Mono- and Bi-nuclear Complexes of Ruthenium(II) with the Ligand 1-(Diphenylphosphino)-2-(2-pyridyl)ethane†

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The ligand 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye) forms six-co-ordinate species [RuX$_2$(ppye-*P,N*)$_2$] (X = Cl, Br or I), the solution behaviour of which has been investigated by ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR, UV/VIS spectroscopy, and conductivity measurements. Halide dissociation from the neutral species yields the five-co-ordinate cations [RuX(ppye-*P,N*)$_2$]$^+$ which can dimerize to [Ru$_2$X$_2$(ppye-*P,N*)$_4$]$^{2+}$ depending on the size of the halide. The chloro derivative [Ru$_2$Cl$_2$(ppye)$_4$][PF$_6$]$_2$ has been characterized crystallographically. Both the five-co-ordinate cations and the dimeric species react with carbon monoxide forming cationic monocarbonyls, while the octahedral species undergo rupture of the Ru–N bond and neutral carbonyl derivatives are formed containing a dangling, P-bound ppye ligand. All these carbonyl derivatives are formed as the kinetically preferred species with a P atom *trans* to CO, and are converted in solution at room temperature into the thermodynamically preferred isomers in which the P and CO groups are mutually *cis*.

Several complexes of ruthenium(II) with diphosphine ligands have been reported and extensively studied,[1] in particular with respect to their use in the activation of molecular hydrogen[2] and their relevance to homogeneous catalysis.[3] The majority of the compounds reported are six-co-ordinate species of the type [RuX$_2$(L–L)$_2$] (X = halide, L–L = diphosphine).[4] However, the unsaturated, five-co-ordinate derivatives [RuX(L–L)$_2$]$^+$ can also be obtained. The tendency of the six-co-ordinate complexes [RuX$_2$(L–L)$_2$] [L–L = R$_2$P(CH$_2$)$_n$PR$_2$, R = aryl or alkyl, n = 1–3] to dissociate one halide ligand giving [RuX(L–L)$_2$]$^+$ increases with increasing chelate ring size in the order six- > five- ≫ four-membered.[4b,c,e] A similar stereochemical effect of the alkyl chain length has also been observed in the case of the six-co-ordinate, d^6 analogues [OsX$_2$(L–L)$_2$].[5] These results are noteworthy in view of the scarcity of five-co-ordinate complexes of riuthenium(II) and in general of d^6 metal ions. In this context we have been investigating ruthenium(II) complexes with the ligand 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye), which forms a six-membered chelate ring. A preliminary communication on the synthesis of [RuCl$_2$(ppye-*P,N*)$_2$] was made some years ago.[6] We proposed therein that there might be some analogies between the chemical behaviour of the complexes with this P,N-donor ligand and those with the diphosphine Ph$_2$P(CH$_2$)$_3$PPh$_2$(dppp). Also, the former species were expected to be more electron-rich than the dppp analogues and thereby facilitate oxidative-addition reactions.

On the other hand, we decided to study the co-ordinating behaviour of ppye toward ruthenium also in view of the general interest in complexes with unsymmetrical, bidentate ligands containing both P and hard donor atoms such as N[7a–e] and O,[8] in particular with respect to the development of novel homogeneous catalysts. An important feature of these potentially chelating ligands is the ease with which their weakly co-ordinating, hard end can be displaced from the metal in solution to provide a vacant co-ordination site for substrate binding. In the case of ruthenium(II) most work has been done with complexes of hybrid ligands containing P and O donor sites,[9] whereas little has been reported with the P,N-donor ligands.[7c,10] To date the ppye ligand has been used to prepare complexes of nickel,[11–13] palladium,[14] copper,[11] rhodium,[15] and iridium,[15,16] in which it acts either as a chelating bidentate or as a P-bound, unidentate ligand. It should be noted that this ligand exhibits a very different co-ordinating ability when compared to the related 2-(diphenylphosphino)pyridine, which has been used as a convenient building block for binuclear complexes.[17]

The ppye ligand looked attractive in that the six-co-ordinate derivatives [RuX$_2$(ppye-*P,N*)$_2$] were expected to dissociate in solution yielding an open site at the metal by alternative rupture either of the Ru–N or of the Ru–X bonds, depending on the experimental conditions. In this paper we describe the synthesis and reactivity of the complexes [RuX$_2$(ppye-*P,N*)$_2$] and of the dicationic dimers [Ru$_2$X$_2$(ppye-*P,N*)$_4$][PF$_6$]$_2$, which have been characterized by means of UV/VIS and NMR spectroscopy. The dimeric structure of [Ru$_2$Cl$_2$(ppye-*P,N*)$_4$][PF$_6$]$_2$ in the solid state has been assessed crystallographically.

Results and Discussion

Octahedral Complexes trans,cis,cis-[RuX$_2$(ppye-*P,N*)$_2$] **1a**–**1c**.‡ —The ligand ppye reacts with [RuX$_2$(dmso)$_4$][18] (dmso = dimethyl sulfoxide, X = Cl or Br) in a 2 : 1 molar ratio in boiling toluene to yield the yellow-orange or brick-red, diamagnetic complexes *trans,cis,cis*-[RuX$_2$(ppye-*P,N*)$_2$] (X = Cl **1a** or Br **1b**). The iodo analogue **1c** was obtained as a purple solid by refluxing **1a** in acetone with an excess of NaI. The geometry of the dihalide derivatives **1** was established by UV/VIS, IR and NMR spectroscopy. Their solid-state electronic spectra are very similar to each other, with a band in the 470–535 nm region and a shoulder at about 400 nm (Table 1), suggesting that they have the same structure. The energies of the maxima produce the usual spectrochemical series I < Br < Cl. The spectral pattern is related to those of similar six-co-ordinate complexes of ruthenium(II) with a P$_4$X$_2$ donor

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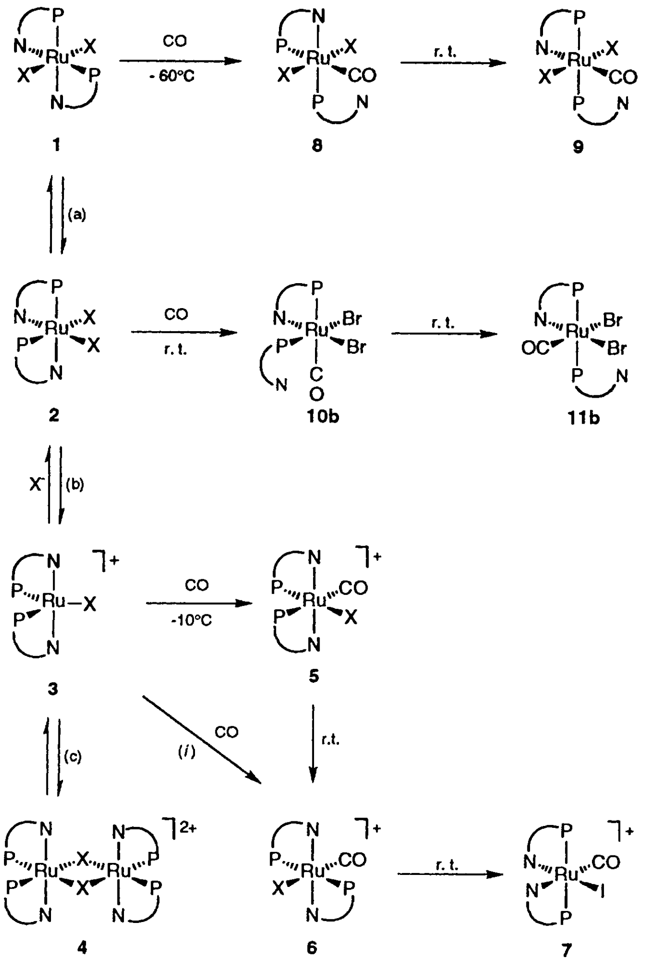
‡ Throughout this paper the *cis* and *trans* notation refers to the pairs of X, P or N atoms bound to the metal.



