b** and **6a**, **6b** show that both chelate and monodentate ppye ligands are present, as the pyridine-ring stretching absorptions appear as two bands of comparable intensity in the 1585–1605 cm^{-1} region (Table 1). The band shifted to higher frequency relative to the free ppye is attributed to chelate ppye, while the second one can be assigned to a P-bound, dangling ppye ligand.[1,4–8] Moreover, the far-infrared spectra of **5a** and **6a** exhibit Os–Cl stretching vibrations at 302 and 306 cm^{-1}, respectively, which can be assigned to terminal chloride ligands in mutually *trans* positions. In agreement with structure **6**, the carbonyl signal in the ^{13}C NMR spectra appears as a pseudo-triplet at *ca.* δ 182 due to coupling to two P atoms in *cis* positions. Unfortunately, the low solubility of **5a**, **5b** prevents $^{13}C\text{-}\{^1H\}$ NMR investigations. A further assessment of the geometry of **5** and **6** can be made from NMR data. The $^{31}P\text{-}\{^1H\}$ spectra of **5a**, **5b** reveal AX spin systems [$^2J(P\text{-}P') \approx 22$ Hz], indicative of a *cis* arrangement of two inequivalent P atoms. The *trans* arrangement of the P atoms in isomers **6a**, **6b** is suggested by the AB spin systems with large coupling constants of about 300 Hz. Geometries **5** and **6** have been proposed also for the analogous ruthenium(II)–ppye derivatives. The initial formation of carbonyl complexes of type **5** in the reaction of **1a**, **1b** with CO is apparently related to the high *trans* effect of the P atom, which favours dissociation of the pyridyl arm of ppye. The isomers **6** appear thermodynamically stabilized with respect to **5** since in the former the CO and PPh_2 groups in mutually *cis* positions do not compete for the same set of metal π orbitals. In agreement with a substantial increase in the Os–CO back bonding, the ν(CO) absorption of **6** is shifted by *ca.* 25 cm^{-1} to lower frequencies with respect to the corresponding isomers **5** (Table 1). It should be noted that the ^{31}P NMR chemical shifts of the chelate and monodentate ppye ligands in **5** and **6** are not very different, consistent with the ring contribution to the co-ordination chemical shift being small or negative for ligands which form a six-membered chelate ring.[15] Moreover, it is an established fact that ligands with a large *trans* influence cause an upfield shift in the resonance of a P atom occupying the *trans* position.[16] Thus it is surprising that the ^{31}P