Scheme 1 r.t. = Room temperature. In CH_2Cl_2 solution, unless otherwise stated. (*i*) Heat, EtOH

Table 1 The UV/VIS data for complexes **1** and **4**

	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1} for solution)	
Complex	CH_2Cl_2 solution	Nujol mull
1a	390 (sh), 475 (550)	400 (sh), 470
1b	400 (sh), 490 (220)[a]	410 (sh), 505
1c[b]	360 (sh), 460 (1540)	385 (sh), 535
4a[c]	360 (sh), 440 (1760)	385 (sh), 440 (sh)
4b[c]	360 (sh), 450 (1720)	390 (sh), 450 (sh)
4c[c]	360 (sh), 460 (1520)	380 (sh), 460 (sh)

[a] In toluene solution. [b] In solution complex **1c** dissociates quantitatively to **3c**. [c] In 10^{-3} mol dm^{-3} solution, the predominant species is **3** (see text); ε calculated assuming quantitative dissociation.

set.[4b,c,19] Six-co-ordination is also supported by the IR spectra which show a band in the 1600–1605 cm^{-1} region (Table 2), attributable to the ring stretching vibration of the co-ordinated pyridyl groups.[11,12,15,20]

The solution chemistry of complexes **1a**–**1c** is markedly dependent upon the nature of the solvent. In the case of **1a** the toluene or dichloromethane solution spectra are similar to the solid-state ones, suggesting that the complex does not undergo structural rearrangements upon dissolution in these solvents. The stereochemistry of **1a** was assessed on the basis of IR and NMR spectroscopy. The IR spectrum in Nujol mull exhibits a single Ru–Cl stretching at 325 cm^{-1}, which can be assigned to terminal chlorines in mutually *trans* positions.[21] The presence of two equivalent phosphorus atoms can be inferred from the single signal at δ 34.8 in the ^{31}P-{^{1}H} NMR spectrum (Table 3). Moreover, the ^{13}C-{^{1}H} NMR spectrum shows two different pairs of equivalent phenyl groups, whose *ipso*-^{13}C atoms appear as five-line multiplets (X part of an AA'X spin system) due to coupling to the P atoms. While one of the multiplets is overlapped with other resonances, the other one is clearly visible. Its simulation gives a value of 36.2 Hz for ^2J(P–P'), which is consistent with a *cis* arrangement of the P atoms.[22] A similar geometry has been reported recently for the related [$RuCl_2\{Ph_2P(CH_2)_2OMe$-*P*,*O*$\}_2$].[9c] Upon standing in CH_2Cl_2 solution at room temperature, **1a** slowly undergoes partial isomerization to all-*cis*-[$RuCl_2$(ppye-*P*,*N*)$_2$] **2a**, in which the P atoms of the ppye ligands occupy inequivalent *cis* positions, as indicated by the appearance of two doublets at δ 32.5 and 38.2 [^2J(P–P') = 36.1 Hz] in the ^{31}P NMR spectrum of aged solutions of **1a**. In co-ordinating solvents such as acetonitrile, complex **1a** gives rise to conducting solutions with formation of the solvates [RuCl(solvent)(ppye-*P*,*N*)$_2$]$^+$.

Visible and ^{31}P NMR spectral measurements (Tables 1 and 3) suggest that the dibromo complex **1b** possesses a similar structure in non-polar solvents such as toluene. These data were obtained for saturated solutions due to the very low solubility of this species. By contrast, the ^{31}P NMR spectrum in dichloromethane solution shows, along with the signal assigned to **1b** at δ 36.2, two doublets centred at δ 30.3 and 38.9 [^2J(P–P') = 32.4 Hz], which can be attributed to the all-*cis* isomer **2b**. Thus partial isomerization of **1b** to **2b** occurs on the time-scale of dissolution in the solvent. The integrated intensities of the signals indicate that **1b** and **2b** are in an approximate 1 : 2 molar ratio in a *ca.* 0.1 mol dm^{-3} solution at room temperature. The doublets assigned to **2b** are rather broad, and sharpen upon addition of bromide ions, thus suggesting an exchange process between free and co-ordinated bromide which is fast on the NMR time-scale. As the temperature is lowered the doublets of **2b** lose intensity and two new, broad signals appear at δ 36.5 and 64.0 (−20 °C), suggesting the occurrence of equilibria (b) and (c) (Scheme 1). Equilibrium (b) involves the dissociation of **2b** to give the five-co-ordinate cation [RuBr(ppye-*P*,*N*)$_2$]$^+$ **3b**, which gives rise to the signal at δ 64.0. The latter species partially dimerizes forming [(ppye-*P*,*N*)$_2$Ru(μ-Br)$_2$Ru(ppye-*P*,*N*)$_2$]$^{2+}$ **4b**, as indicated by the singlet at δ 36.5 (see below). Direct evidence for a dissociative process involving bromide also comes from the molar conductivity of a 10^{-3} mol dm^{-3} dichloromethane solution, which increases with time from a starting value close to zero to about 15 Ω^{-1} cm^2 mol^{-1}. The labilization of the bromide in **2b** provides another example of the high *trans* effect of the P donor in six-co-ordinate ruthenium(II) complexes.[5]

Finally, the diiodo derivative **1c** is insoluble in non-polar solvents such as toluene, but dissolves in dichloromethane with quantitative conversion into the cationic, five-co-ordinate species [RuI(ppye-*P*,*N*)$_2$]$^+$ **3c**, as indicated by conductivity and spectroscopic data. The molar conductance of a 10^{-3} mol dm^{-3} dichloromethane solution of **1c** is near to the typical values of a 1 : 1 electrolyte (Table 4).[23] The UV/VIS spectrum in CH_2Cl_2 solution shows a band at 460 nm which is not present in the solid-state spectrum. Such a spectral pattern rules out the formation of a dimeric structure containing halide bridges (see below), as well as the possibility of strong solvation, since the yellow, six-co-ordinate solvates [RuX(solvent)(ppye-*P*,*N*)$_2$]$^+$ do not exhibit definite absorptions in the visible region. Moreover, the ^{31}P NMR spectra of a CH_2Cl_2 solution of **1c** (concentration range 10^{-3}–10^{-1} mol dm^{-3}) show a single resonance at δ 62.1, attributable to **3c**, which remains unchanged upon lowering the temperature to −90 °C. No other species are present at concentrations detectable by NMR spectroscopy. The six-co-ordinate adducts [RuI(solvent)(ppye-*P*,*N*)$_2$]$^+$ are formed in more co-ordinating solvents such as acetonitrile or nitromethane, as indicated by the ^{31}P NMR resonances in the range δ 30–50.