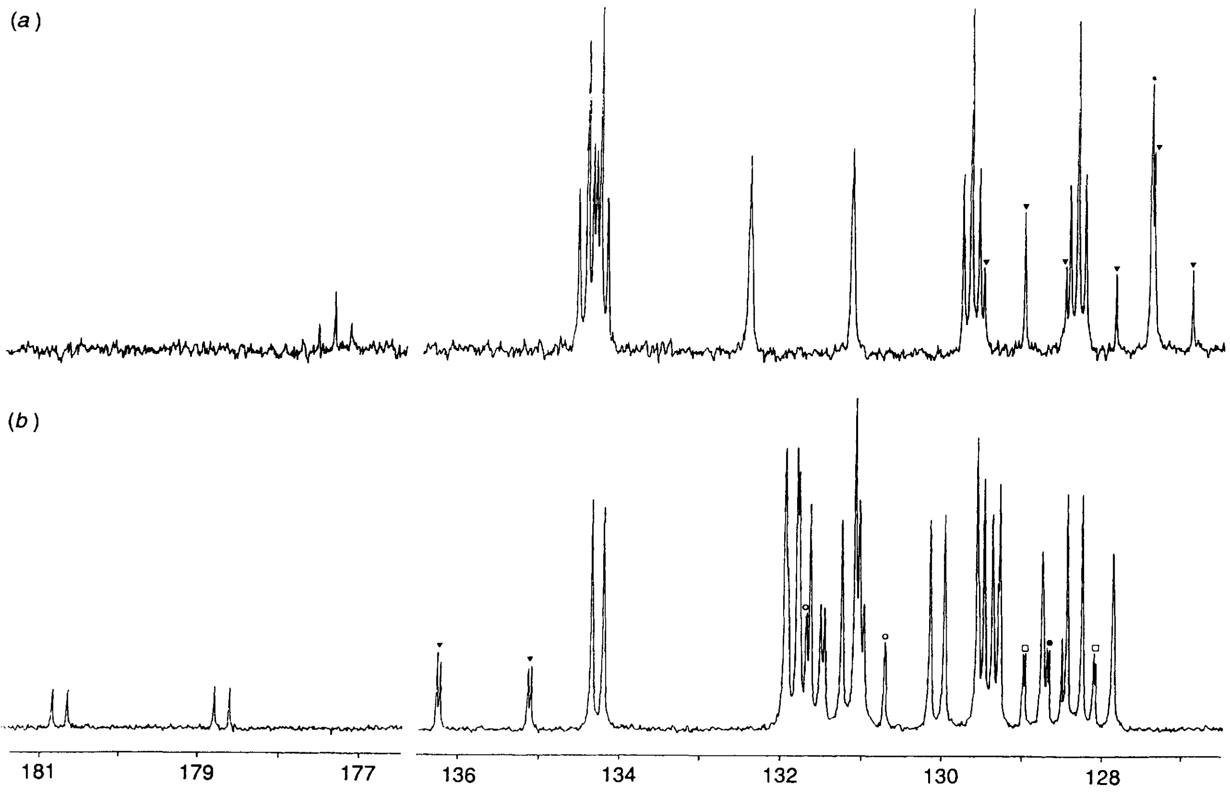


Fig. 1 The ^{13}C NMR spectra (phenyl carbons and CO) of (*a*) *trans,trans*-[OsCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$ **8a** and (*b*) *cis,trans*-[OsCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$ **7a** (CD$_2$Cl$_2$, 20 °C). The $^{13}C_{ipso}$ multiplets are marked (one of the four doublets of doublets in the spectrum of **7a** is partially overlapped by the signal at δ 129.3). The singlet marked by * on (*a*) is attributed to the C^3 resonance of pyridine

NMR signals of **6** (P *trans* to P) are at lower field with respect to those of isomers **5** (P *trans* to CO or pyridine). This would suggest that the pyridyl ligand has a larger *trans* influence than that of phosphorus. Also for other complexes reported in this paper (Table 1) there is not a satisfactory correlation between observed chemical shifts and the previously reported *trans*-influence order of various ligands.[16,17] This failure, which was not evident for the analogous ruthenium(II) derivatives,[8] clearly shows that one must be cautious when making correlations between *trans* influence and chemical shift data.[18]

Complexes **1a**, **1b** are insoluble in ethanol, but clear yellow solutions are obtained when the suspension is heated to 50 °C for about 15 min under a carbon monoxide atmosphere. Cationic carbonyl derivatives of the type *cis,trans*-[OsX(CO)-(ppye-*P*,*N*)$_2$]PF$_6$ (X = Cl **7a** or Br **7b**) precipitate from the cold solutions on addition of an excess of NH$_4$PF$_6$. The same products can be obtained when the binuclear complexes **2a**, **2b** are treated with carbon monoxide in dichloromethane solution (Scheme 2). It is likely that in both cases the reaction proceeds *via* the five-co-ordinate **4** which rapidly add CO to yield the monocarbonyl adducts **7**. Compounds **7** are cream-coloured, crystalline materials which are air stable both in the solid state and in solution, where they behave as 1 : 1 electrolytes. The IR spectra contain a strong absorption at *ca.* 1970 cm^{-1}, which can be assigned to the CO stretching vibration. Consistent with the presence of two inequivalent P atoms occupying mutually *cis* positions, the ^{31}P-{^{1}H} NMR spectra show AX (**7a**) or AB (**7b**) patterns with ^2J(P–P′) *ca.* 15 Hz. Structure **7** where a P atom is *trans* to a halogen seems to be more consistent with the ^{31}P chemical shift data (Table 1) than one in which the P atom is *trans* to a pyridine. It should be emphasized that the addition of CO occurs stereoselectively *trans* to a P atom as observed in the case of the five-co-ordinate analogues [RuX(ppye)$_2$]$^+$ (X = Cl, Br or I)[8] and [MX(dcpe)$_2$]$^+$ [M = Ru or Os, X = Cl or Br, dcpe = 1,2-bis(dicyclohexylphosphino)ethane].[14]

The ^{13}C-{^{1}H} NMR spectra of both complexes **7a**, **7b** show, in the CO region, a doublet of doublets centred at *ca.* δ 180, which unequivocally indicates that the CO ligand is *trans* to a P atom and *cis* to the other one, [$^2J(^{31}P-^{13}C)_{trans} \approx 102$ Hz $\gg$ $^2J(^{31}P-^{13}C)_{cis} \approx 11$ Hz]. The spectral patterns in the phenyl region show the inequivalent nature of the four phenyl rings in the complex. In particular, each *ipso*-carbon resonance appears as a doublet of doublets due to coupling to chemically inequivalent P atoms in *cis* positions. The spectra show also the presence of inequivalent pyridine and CH$_2$CH$_2$ groups. The ^{13}C-{^{1}H} NMR spectrum of **7a** is shown in Fig. 1(*b*).