Also the ^{1}H and ^{13}C NMR spectra of complex **3c**, which are invariant between 30 and −90 °C, suggest that the five-co-

Table 2 Selected IR and ^{13}C-{^1H} NMR data

	IR[a]			^{13}C-{^1H}[b]	
Complex	ν(CO)	ν(Ru–Cl)	ν(py CN)	δ(CO)	^2J(C–P)/Hz
1a		325	1603		
1b			1602		
1c			1603		
4a		280	1603		
4b			1606		
4c			1603		
5a	1996	329	1604	197.9 (dd)	13.0, 107.6
5b	1990		1605	198.3 (dd)	12.6, 105.4
5c	1989			199.8 (dd)	10.9, 103.2
6a	1939	308	1603	199.4 (t)	13.8
6b	1938		1606	199.3 (t)	13.2
6c	1956[c]				
7c	1948		1605	204.3 (t)	13.8
8a	1970	331	1604, 1586	*d*	
9a	1950	335	1603, 1587	205.3 (t)	14.9

[a] Nujol mull. [b] In CD_2Cl_2. Multiplicity in parentheses: dd = doublet of doublets, t = triplet. [c] Impure product. [d] Signal of ^{13}CO not detected due to low solubility.

Table 3 ^{31}P-{^1H} NMR data[a]

	^{31}P-{^1H}	
Complex	δ	^2J(P–P′)/Hz
1a	34.8 (s)	36.2[b]
1b	36.2 (s)	
1c	62.1 (s)[c]	
2a	32.5 (d), 38.2 (d)	36.1
2b	30.3 (d), 38.9 (d)	32.4
3a	70.5 (s)	
3b	68.3 (s)	
3c	62.1 (s)	
4a	36.7 (s)	
4b	37.3 (s)	
4c	62.1 (s)[c]	
5a	5.8 (d), 29.5 (d)[d]	25.4
5b	4.5 (d), 31.2 (d)[d]	24.6
5c	2.3 (d), 30.3 (d)[d]	28.8
6a	27.1 (s)	
6b	24.8 (s)	
6c	21.5 (s)	
7c	13.7, 22.2[e]	283.0
8a	6.6 (d), 35.0 (d)[f]	30.5
9a	18.2, 27.8[e]	332.4
9b	16.5, 27.3[e]	328.0
10b	−4.5 (d), 37.7 (d)	26.4
11b	14.5, 22.3[e]	292.5

[a] In CD_2Cl_2 at room temperature, unless otherwise stated. Multiplicity in parentheses: s = singlet, d = doublet. [b] Computer simulation of multiplet of one of phenyl *ipso*-C atoms of ppye (X part of AA′X spin system) gives: $\delta_X = 144.9$, $J(A\text{–}A') = -36.2$, $J(A\text{–}X) = 41.9$, $J(A'\text{–}X) = -1.4$ Hz. [c] Only complex **3c** present in solutions of **1c** or **4c**. [d] $T = 253$ K. [e] AB spin system. [f] $T = 233$ K.

ordinate $[RuI(ppye\text{-}P,N)_2]^+$ is stereochemically rigid. If cation **3c** is assigned a trigonal-bipyramidal structure as that of the related $[RuX(L\text{–}L)_2]^+$ (L–L = diphosphine),[4c,e,24] then we favour structure **3**, in which the two equivalent P atoms are in the equatorial plane. This structure is supported by the presence of two types of phenyl groups in the ^{13}C NMR spectrum, with the form of the two *ipso*-^{13}C multiplets indicating that the value of ^2J(P–P′) is lower than required for a *trans* arrangement of the P atoms.[22] It should be noted that the analogues $[RuX(dppp)_2]^+$ give a static ^{31}P NMR spectrum at room temperature.[4c] Finally, no changes were observed in the UV/VIS and ^{31}P NMR spectra of CH_2Cl_2 solutions of **1c** upon addition of an excess of NBu_4I. The solution behaviour of complexes **1a**–**1c** clearly indicates that the tendency of the six-co-ordinate $[RuX_2(ppye\text{-}P,N)_2]$ derivatives to dissociate markedly increases with increasing size of the halogen, as found for the diphosphine analogues $[RuX_2(L\text{–}L)_2]$.[4e]

Dihalide-bridged Complexes $[Ru_2X_2(ppye\text{-}P,N)_4][PF_6]_2$.—Attempts to isolate the five-co-ordinate cations **3** in the solid state as the hexafluorophosphate salts invariably led to the binuclear compounds $[(ppye\text{-}P,N)_2Ru(\mu\text{-}X)_2Ru(ppye\text{-}P,N)_2][PF_6]_2$ (X = Cl **4a**, Br **4b** or I **4c**). Thus, when the six-co-ordinate complexes **1a**–**1c** are refluxed in ethanol in the presence of NH_4PF_6, yellow-to-ochre, air-stable crystals of **4a**–**4c** are rapidly formed. The chloro and bromo derivatives are more directly prepared by reaction of the appropriate $[RuX_2(dmso)_4]$ species with 2 equivalents of the ppye ligand in boiling ethanol in the presence of an excess of NH_4PF_6.

The binuclear structure of complex **4a** has been assessed by means of a single-crystal X-ray analysis (see below). As the solid-state electronic spectra of **4a**–**4c** closely resemble each other (Table 1), we assume that these species all possess the same binuclear structure. The solution behaviour of the binuclear complexes depends on the temperature, size of the halogen, and nature of the solvent. Evidence was obtained from visible and ^{31}P NMR data that **4a**–**4c** dissociate in CH_2Cl_2 solution to give the five-co-ordinate species $[RuX(ppye\text{-}P,N)_2]^+$ (X = Cl **3a**, Br **3b** or I **3c**) in agreement with equilibrium (c) (Scheme 1). The presence of the $[RuX(ppye\text{-}P,N)_2]^+$ chromophore in diluted CH_2Cl_2 solutions (10^{-3} mol dm^{-3}) of **4** is suggested by the appearance of a well defined UV/VIS band in the 440–460 nm region, which is absent in the solid-state spectra. Moreover, the ^{31}P-{^1H} NMR spectra of 10^{-3} mol dm^{-3} solutions of **4a**–**4c** exhibit a sharp singlet in the range δ 62–71, which can be attributed to the five-co-ordinate cations **3a**–**3c**. The position of this equilibrium, however, depends markedly on the size of the halide. Thus, the ^{31}P NMR spectrum of a 10^{-3} mol dm^{-3} solution of **4a** shows, along with the signal of **3a** at δ 70.5, a singlet at δ 36.7 which can be attributed to undissociated **4a**. The integrated intensities of these signals indicate that dissociation of dimer **4a** is about 75% complete. Upon increasing the concentration of the solutions, the signal of the binuclear species gains in intensity, and in a 10^{-1} mol dm^{-3} solution of **4a** dissociation is depressed to *ca.* 5%. In the case of the bromo derivative **4b** the signal attributable to the dimeric species appears only in concentrated solutions, the ^{31}P NMR spectrum of a 10^{-1} mol dm^{-3} solution indicating that dissociation of **4b** as high as 95% complete. Finally, complex **3c** is quantitatively formed even in saturated dichloromethane solutions and no evidence for the presence of **4c** was obtained.

Table 4 Analytical and physical data

Complex	Colour	$\Lambda_M{}^a/\Omega^{-1}$ cm^2 mol^{-1}	Analysis^b (%)		
			C	H	N
1a *trans,cis,cis*-[RuCl$_2$(ppye-*P*,*N*)$_2$]	Yellow-orange	1	60.40 (60.50)	4.80 (4.80)	3.70 (3.70)
1b *trans,cis,cis*-[RuBr$_2$(ppye-*P*,*N*)$_2$]	Brick-red	15^c	54.10 (54.10)	4.30 (4.30)	3.25 (3.30)
1c *trans,cis,cis*-[RuI$_2$(ppye-*P*,*N*)$_2$]	Purple	41^d	47.60 (48.70)	3.85 (3.85)	2.95 (3.00)
4a [Ru$_2$Cl$_2$(ppye-*P*,*N*)$_4$][PF$_6$]$_2$	Yellow	48^d	52.80 (52.80)	4.20 (4.20)	3.25 (3.25)
4b [Ru$_2$Br$_2$(ppye-*P*,*N*)$_4$][PF$_6$]$_2$	Ochre-yellow	46^d	49.80 (50.25)	4.05 (4.00)	2.95 (3.10)
4c [Ru$_2$I$_2$(ppye-*P*,*N*)$_4$][PF$_6$]$_2$	Ochre	46^d	47.50 (47.75)	3.80 (3.80)	2.85 (2.95)
5a *cis,trans*-[RuCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$	Pale yellow	73^e	52.45 (52.50)	4.05 (4.05)	3.15 (3.15)
5b *cis,trans*-[RuBr(CO)(ppye-*P*,*N*)$_2$]PF$_6$	Pale yellow	74^e	49.45 (50.00)	3.80 (3.85)	3.00 (3.00)
5c *cis,trans*-[RuI(CO)(ppye-*P*,*N*)$_2$]PF$_6$	Yellow	73^e	47.35 (47.60)	3.65 (3.70)	2.80 (2.85)
6a *trans,trans*-[RuCl(CO)(ppye-*P*,*N*)$_2$]PF$_6$	White	76^e	52.40 (52.50)	4.10 (4.05)	3.15 (3.15)
6b *trans,trans*-[RuBr(CO)(ppye-*P*,*N*)$_2$]PF$_6$	White	75^e	49.05 (50.00)	3.85 (3.85)	3.05 (3.00)
7c *trans,cis*-[RuI(CO)(ppye-*P*,*N*)$_2$]PF$_6$	White	76^e	47.25 (47.60)	3.60 (3.70)	2.80 (2.85)
8a [RuCl$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)]	Yellow	—	59.45 (59.85)	4.60 (4.65)	3.70 (3.70)
9a [RuCl$_2$(CO)(ppye-*P*)(ppye-*P*,*N*)]	Pale yellow	—	58.90 (59.85)	4.65 (4.65)	3.50 (3.70)

[a] In 10^{-3} mol dm^{-3} CH$_2$Cl$_2$ solution, unless otherwise stated. [b] Required values are given in parentheses. [c] 30 min after dissolution. [d] Species **3** present in solution. [e] In 10^{-3} mol dm^{-3} MeNO$_2$ solution.

This observation shows that the stability of the binuclear species **4** decreases with increasing halide size.

Moreover, ^{31}P NMR measurements indicate that equilibrium (c) is shifted toward dimer **4** by lowering the temperature. Accordingly, the signal of complex **3a** is not detected in the ^{31}P NMR spectrum of a 10^{-1} mol dm^{-3} solution of **4a** recorded at −60 °C. The dissociation of **4b** is depressed to about 30% under the same experimental conditions. The iodo derivative **4c** is completely dissociated to five-co-ordinate **3c** even at −80 °C, as no evidence for the presence of a dimeric species was obtained from the low-temperature ^{31}P NMR spectra.

The addition of an excess of halide ions to a dilute dichloromethane solution of complex **4a** or **4b** results in the formation of a mixture of the six-co-ordinate isomers **1a**, **2a** or **1b**, **2b** according to equilibria (b) and (a) (Scheme 1). It is probable that the addition reaction to five-co-ordinate **3** occurs stereoselectively with fast formation of the all-*cis*, six-co-ordinate adducts **2a**, **2b**, as already found for [RuX(dcpe)$_2$]$^+$ [dcpe = (C$_6$H$_{11}$)$_2$P(CH$_2$)$_2$P(C$_6$H$_{11}$)$_2$].[4e] The all-*cis* complexes isomerize into the *trans*, *cis*, *cis* species **1a**, **1b** giving the observed equilibrium mixture. In the case of the five-co-ordinate **3c**, no change is observed in the visible and ^{31}P NMR spectral patterns upon addition of an excess of iodide to the solution.

Complexes **4a**–**4c** dissolve in more co-ordinating solvents such as MeCN forming the solvates [RuX(MeCN)(ppye-*P*,*N*)$_2$]$^+$.

Carbonyl Complexes.—Complexes **1a**–**1c** and **4a**–**4c** react with carbon monoxide to give the carbonyl derivatives summarized below. The cationic isomeric pairs **5a**–**5c** and **6a**–**6c**, as well as the neutral isomers **8a**, **8b**, **9a**, **9b**, **10b** and **11b** were either isolated or observed in solution.

The carbonyl adducts [RuX(CO)(ppye-*P*,*N*)$_2$]$^+$ are formed when a CH$_2$Cl$_2$ solution of the binuclear complexes **4** is treated with carbon monoxide. The kinetic products **5** are stereoselectively formed at low temperature, while the thermodynamically stable isomers **6** are obtained at room temperature. The carbonylation reaction, which can be conveniently followed by ^{31}P NMR spectroscopy, apparently occurs *via* addition of the CO ligand to the co-ordinatively unsaturated, five-co-ordinate **3** which are present in the solutions of **4** according to equilibrium (c) (Scheme 1). It should be noted that the addition of CO occurs stereoselectively *trans* to a P atom also in the case of the five-co-ordinate analogues [MX(dcpe)$_2$]$^+$ (M = Ru or Os).[5] The resulting adducts are then thermally converted into the corresponding derivatives in which the CO and halide ligands occupy mutually *trans* positions.

The complexes **5a**–**5c** were prepared by stirring a CH$_2$Cl$_2$ solution of **4a**–**4c** under a carbon monoxide atmosphere at −10 °C. Addition of propan-2-ol to the cold solution affords yellow crystals. These compounds are 1 : 1 electrolytes in nitromethane, and their Nujol-mull IR spectra show a strong absorption in the 1989–1996 cm^{-1} region, attributed to the CO stretching vibration. The presence of *cis*-P atoms is inferred from the ^{31}P NMR spectra of freshly prepared CH$_2$Cl$_2$ solutions at −20 °C, which show two doublets in the regions δ 2.3–5.8 and 29.5–31.2, respectively, with a ^2J(P–P′) of about 25 Hz. In agreement with structure **5**, the ^{13}CO NMR resonance appears as a doublet of doublets with $^2J(\mathrm{P–C})_{trans} \gg {}^2J(\mathrm{P–C})_{cis}$ (Table 2).

The all-*trans* isomers **6a**, **6b** can be obtained as white products by refluxing **4a**, **4b** in ethanol under a carbon monoxide atmosphere. Consistently with a *trans* arrangement of P atoms, the ^{31}P NMR spectra of **6a**, **6b** show a sharp singlet in the region δ 24–27, while the ^{13}CO NMR resonance appears as a triplet. Moreover, the IR spectra show ν(CO) absorptions at about 1938 cm^{-1}, with a significant lowering in energy with respect to the *cis* analogues **5a**, **5b**, in agreement with a substantial increase in the Ru-to-CO back bonding. The higher stability of isomers **6** with respect to **5** is ascribed to the overall enhancement of the metal-to-ligand back donation when the CO and PPh$_2$ groups do not compete for the same set of metal π electrons. The iodo derivative **4c** reacts with CO forming first **5c** and then **6c**. The latter product cannot be obtained pure in the solid state, as it isomerizes giving a final species which probably possesses structure **7**, the CO group being *trans* to a pyridyl ring. Thus the ^{31}P NMR spectrum of a CH$_2$Cl$_2$ solution of **4c** under CO shows the stepwise appearance of the two doublets typical of isomer **5c**, followed by the increase of a sharp singlet at δ 21.5, which is attributed to **6c**. In turn, this species is converted into a new product showing an AB NMR pattern with a ^2J(P–P′) of 283 Hz, indicative of the presence of inequivalent P atoms occupying mutually *trans* positions. The values of the CO stretching frequencies are 1956 and 1948 cm^{-1} for **6c** and **7c**, respectively. The ^{13}C NMR data for **7c** are consistent with the assigned geometry (Table 2).