Unlike the ruthenium analogues,[8] complexes **7** do not isomerize at room temperature, as their ^{31}P-{^{1}H} NMR spectra in dichloromethane solution remain unchanged over several days. However, the white isomers *trans,trans*-[OsX(CO)(ppye-*P*,*N*)$_2$]PF$_6$ (X = Cl **8a** or Br **8b**) have been prepared in high yield by treating **2a**, **2b** with CO in boiling 2-methoxyethanol or by refluxing **7a**, **7b** in the same solvent. Complexes **8a**, **8b** are 1 : 1 electrolytes in MeNO$_2$ solution and their IR spectra in Nujol mull show an intense absorption at 1918 cm^{-1} identifiable as the CO stretching vibration. The presence of equivalent P atoms is inferred from the ^{31}P-{^{1}H} NMR spectra which exhibit a single signal at δ 2.1 and −1.2 for **8a** and **8b**, respectively. Moreover, the ^{13}C-{^{1}H} NMR spectra show two different pairs of equivalent phenyl rings, the *ipso*-carbons of which appear as triplets (X part of an AXX′ spin system) due to virtual coupling[19] between two equivalent *trans* phosphorus atoms (Table 3). Consistently, with the all-*trans* structure **8**, the ^{13}CO signal appears as a triplet at about δ 177. The ^{13}C-{^{1}H} NMR spectrum of **8a** is shown in Fig. 1(*a*).

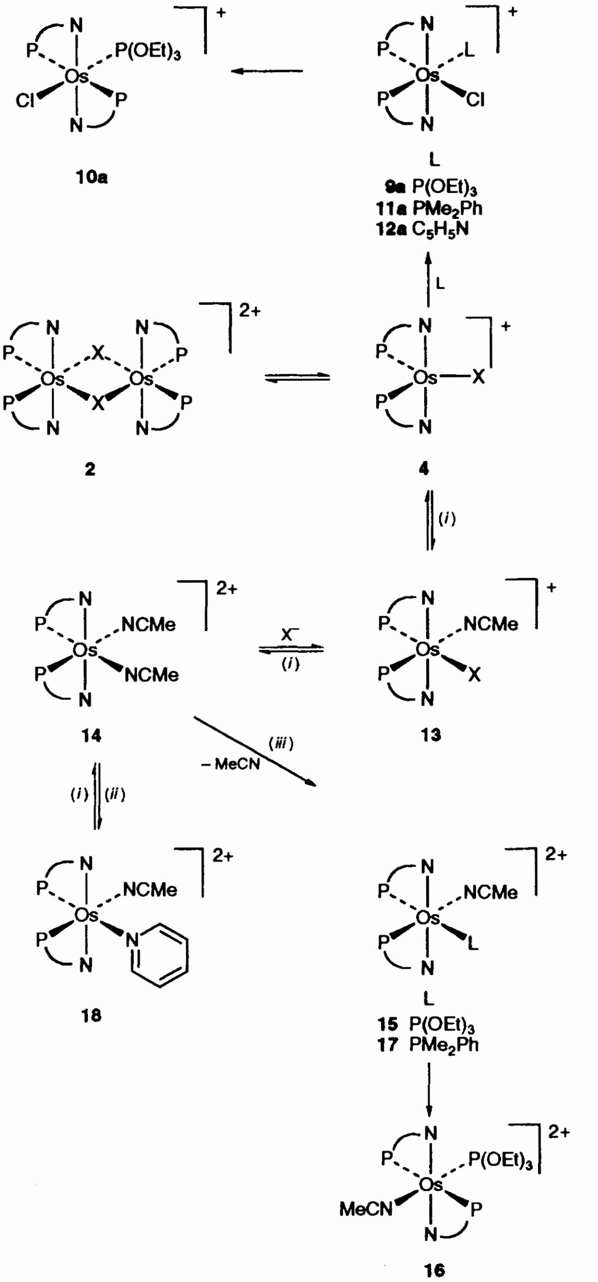
Reactions of the Dihalide-bridged Complexes with Neutral Ligands.—Owing to the presence of the five-co-ordinate, unsaturated species **4**, complexes **2a**, **2b** easily react in dichloromethane solution with neutral ligands (L) giving the