Complexes **5** and **6** can be also obtained by direct reaction of carbon monoxide with the six-co-ordinate **1** under conditions favouring halide-ion dissociation. Though the octahedral species **1** are only sparingly soluble in methanol at room temperature, they readily dissolve upon stirring at 40 °C. In agreement with equilibrium (c) (Scheme 1), derivatives **3** and **4** are the main components of these solutions, as can be inferred from the ^{31}P NMR spectra. Accordingly, these solutions react with carbon monoxide to give the carbonyl derivatives **5** or **6** depending on the reaction temperature.

As expected on the basis of the semilabile character of ppye, complexes **1** react with carbon monoxide also with dissociation of the Ru–N bond. Thus, **8a** is formed as a yellow, microcrystalline powder when an alcoholic suspension of **1a** is stirred under a carbon monoxide atmosphere for 3 h at −10 °C. The product is stable in the solid state and its Nujol-mull IR spectrum shows a strong ν(CO) band at 1970 cm^{-1}. The isomer **9a**, obtained when CH_2Cl_2 solutions of **1** are treated with carbon monoxide at room temperature, exhibits a ν(CO) absorption at 1950 cm^{-1} (Nujol mull).

The stepwise formation of the neutral species **8a** and **9a** in the reaction between **1a** and carbon monoxide in dichloromethane can be conveniently followed by IR and ^{31}P NMR spectroscopy. When carbon monoxide is bubbled through a CH_2Cl_2 solution of the chloro derivative **1a** at room temperature the orange colour fades and a strong absorption appears in the IR spectrum at 1976 cm^{-1}. Within a few minutes this band is replaced by a new strong absorption at 1950 cm^{-1}. If the solution is cooled to −60 °C before bubbling CO a pale yellow solution is obtained, the ^{31}P NMR spectrum of which exhibits two doublets centred at δ 6.6 and 35.0, with a ^2J(P–P′) of 30.5 Hz, in agreement with the presence of two inequivalent P atoms occupying mutually *cis* positions. An identical spectral pattern is obtained when **8a** is dissolved in CH_2Cl_2 at low temperature. When the sample temperature is raised, the two doublets are eventually replaced by an AB system (δ_A 18.2, δ_B 27.8). The ^2J(P–P′) value of 332 Hz suggests that the P atoms occupy mutually *trans* positions. Addition of hexane to these solutions gives pale yellow crystals of the carbonyl derivative **9a**.

A further assessment of the geometry of complexes **8a** and **9a** comes from their IR and ^{13}C NMR spectra (Table 2). The observation of a single Ru–Cl stretching vibration in the far-IR spectra of both complexes at about 330 cm^{-1} strongly suggests that the chlorine atoms are mutually *trans*. Moreover, the appearance of two different pyridyl ring vibrations in the spectra of **8a** and **9a** indicates the presence both of co-ordinated and of dangling pyridyl groups.[11,12,15,20] Accordingly, the ^{13}C NMR spectra of both isomers exhibit two non-equivalent pyridyl groups. The carbonyl carbon atom *cis* to both PPh_2 groups in **9a** appears as a triplet, while no ^{13}CO signals were detected in the ^{13}C NMR spectrum of **8b** at −20 °C, owing to the low solubility of this complex. These data suggest that the co-ordination of CO involves the dissociation of a pyridyl arm and the formation of a six-co-ordinate adduct in which one ppye ligand is bidentate and the other is P-bound, unidentate. It is likely that an adduct of type **8**, with the CO group *trans* to the P atom of the chelating ppye, is initially formed also in the room-temperature reaction. Complex **8** isomerizes in solution at room temperature giving **9**, in which CO is *trans* to N. This isomer appears to be favoured with respect to **8**, in which the CO and P groups are mutually *trans* and compete for the electron density residing in the same metal orbital. The isomerization rate is not affected by the presence of CO, and no retardation effect is observed in the presence of large excesses of halide ions. Therefore, it appears probable that the *cis* to *trans* isomerization involves cleavage of the Ru–N bond *trans* to P, with the formation of a five-co-ordinate intermediate which contains two unidentate ppye ligands.

The reaction of the six-co-ordinate bromo derivative **1b** with carbon monoxide in CH_2Cl_2 solution gives rise to a mixture of different carbonyl adducts, the nature of which can be tentatively inferred from the ^{31}P NMR data. After a few minutes, the spectrum of a CH_2Cl_2 solution of **1b** under CO shows signals attributable to **9b** and **5b**, together with another doublet of doublets at δ 37.7 and −4.5 [^2J(P–P′) = 26.4 Hz], which can be attributed to the presence of an isomer of type **10b**. The upfield chemical shift value of the resonance at δ −4.5 suggests a *trans* arrangement of one P atom with respect to the CO ligand.[25] With time complex **5b** isomerizes to the corresponding *trans* isomer **6b** (singlet at δ 24.8), while **10b** is converted into a stabler isomer, probably **11b**, in which the two inequivalent P atoms occupy mutually *trans* positions. In the IR spectrum (CH_2Cl_2 solution), only two very broad carbonyl absorptions were observed at 1990 and 1950 cm^{-1}. The equilibria in Scheme 1 can account for the different types of carbonyl derivatives formed in this reaction. The isomeric pair **10b** and **11b**, which was not isolated in the solid state, probably arises from the all-*cis* complex **2b** *via* dissociation of the Ru–N bond *trans* to the P atom. The other carbonyl adducts which are present in the reaction mixture are those expected to arise from the stepwise carbonylation of complexes **1b** and **3b**.

In the case of iodo derivative **1c**, which is completely dissociated in CH_2Cl_2 solution to give the five-co-ordinate **3c**, the reaction with CO leads to the same products as obtained starting from **4c**.

Crystal and Molecular Structure of $[Ru_2Cl_2(ppye\text{-}P,N)_4][PF_6]_2$.—An ORTEP[26] drawing of the core of the binuclear cation $[(ppye\text{-}P,N)_2Ru(\mu\text{-}Cl)_2Ru(ppye\text{-}P,N)_2]^{2+}$ is shown in Fig. 1 with the atom numbering scheme, the phenyl rings being omitted for clarity. Final fractional coordinates of non-H atoms are in Table 5 and selected bond lengths and angles in Table 6. The Ru atoms present a pseudo-octahedral co-ordination with the two octahedra sharing an edge *via* the Cl atoms, which lie on a crystallographic two-fold axis. The chlorine atoms bridge the metallic centres at a mean bond length of 2.490(1) Å, with Cl(1)–Ru–Cl(2) and Ru–Cl–Ru′ bond angles of 78.15(4) and 101.85(6)° (mean value), respectively, which provide a clear indication of the distorted co-ordination about the metal. The Ru–P distances are similar within experimetal errors, while the Ru–N bond lengths are slightly different (Table 6). The plane defined by Ru and the co-ordinated P atoms makes a dihedral angle of 7.3(4)° with the $RuCl_2Ru$ mean plane, which is similar to that found in other dimeric, doubly halide-bridged Ru complexes.[27a] The P atoms are displaced by −0.230(3) and +0.199(3) Å from the $RuCl_2Ru$ mean plane.