Table 3 Selected $^{13}C-\{^1H\}$ NMR data for complexes **6**–**8** and **14**[a]

Complex	δ(CO)	δ(C_{ipso})
6a	182.0 (t, 10.3)	132.1 (dd, 32.5, 11.9), 133.9 (dd, 39.4, 12.9)
6b	182.2 (t, 10.2)	132.4 (dd, 37.2, 7.5)[b]
7a	179.7 (dd, 101.7, 9.8)	128.5 (dd, 44.3, 1.2), 129.1 (dd, 31.0, 1.5), 131.2 (dd, 49.2, 0.7), 135.7 (dd, 56.6, 2.0)
7b	180.1 (dd, 101.8, 11.5)	135.5 (dd, 58.4, 1.6)[c]
8a	177.4 (t, 9.9)	127.4 (t, 24.0), 129.9 (t, 25.6)
8b	176.1 (t, 10.0)	127.8 (t, 24.2), 129.1 (t, 25.3)
14	*d*	133.3 (qnt, 56.5, 7.0), 134.0 (qnt, 56.9, 8.1)

[a] In dichloromethane solution, at 293 K; qnt = non-binomial quintet, $J(^{13}C-^{31}P)$/Hz in parentheses. [b] The second C_{ipso} signal is obscured by the resonances of the C_{ortho} carbons. [c] The other three C_{ipso} signals are partially overlapped by the resonances of phenyl carbons. [d] δ(CN) 122.7 (qnt), $^3J(^{31}P_{trans}-^{13}C)$ = 12.7, $^3J(^{31}P_{cis}-^{13}C)$ = 1.9, ^2J(P–P) = 9.6 Hz, from computer simulation.

corresponding six-co-ordinate adducts $[OsX(L)(ppye\text{-}P,N)_2]^+$. For example, addition of a slight excess of $P(OEt)_3$ to a solution of **2a** leads to the immediate formation of *cis,trans*-$[OsCl\{P(OEt)_3\}(ppye\text{-}P,N)_2]^+$ **9a** (Scheme 3). The $^{31}P-\{^1H\}$ NMR spectrum of the solution shows a doublet of doublets centred at δ 68.9 for the phosphorus atom of $P(OEt)_3$ (P*) together with an eight-line multiplet in the range δ −22 to −29 for the two P atoms of the ppye ligands, which is the AB part of an ABX spin system [$^2J(P_A-P^*)$] = 28.5, $^2J(P_B-P^*)$ = 431.1, $^2J(P_A-P_B)$] = 8.8 Hz]. The whole spectral pattern is consistent with structure **9** where the P atoms of inequivalent ppye ligands are respectively *trans* and *cis* to $P(OEt)_3$ in a meridional arrangement. With time **9a** is converted into the all-*trans* isomer *trans,trans*-$[OsCl\{P(OEt)_3\}(ppye\text{-}P,N)_2]^+$ **10a**, as shown by the appearance in the $^{31}P-\{^1H\}$ NMR spectrum of a doublet and a triplet at δ −3.7 and 57.7, respectively [$^2J(P-P^*)$ = 27.6 Hz], which indicate that the equivalent P atoms of the ppye ligands are both *cis* to $P(OEt)_3$. In turn **10a** is slowly transformed into a new product which was not identified. Attempts to isolate these $P(OEt)_3$ derivatives in the solid state led to a mixture of products. The ^{31}P NMR investigations (Table 1) indicate that **2a** reacts also with PMe_2Ph and pyridine to give adducts of the type *cis,trans*-$[OsCl(PMe_2Ph)(ppye\text{-}P,N)_2]^+$ **11a** and *cis,trans*-$[OsCl(py)(ppye\text{-}P,N)_2]^+$ **12a** (py = pyridine). These complexes were found to be stable in solution at room temperature for several days, but only **11a** was isolated in pure form in the solid state as the hexafluorophosphate salt and has been fully characterized by elemental analysis and conductivity measurements. The $^{31}P-\{^1H\}$ NMR spectral pattern is consistent with a meridional arrangement of the P atoms of the ligands.



Scheme 3 In dichloromethane; (*i*) MeCN; (*ii*) pyridine; (*iii*) L = $P(OEt)_3$ or PMe_2Ph

Furthermore, the dihalide-bridged complexes **2a**, **2b** dissolve in co-ordinating solvents such as acetonitrile forming six-co-ordinate *cis,trans*-$[OsX(MeCN)(ppye\text{-}P,N)_2]^+$ (X = Cl **13a** or Br **13b**) and *cis,trans*-$[Os(MeCN)_2(ppye\text{-}P,N)_2]^{2+}$ **14** (Scheme 3). The stepwise formation of both species can be conveniently followed by ^{31}P NMR spectroscopy. When complexes **2a**, **2b** are dissolved in MeCN pale yellow solutions are obtained, the spectra of which exhibit two doublets (Table 1) attributed to the monosolvates **13**. The signals at δ −9.1 can be attributed to P atoms *trans* to MeCN. The formation of these species probably occurs *via* stereoselective addition of the solvent molecule to the five-co-ordinate complex **4**. With time a new singlet appears at δ −12.1, which can be attributed to the disolvate **14**. This derivative is formed slowly and its concentration, at equilibrium, depends on the starting complex **2**. For a 5 × 10^{-2} mol dm^{-3} solution, about 7% **14** is formed from **2a** and 33% from **2b**, respectively. Attempts to isolate both species **13** in the solid state led to products slightly contaminated with **2** and **14**. By contrast, **14** has been obtained in pure form by treating **2a** or **2b** with $AgPF_6$ in acetonitrile solution. This cream-white complex behaves as a 1:2 electrolyte in MeCN and its IR spectrum in KBr shows two weak absorptions at 2320 and 2285 cm^{-1}, which can be attributed to the stretching mode of mutually *cis* CN groups. The *cis,trans* structure **14** is also supported by the $^{13}C-\{^1H\}$

NMR spectrum in CD_2Cl_2 solution, which shows two different pairs of equivalent phenyl groups. The *ipso*-carbons appear as non-binomial quintets arising from spin–spin coupling with two equivalent P atoms in *cis* position. The ^{13}CN resonance at δ 122.7 (*ca.* 5 ppm downfield from free MeCN) also appears as a non-binomial quintet. The spectral pattern of the *ipso* and nitrile carbons was reproduced by computer simulation giving a ^2J(P–P) of 9.6 Hz; the calculated $J(^{31}P-^{13}C)$ values are given in Table 3. The chemical shift of the ^{31}P resonance is also consistent with P atoms *trans* to MeCN. The acetonitrile ligands in **14** are tightly bound to osmium since they cannot be removed under vacuum even upon prolonged treatment. In solution, at room temperature, one solvent molecule is displaced by X^- ions, while the second is not removed even in the presence of a large excess of halide.

Complex **14** has been used as starting material for the synthesis of dicationic derivatives with some neutral ligands in dichloromethane solution. Thus $P(OEt)_3$ reacts with **14** to generate monosubstituted *cis,trans*-$[Os(MeCN)\{P(OEt)_3\}$(ppye-*P*, *N*)$_2]^{2+}$ **15**. No evidence of displacement of the second nitrile is observed even in the presence of a large excess of phosphite. A confirmation of structure **15** is provided by the ^{31}P NMR spectral pattern which is characteristic of an ABX spin system. Complex **15** is then slowly transformed into the thermodynamically preferred isomer *trans,trans*-$[Os(MeCN)\{P(OEt)_3\}$(ppye-*P*,*N*)$_2]^{2+}$ **16** in which the $P(OEt)_3$ ligand is *cis* to both P atoms of the ppye ligands. The ^{31}P-$\{^1H\}$ NMR spectrum, which shows a triplet at δ 62.5 and a doublet at δ −6.9, is consistent with the P atoms of the ppye ligands in a mutual *trans* arrangement.

The ^{31}P NMR studies in dichloromethane solution indicate that also PMe_2Ph and pyridine react with **14** to give monosubstituted adducts *cis,trans*-[Os(MeCN)L(ppye-*P*,*N*)$_2]^{2+}$(L = PMe_2Ph **17** or pyridine **18**). The former is quantitatively obtained, while the latter is present in an equilibrium mixture also in the presence of a large excess of pyridine. Both complexes do not isomerize to the corresponding *trans,trans* isomers over several days.