The two chelating ppye ligands co-ordinate the Ru atom with the pyridine donors in *trans* positions, which allows minimization of non-bonded interactions between the two monomeric units. The shortest contact between the facing pyridyls is N(2)···C(1) 3.35(1) Å. The mean planes of the two independent pyridine rings make an angle of 37.5(5)° and are essentially perpendicular to the plane defined by the bridging Cl and the Ru atoms, the dihedral angles being 89.4(2) and 87.6(2)°. The phenyl rings at either side of the binuclear cation are parallel and face each other (Fig. 2) with non-bonded interactions of about 3.5 Å. The ppye ligands exhibit bite angles in the range observed for complexes of Rh^I and Ir^I (83.4–93.7°].[15] The bond lengths and angles within each ppye ligand are not unusual and are similar to those in other ppye complexes.[15]

The most striking feature of the structure is the long Ru···Ru distance of 3.867(1) Å indicating no intermetallic interaction is present. This distance is considerably longer than those found in other ruthenium(II) complexes containing a $RuCl_2Ru$ fragment (3.515–3.680 Å).[27] Also, the Ru–Cl bond distances in **4a** are significantly longer than those found in the same group (mean value 2.443 Å), and both Ru–Cl–Ru and Cl–Ru–Cl angles fall outside the range observed before (93.3–95.7 and 83.1–86.6°, respectively).[27] The non-bonded interactions between the pyridyl rings of the ppye ligands appear to be responsible for the strain in the chloride bridge, which might also account for the dissociation of dimers **4** in solution.

Conclusion

These results show that the chemistry of the six-co-ordinate ppye complexes of ruthenium(II) parallels that of the diphosphine derivatives $[RuX_2(dppp)_2]$, with the same strong tendency to dissociate (even in solvents of fairly low relative permittivity such as CH_2Cl_2) giving the five-co-ordinate species $[RuX(ppye\text{-}P,N)_2]^+$. Both ligands form six-membered rings

Table 5 Fractional atomic coordinates with estimated standard deviations in parentheses for the non-hydrogen atoms of complex **4a**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	0.097 04(6)	0.211 41(3)	0.181 04(3)	C(22)	0.100(1)	0.050 7(5)	0.290 8(5)
Cl(1)	0.215 4(3)	0.250	0.250	C(23)	0.012(1)	0.065 7(5)	0.266 9(5)
Cl(2)	−0.021 4(3)	0.250	0.250	C(24)	0.003 9(9)	0.111 8(4)	0.238 0(4)
P(1)	0.219 4(2)	0.171 9(1)	0.129 0(1)	C(25)	−0.094(1)	0.127 9(4)	0.212 3(4)
P(2)	−0.033 1(2)	0.187 9(1)	0.123 1(1)	C(26)	−0.097 1(9)	0.130 3(4)	0.148 5(4)
N(1)	0.112 3(6)	0.282 8(3)	0.136 5(3)	C(27)	−0.140 0(8)	0.233 1(4)	0.119 3(4)
N(2)	0.085 8(6)	0.143 3(3)	0.233 0(3)	C(28)	−0.153(1)	0.266 6(5)	0.073 5(5)
C(1)	0.031 0(9)	0.314 8(4)	0.138 2(5)	C(29)	−0.230(1)	0.302 3(6)	0.074 2(6)
C(2)	0.025(1)	0.360 5(5)	0.109 9(5)	C(30)	−0.295(1)	0.305 3(6)	0.119 3(6)
C(3)	0.104(1)	0.376 2(5)	0.078 4(5)	C(31)	−0.285(1)	0.274 1(6)	0.162 1(6)
C(4)	0.190(1)	0.346 9(5)	0.078 3(5)	C(32)	−0.208 5(9)	0.236 6(5)	0.160 5(5)
C(5)	0.192 6(9)	0.300 2(4)	0.106 9(4)	C(33)	−0.009 7(8)	0.175 5(4)	0.049 3(4)
C(6)	0.287 8(9)	0.270 2(5)	0.106 9(5)	C(34)	0.043 1(8)	0.211 8(5)	0.017 9(4)
C(7)	0.278 6(8)	0.216 2(5)	0.080 6(4)	C(35)	0.063 8(8)	0.203 0(6)	−0.038 8(4)
C(8)	0.331 8(8)	0.147 1(5)	0.166 3(4)	C(36)	0.032 3(9)	0.157 0(5)	−0.063 6(5)
C(9)	0.394 3(9)	0.180 3(5)	0.195 0(5)	C(37)	−0.021 8(9)	0.122 6(5)	−0.033 2(4)
C(10)	0.481(1)	0.162 4(7)	0.223 9(6)	C(38)	−0.043 2(8)	0.130 7(4)	0.022 7(4)
C(11)	0.502(1)	0.111 0(7)	0.222 1(6)	P(3)	0.750	0.000	0.158 2(2)
C(12)	0.441(1)	0.077 8(6)	0.194 5(5)	F(31)	0.716 3(7)	0.056 8(3)	0.157 4(5)
C(13)	0.357 6(9)	0.096 1(6)	0.166 5(5)	F(32)	0.833(1)	0.013 6(4)	0.198 8(5)
C(14)	0.185 0(8)	0.116 1(4)	0.087 3(5)	F(33)	0.824 3(8)	0.014 6(4)	0.109 1(5)
C(15)	0.213 7(8)	0.110 9(5)	0.031 7(4)	P(4)*	0.471(1)	0.065 4(7)	0.422 4(6)
C(16)	0.188 3(9)	0.066 6(5)	0.001 8(5)	F(41)*	0.492(3)	0.010(1)	0.435(1)
C(17)	0.132 7(9)	0.028 0(5)	0.027 6(5)	F(42)*	0.533(3)	0.052(1)	0.367(1)
C(18)	0.108(1)	0.032 7(4)	0.082 1(5)	F(43)*	0.580(3)	0.071(1)	0.447(1)
C(19)	0.133 4(9)	0.076 1(4)	0.113 8(5)	F(44)*	0.359(3)	0.041(1)	0.399(1)
C(20)	0.170 0(8)	0.128 5(4)	0.258 7(4)	F(45)*	0.409(3)	0.069(1)	0.474(1)
C(21)	0.182(1)	0.083 0(5)	0.288 2(5)	F(46)*	0.456(3)	0.110(1)	0.390(1)

* Isotropically refined atoms with occupancy 0.5.

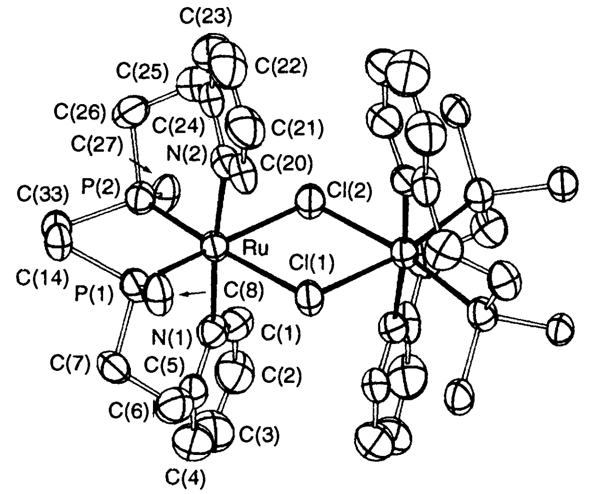


Fig. 1 An ORTEP drawing (ellipsoids at 50% probability) of the cation $[Ru_2Cl_2(ppye\text{-}P,N)_4]^{2+}$ with phenyl rings omitted for clarity (C atoms numbered according to Table 5)

Table 6 Selected bond distances (Å) and angles (°) for complex **4a**

Ru ••• Ru′	3.867(1)	Ru–P(2)	2.297(1)
Ru–Cl(1)	2.490(1)	Ru–N(1)	2.152(4)
Ru–Cl(2)	2.491(1)	Ru–N(2)	2.172(3)
Ru–P(1)	2.290(1)		
Cl(1)–Ru–Cl(2)	78.15(4)	P(1)–Ru–P(2)	94.82(4)
Cl(1)–Ru–P(1)	95.51(4)	P(1)–Ru–N(1)	92.9(1)
Cl(1)–Ru–P(2)	168.94(4)	P(1)–Ru–N(2)	89.7(1)
Cl(1)–Ru–N(1)	85.48(9)	P(2)–Ru–N(1)	90.2(1)
Cl(1)–Ru–N(2)	89.6(1)	P(2)–Ru–N(2)	94.4(1)
Cl(2)–Ru–P(1)	171.46(4)	N(1)–Ru–N(2)	174.6(1)
Cl(2)–Ru–P(2)	91.95(4)	Ru–Cl(1)–Ru′	101.89(6)
Cl(2)–Ru–N(1)	92.29(9)	Ru–Cl(2)–Ru′	101.82(6)
Cl(2)–Ru–N(2)	84.59(9)		

Ru′ unit at $x, \frac{1}{2} - y, \frac{1}{2} - z$.

and probably the steric crowding around the metal centre due to the chelate ring size determines the formation of unsaturated species. However, substitution of a PPh_2 group by 2-pyridyl causes a decrease in the steric hindrance in the d^6, five-co-ordinate cations **3**, thus allowing dimerization to the binuclear species **4**. Both for the Ru–X bond and for the RuX_2Ru bridge, the tendency to dissociate increases with increasing halide size, namely in the order Cl < Br < I. Thus, the five-co-ordinate species **3c** predominates in solutions of **1c** and of **4c**. These results also indicate that the nature of the solvent plays a crucial role in determining different reaction pathways.

The semilabile character of ppye is apparent in the reactivity of complexes **1**, which readily undergo carbonylation in CH_2Cl_2 solution with concomitant dissociation of one pyridyl arm of the chelate. This behaviour can be compared with that of the related complexes $[RuX_2(L\text{–}L')_2]$ containing other P,N-donor ligands, such as *o*-diphenylphosphino-*N*,*N*-dimethylaniline and *o*-diphenylphosphino-*N*,*N*-dimethylbenzylamine, which do not react with CO under ambient conditions.[7c] Apparently the dissociation of the pyridyl moiety is favoured with respect to that of the dimethylamino groups, and therefore the ppye ligand may have greater potential in Ru-based homogeneous catalysis than the aminophosphine ligands.

The second pyridine nitrogen is not displaced by CO, and there is no evidence for the formation of dicarbonyl derivatives in which both ppye molecules act as P-bound ligands. By contrast the $[RuX_2(L\text{–}L')_2]$ complexes containing P,O-donor ligands such as $Ph_2P(CH_2)_2OMe$, *o*-(diphenylphosphino)-anisole or *o*-(diphenylphosphino)benzylmethyl ether readily react with CO to give dicarbonyl derivatives with rupture of both Ru–O bonds.[7c,9c,f] The factors affecting the ease of dissociation of the hard end of these hybrid ligands in the

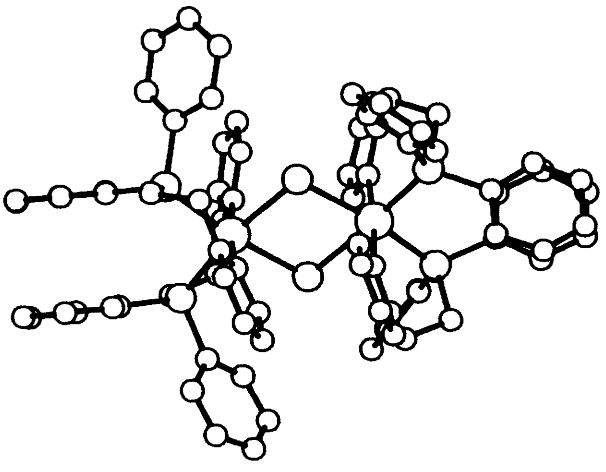


Fig. 2 Side view of the cation $[Ru_2Cl_2(ppye\text{-}P,N)_4]^{2+}$

ruthenium(II) complexes are not yet fully understood. However, bulkiness and basicity as well as the steric strain of the chelate ring appear to be significant factors.

Finally, there is evidence that addition of CO to the cationic or neutral five-co-ordinate, d^6 intermediates occurs stereoselectively to give the corresponding adducts with P and CO groups in mutually *trans* positions. These kinetic products can then isomerize to the thermodynamically preferred isomers in which P and CO are mutually *cis*.

Experimental

All manipulations were performed under argon with use of standard Schlenk-line techniques. All chemicals used were of reagent grade or comparable purity. Solvents were purified by standard procedures. The starting complexes *cis*-$[RuCl_2(dmso)_4]$[18a,b] and *trans*-$[RuBr_2(dmso)_4]$[18c] were prepared by published methods. The ligand ppye was prepared according to Uhlig and Maaser.[11] Infrared spectra were recorded on a JASCO DS 702 G spectrophotometer, UV/VIS spectra on JASCO UVDEC 505 or Varian CARY 2300 spectrophotometers, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR spectra on a Bruker AC 200 F instrument equipped with a variable-temperature QNP probe. 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 simulation for complex **1a** performed with PANIC[28] assuming an AA'X spin system and a negative value for *cis*-^2J(P–P).[29] The X part of the spectrum, however, is invariant with respect to the signs of the coupling constants, provided that ^1J(C–P) and ^3J(C–P') have opposite signs. Molar conductivities at 20 °C were obtained on 10^{-3} mol dm^{-3} nitromethane or dichloromethane solutions with a Metrohm E 518 conductivity bridge. As complexes **1**–**4** form solvates in nitromethane solution, their conductivities were measured in dichloromethane because of its very weak ability to act as donor.[23] Elemental analyses were performed by the Microanalytical Laboratory of Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine.

Preparations.—*trans,cis,cis*-$[RuCl_2(ppye\text{-}P,N)_2]$ **1a**. A slurry of *cis*-$[RuCl_2(dmso)_4]$ (0.97 g, 2.0 mmol) and ppye (1.17 g, 4.0 mmol) in toluene (25 cm^3) was refluxed for 1 h. Upon cooling to 0 °C the deep red solution deposited yellow-orange *crystals* which were filtered off, washed with toluene and light petroleum, and dried *in vacuo*. Recrystallization was from dichloromethane–propan-2-ol. Yield: 1.45 g, 96%.

trans,cis,cis-$[RuBr_2(ppye\text{-}P,N)_2]$ **1b**. A slurry of *trans*-$[RuBr_2(dmso)_4]$ (1.15 g, 2.0 mmol) and ppye (1.17 g, 4.0 mmol) in toluene (25 cm^3) was refluxed for 2 h. After cooling to room temperature, the resulting brick-red solid was filtered off, washed with toluene and light petroleum (b.p. 30–60 °C), and dried *in vacuo*. Recrystallization was from dichloromethane–hexane. Yield: 1.33 g, 79%.

trans,cis,cis-$[RuI_2(ppye\text{-}P,N)_2]$ **1c**. (*a*) Complex **1a** (0.75 g, 1.0 mmol) and NaI (3.0 g, 20 mmol) were suspended in acetone (30 cm^3) and the slurry was refluxed for 48 h. The purple solid formed thereby was filtered off, washed with acetone, and dried *in vacuo*. Recrystallization from dichloromethane–propan-2-ol. Yield: 0.67 g, 72%.