Conclusion

These results show that the chemistry of the ppye complexes of osmium(II) parallels that of the corresponding ruthenium(II) analogues.[8] In both cases the $[MX_2(ppye)_2]$ (M = Ru or Os) derivatives were found to react with CO with formation of neutral or cationic monocarbonyl adducts probably *via* a five-co-ordinate intermediate. The nature of the solvent plays a crucial role in determining the reaction pathway. In polar solvents the rupture of the M–X bond is favoured and the cationic monocarbonyls [MX(CO)(ppye-*P*,*N*)$_2]^+$ are obtained. In less-polar solvents dissociation of the M–N bond occurs with formation of neutral derivatives of the type $[MX_2(CO)$(ppye-*P*)(ppye-*P*,*N*)] containing a P-bound, monodentate ppye ligand.

The formation of unsaturated species is probably related to the steric crowding around the metal centre. It should be noted that the six-co-ordinate complexes $[MX_2(dppp)_2]$ [X = Cl or Br; dppp = 1,3-bis(diphenylphosphino)propane] easily dissociate a halide ion in solution with formation of five-co-ordinate $[MX(dppp)_2]^+$.[20] The ditertiary phosphine ligand dppp forms a six-membered chelate ring with a bite angle which is similar to that of ppye.[6] In the case of the $[MX_2(ppye)_2]$ complexes apparently an additional route to unsaturated species comes from the labile nature of the M–N bond.

Dihalide-bridged complexes of type **2** were obtained with both metals. These species dissociate in solution with formation of the five-co-ordinate **4**. The co-ordinatively unsaturated complexes **4** readily add neutral ligands to give in a first step the corresponding six-co-ordinate *cis,trans*-[MX(L)(ppye-*P*,*N*)$_2]^+$ [M = Ru, L = CO or MeCN; M = Os, L = CO, MeCN, $P(OEt)_3$, PMe_2Ph or pyridine], in which L is *trans* to a P atom of the ppye ligand. The *cis,trans* derivatives can, in some cases, isomerize into the *trans,trans* analogues in which the L ligand is *cis* to the phosphorus atom. The rates of isomerization of the osmium(II) complexes are slower than those of the corresponding ruthenium(II) analogues.

Experimental

General Procedures.—Solvents were purified by standard methods and stored over molecular sieves under an argon atmosphere. All chemicals used were of reagent grade or comparable purity. The salt $[NH_4]_2[OsCl_6]$ was obtained from Aldrich; $[NH_4]_2[OsBr_6]$ was prepared from OsO_4 (Johnson Matthey) according to a literature method.[21] The complex $[OsCl_2(PPh_3)_3]$ was prepared as previously described[22] and the analogue $[OsBr_2(PPh_3)_3]$ was obtained from $[NH_4]_2[OsBr_6]$ in high yield (> 90%) by the same procedure. The ligand ppye was synthesised according to the method of Uhlig and Maaser[1] and purified on a silica gel column with diethyl ether as eluent.

Infrared spectra were recorded on JASCO DS 702 G or Nicolet-FT 550 spectrometers, UV/VIS spectra on a Cary 2300 spectrophotometer, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR spectra on a Bruker AC 200 F QNP spectrometer equipped with a VT 1000 variable-temperature probe. Temperatures were calibrated either with methanol or with ethylene glycol. Positive ^{31}P chemical shifts are downfield from 85% H_3PO_4 as external standard; ^{13}C chemical shifts are referenced to $SiMe_4$. Spectral simulations were performed on an Aspect 3000 computer using the program PANIC.[23] Conductance data (see Table 4), obtained at 293 K on 10^{-3} mol dm^{-3} nitromethane solutions of the complexes, were measured with a Metrohm E 518 conductivity bridge. Elemental analyses were performed by the Microanalytical Laboratory of our Department.

Syntheses.—All manipulations were performed under argon with standard Schlenk-line techniques.

trans,cis,cis-$[OsCl_2$(ppye-*P*,*N*)$_2]$ **1a**. The complex $[OsCl_2(PPh_3)_3]$ (0.524 g, 0.5 mmol) and ppye (0.291 g, 1.0 mmol) were suspended in toluene (20 cm^3) and the slurry was then refluxed for 2 h. Upon cooling to 0 °C the red solution deposited yellow-orange *crystals* which were filtered off, washed with diethyl ether and vacuum-dried. Yield: 0.290 g, 68%.

trans,cis,cis-$[OsBr_2$(ppye-*P*,*N*)$_2]$ **1b**. The complex $[OsBr_2(PPh_3)_3]$ (0.568 g, 0.5 mmol) and ppye (0.291 g, 1.0 mmol) were suspended in toluene (20 cm^3) and the slurry was refluxed for 4 h. The suspension was allowed to cool and the resulting orange-red solid was collected, washed with diethyl ether, and vacuum-dried. Yield: 0.415 g, 89%.

[(ppye-*P*,*N*)$_2$Os(μ-Cl)$_2$Os(ppye-*P*,*N*)$_2$][$PF_6]_2$ **2a**. A mixture of $[OsCl_2(PPh_3)_3]$ (0.524 g, 0.5 mmol), ppye (0.291 g, 1.0 mmol) and NH_4PF_6 (0.163 g, 1.0 mmol) was refluxed in ethanol (20 cm^3) for 1 h. After cooling to room temperature, the yellow solid formed was collected, washed with cold ethanol, and dried *in vacuo*. Recrystallization was from dichloromethane–propan-2-ol. Yield: 0.416 g, 87%.

[(ppye-*P*,*N*)$_2$Os(μ-Br)$_2$Os(ppye-*P*,*N*)$_2$][$PF_6]_2$ **2b**. This yellow-green complex was prepared from $[OsBr_2(PPh_3)_3]$ (0.569 g, 0.5 mmol), ppye (0.291 g, 1.0 mmol) and NH_4PF_6 (0.163 g, 1.0 mmol) by a route analogous to that for **2a**. Yield: 0.455 g, 91%.

trans,cis-$[OsCl_2(CO)$(ppye-*P*)(ppye-*P*,*N*)] **5a**. Complex **1a** (0.169 g, 0.2 mmol) was dissolved in dichloromethane (10 cm^3) and the solution cooled to −20 °C before saturating with CO. Hexane (20 cm^3) was added after 16 h and dichloromethane pumped off until a pale yellow precipitate formed, which was filtered off and dried *in vacuo*. Yield: 0.160 g, 92%.

trans,cis-$[OsBr_2(CO)$(ppye-*P*)(ppye-*P*,*N*)] **5b**. Complex **1b** (0.186 g, 0.2 mmol) was dissolved in dichloromethane (10 cm^3) and the solution stirred under an atmosphere of CO for 30 min.

Table 4 Analytical and physical data

Complex	Colour	Λ_M[a]/ Ω^{-1} cm^2 mol^{-1}	Analysis (%) C	H	N
1a *trans,cis,cis*-[OsCl$_2$(ppye-*P*,*N*)$_2$]	Yellow-orange		53.90 (54.10)	4.35 (4.30)	3.20 (3.30)
1b *trans,cis,cis*-[OsBr$_2$(ppye-*P*,*N*)$_2$]	Orange-red		49.25 (48.95)	3.90 (3.90)	2.90 (3.00)
2a [Os$_2$(μ-Cl)$_2$(ppye-*P*,*N*)$_4$][PF$_6$]$_2$	Yellow	64,[b] 31[b,c]	47.60 (47.90)	3.85 (3.80)	2.90 (2.95)
2b [Os$_2$(μ-Br)$_2$(ppye-*P*,*N*)$_4$][PF$_6$]$_2$	Yellow-green	87,[b] 49[b,c]	45.65 (45.75)	3.65 (3.65)	2.70 (2.80)
5a *trans,cis*-[OsCl$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)]	Pale yellow		53.40 (53.75)	4.25 (4.15)	3.15 (3.20)
5b *trans,cis*-[OsBr$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)]	Pale yellow		48.35 (48.75)	3.85 (3.80)	2.80 (2.90)
6a *trans,trans*-[OsCl$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)]	Cream-white		53.45 (53.75)	4.20 (4.15)	3.15 (3.20)
6b *trans,trans*-[OsBr$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)]	Cream-white		48.40 (48.75)	3.80 (3.80)	3.00 (2.90)
7a *cis,trans*-[OsCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$	Cream-white	78	47.30 (47.75)	3.75 (3.70)	2.75 (2.85)
7b *cis,trans*-[OsBr(CO)(ppye-*P*,*N*)$_2$]PF$_6$	Cream-white	81	45.75 (45.65)	3.60 (3.55)	2.60 (2.75)
8a *trans,trans*-[OsCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$	White	82	47.45 (47.75)	3.70 (3.70)	2.80 (2.85)
8b *trans,trans*-[OsBr(CO)(ppye-*P*,*N*)$_2$]PF$_6$	White	79	45.35 (45.65)	3.55 (3.55)	2.65 (2.75)
11a *cis,trans*-[OsCl(PMe$_2$Ph)(ppye-*P*,*N*)$_2$]PF$_6$	Lemon-yellow	84	50.35 (50.60)	4.40 (4.35)	2.50 (2.55)
14 *cis,trans*-[Os(MeCN)$_2$(ppye-*P*,*N*)$_2$][PF$_6$]$_2$	Cream-white	164	44.10 (44.05)	3.65 (3.70)	4.95 (4.90)