(*b*) Complex **4a** (0.86 g, 0.5 mmol) was used instead of **1a**. Yield: 0.83 g, 89%.

$[Ru_2(\mu\text{-}X)_2(ppye\text{-}P,N)_4][PF_6]_2$ (X = Cl **4a** *or* Br **4b**. (*a*) An ethanol solution (30 cm^3) of $[RuX_2(dmso)_4]$ (1.0 mmol) (X = Cl, 0.48; Br, 0.49 g), ppye (0.59 g, 2.0 mmol), and NH_4PF_6 (0.82 g, 5.0 mmol) was refluxed for 3 h. The precipitate formed upon cooling was filtered off, washed with ethanol and light petroleum, and dried *in vacuo*. Recrystallization was from dichloromethane–propan-2-ol. Yields: **4a**, 97; **4b**, 80%.

(*b*) *For* **4a**. The complex $[RuCl_2(PPh_3)_3]$ (0.96 g, 1.0 mmol) was used instead of *cis*-$[RuCl_2(dmso)_4]$. Yield: 0.81 g, 94%.

$[Ru_2(\mu\text{-}I)_2(ppye\text{-}P,N)_4][PF_6]_2$ **4c**. Complex **1c** (0.94 g, 1.0 mmol) and NH_4PF_6 (1.64 g, 10.0 mmol) were suspended in acetone (20 cm^3) and refluxed for 2 h. Ochre *crystals* were formed, which were filtered off, washed with acetone and hexane, and dried *in vacuo*. Recrystallization was from dichloromethane–propan-2-ol. Yield: 0.70 g, 73%.

cis,trans-$[RuX(CO)(ppye\text{-}P,N)_2]PF_6$ (X = Cl **5a**, Br **5b** *or* I **5c**. (*a*) A dichloromethane solution (10 cm^3) of $[Ru_2(\mu\text{-}X)_2(ppye\text{-}P,N)_4][PF_6]_2$ (0.30 mmol) (X = Cl, 0.52; Br, 0.54; I, 0.57 g) was cooled to −10 °C and then saturated with carbon monoxide. Addition of propan-2-ol (20 cm^3) and evaporation of dichloromethane *in vacuo* afforded yellow *crystals* which were filtered off, washed with ethanol, and vacuum dried. Yields: **5a**, 68; **5b**, 63; **5c**, 67%.

(*b*) *For* **5a**. Complex **1a** (0.15 g, 0.2 mmol) was refluxed in ethanol (20 cm^3) until a homogeneous, orange solution formed, which was cooled to −10 °C and saturated with carbon monoxide. Addition of NH_4PF_6 (0.16 g, 1.0 mmol) in propan-2-ol (20 cm^3) gave a pale yellow precipitate which was filtered off, washed with ethanol, and vacuum-dried. Yield: 0.12 g, 70%.

trans,trans-$[RuCl(CO)(ppye\text{-}P,N)_2]PF_6$ **6a**. (*a*) A dichloromethane solution (5 cm^3) of complex **4a** (0.35 g, 0.20 mmol) was shaken under carbon monoxide for 72 h. Upon addition of propan-2-ol (20 cm^3) and evaporation of dichloromethane, white *crystals* separated which were filtered off and dried *in vacuo*. Yield: 0.27 g, 77%.

(*b*) Complex **1a** (0.15 g, 0.20 mmol) was refluxed in ethanol (10 cm^3) until a homogeneous, orange solution formed, which was cooled to room temperature. Upon saturation with carbon monoxide the solution instantaneously became colourless. After shaking for 2 h, NH_4PF_6 (0.16 g, 1.0 mmol) in propan-2-ol (20 cm^3) was added, and the resulting white precipitate was filtered off, washed with ethanol, and vacuum-dried. Yield: 0.14 g, 80%.

trans,trans-$[RuBr(CO)(ppye\text{-}P,N)_2]PF_6$ **6b**. Complex **4b** (0.20 mmol, 0.36 g) was refluxed in ethanol (10 cm^3) under carbon monoxide for 1 h. The resulting white precipitate was filtered off, washed with ethanol, and vacuum-dried. Yield: 83%.

trans,cis-$[RuI(CO)(ppye\text{-}P,N)_2]PF_6$ **7c**. As for **6b**, complex **4c** (0.20 mmol, 0.38 g) was used as starting material. Yield: 81%.

trans,cis-$[RuCl_2(CO)(ppye\text{-}P)(ppye\text{-}P,N)]$ **8a**. An ethanol (15 cm^3) suspension of complex **1a** (0.23 g, 0.30 mmol) was cooled to −10 °C and saturated with carbon monoxide. A yellow solid formed within 3 h, which was filtered off, washed with ethanol and light petroleum, and vacuum-dried. Yield: 0.14 g, 61%.

trans,trans-$[RuCl_2(CO)(ppye\text{-}P)(ppye\text{-}P,N)]$ **9a**. A dichloromethane (5 cm^3) solution of complex **1a** (0.23 g, 0.30 mmol) was saturated with carbon monoxide. Addition of hexane (20 cm^3) and evaporation of the dichloromethane *in vacuo* afforded a pale yellow solid which was filtered off, washed with hexane, and vacuum-dried. Yield: 0.16 g, 70%.

Crystal Structure Determination of [Ru_2Cl_2(ppye-*P*,*N*)$_4$][PF_6]$_2$ **4a**.—Crystals of complex **4a** were grown by slow diffusion of propan-2-ol into a CH_2Cl_2 solution of the complex.

Crystal data. $C_{76}H_{72}Cl_2F_{12}N_4P_6Ru_2$, M = 1728.4, orthorhombic, space group *Pnna* (no. 52), a = 13.263(3), b = 26.028(7), c = 23.959(8) Å, U = 8271 Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections in the range $14 \leqslant \theta \leqslant 22°$, λ = 0.710 69 Å), Z = 4, D_c = 1.39 g cm^{-3}, $F(000)$ = 3504. Yellow prisms. Crystal dimensions 0.20 × 0.20 × 0.60 mm, μ(Mo-Kα) = 6.0 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, ω–2θ mode with ω scan width = 0.60 + 0.35 tan θ, graphite-monochromated Mo-Kα radiation; 8873 independent reflections measured ($3 \leqslant 2\theta \leqslant 52°$, $+h, k, l$), giving 3610 with $I > 3\sigma(I)$, corrected for Lorentz-polarization effects. No absorption and secondary extinction correction. Three standard reflections monitored every 4000 s showed no significant variation in intensity.

Solution and refinement. Conventional Patterson and Fourier methods. Only one half of the dication is crystallographically independent, as the Cl atoms sit on a two-fold axis. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, except for a PF_6 anion (see below). Hydrogen atoms included at calculated positions (C–H 0.95 Å) with isotropic $B = 1.3B_{eq}$ of the corresponding C atom. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with unit weights using 451 parameters. Final R and R' values are 0.061 and 0.069. The maximum and minimum electron densities in the final ΔF map are ±0.51 e Å^{-3}. An occupancy factor of 0.5 was assigned to the atoms of the [PF_6]$^-$ anion in general position in order to maintain the electroneutrality of the compound. As this group was found to be disordered, it was isotropically refined with fixed B = 15.0 Å^2 for P and 20.0 Å^2 for F atoms.

Calculations were carried out on a μVAX 2000 computer using the Enraf-Nonius CAD4 system of programs.[30] Sources of f, f' and f'' data are given in ref. 4(*e*).

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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