[a] In 10^{-3} mol dm^{-3} MeNO$_2$ solution, unless otherwise stated. [b] Calculated for monomer **4** (see text). [c] In 10^{-3} mol dm^{-3} CH$_2$Cl$_2$ solution.

Hexane (15 cm^3) was then added and dichloromethane removed under vacuum. The resulting pale yellow precipitate was filtered off and dried *in vacuo*. Yield: 0.164 g, 85%.

trans,trans-[OsCl$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)] **6a**. Complex **1a** (0.169 g, 0.2 mmol) was dissolved in dichloromethane (10 cm^3) and the solution stirred under CO for 24 h. Hexane (15 cm^3) was then added, and the dichloromethane pumped off until a cream-white precipitate formed, which was filtered off and dried *in vacuo*. Yield: 0.153 g, 88%.

trans,trans-[OsBr$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)] **6b**. Complex **1b** (0.186 g, 0.2 mmol) was dissolved in dichloromethane (10 cm^3) and the solution stirred under CO for 6 h. On addition of hexane (15 cm^3) and concentration a cream-white precipitate formed, which was filtered off and dried *in vacuo*. Yield: 0.159 g, 83%.

cis,trans-[OsCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$ **7a**. Complex **2a** (0.381 g, 0.2 mmol) was dissolved in dichloromethane (15 cm^3) and the solution stirred under CO for 30 min. Propan-2-ol (20 cm^3) was then added, and the dichloromethane pumped off until a cream-white precipitate formed, which was filtered off and dried *in vacuo*. Yield: 0.341 g, 87%.

cis,trans-[OsBr(CO)(ppye-*P*,*N*)$_2$]PF$_6$ **7b**. This cream-white product was prepared from complex **2b** (0.399 g, 0.2 mmol) as reported above for **7a**. Yield: 0.372 g, 91%.

trans,trans-[OsCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$ **8a**. Complex **2a** (0.381 g, 0.2 mmol) was suspended in 2-methoxyethanol (20 cm^3), and the mixture refluxed under an atmosphere of CO for 6 h. The solvent was then removed under reduced pressure and the residue dissolved in dichloromethane (20 cm^3). Addition of propan-2-ol (20 cm^3) followed by removal of the dichloromethane afforded a white crystalline solid. Yield: 0.353 g, 90%.

trans,trans-[OsBr(CO)(ppye-*P*,*N*)$_2$]PF$_6$ **8b**. This white complex was prepared from **2b** (0.399 g, 0.2 mmol) by the same procedure used to synthesise **8a**. Yield: 0.376 g, 92%.

cis,trans-[OsCl(PMe$_2$Ph)(ppye-*P*,*N*)$_2$]PF$_6$ **11a**. Complex **2a** (0.381 g, 0.2 mmol) and PMe$_2$Ph (0.069 g, 0.5 mmol) were dissolved in dichloromethane (20 cm^3) and the solution stirred for 10 min. Propan-2-ol (20 cm^3) was added, and the dichloromethane pumped off until a lemon-yellow precipitate formed, which was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield: 0.392 g, 89%.

cis,trans-[Os(MeCN)$_2$(ppye-*P*,*N*)$_2$][PF$_6$]$_2$ **14**. Complex **2a** (0.381 g, 0.2 mmol) and AgPF$_6$ (0.126 g, 0.5 mmol) were stirred in acetonitrile (10 cm^3) for 2 h in the dark. The suspension was filtered over Celite. Addition of propan-2-ol (20 cm^3) to the resulting pale yellow solution and removal of acetonitrile afforded a cream-white product which was filtered off and dried *in vacuo*. Recrystallization was from dichloromethane–propan-2-ol. Yield: 0.409 g, 89%.

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