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Ruthenium ammine complexes of group VB donor ligands

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CONTENTS

ABBREVIATIONS

4-cp	4-cyanopyridine
4-cpH^+	4-cyanopyridinium ion
cys	L-cysteine
dppe	bis(1,2-diphenylphosphino)ethane
DMPP	1-phenyl-3,4-dimethylphosphole
ETPB	4-ethyl-2,6,7-trioxo-1-phospha(III)-bicycle-[2,2,2]octane
fu	furan
gly	glycine
H_2Pcy	cyclohexylphosphine
imN	N-bound imidazole
imC	C-bound imidazole
isn	isonicotinamide

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L-hist	L-histidine
1-Meime	1-methylimidazole
$Mepyr^+$	methylpyrazinium ion
nic^-	nicotinate ion
nic	nicotinamide
pic	picoline
py	pyridine
pyr	pyrazine

A. INTRODUCTION

Tertiary phosphorus ligands have been very useful as ancillary ligands in catalysis [1–5]. However, very little effort has been dedicated to the understanding of the basic chemistry of phosphanes, e.g. the quantification [5,6] of their trans-effect and trans-influence.

At the time we started this work, most of the research dealing with phosphanes as ligands was restricted to phosphines in square planar systems [7–10]. Furthermore, reports referring to systems with the metal centre coordinated to diverse ligands [6–28], in many cases non-innocent ones, made it difficult to establish correlations.

The exploration of the chemistry of phosphanes as ligands in a well-defined octahedral environment was initiated [29] taking the ruthenium ammines as probes. Considering that the σ-bonding and innocent NH_3 ligand was known to be inert to substitution in ruthenium(II) and (III) tetraamines [30–32], *trans*-$[Ru(NH_3)_4L(H_2O)]^{3+,2+}$ species were selected as models [29,33–35] to investigate the mutual influence of the metal centre and the ligand L upon their reactivities.

The systems considered above have advantages over the $[Fe(CN)_5(H_2O)]^{3-}$ and $[Ru(CN)_5(H_2O)]^{3-}$ ions, since in these cyano complexes the metal centre is surrounded by non-innocent ligands. Furthermore, we are aware of unsuccessful attempts [36,37] to prepare the analogue *trans*-$[Fe(CN)_4L(H_2O)]^{3-}$. In addition, the synthetic chemistry in $[Ru(CN)_5(H_2O)]^{3-}$ systems is still under development [38,39].

The phosphorus atom has vacant orbitals with symmetry and energy adequate for back-bonding with the filled $4d_\pi$ orbitals of ruthenium. Sigma donation occurs from the filled 3s orbital of phosphorus, making phosphanes biphilic ligands [4,40,41] in nature and good candidates to interact with ruthenium(II) and (III).

The $M \rightarrow P(III)$ back-bonding has been interpreted [1–4] as a transfer of charge from the filled nd_π metal orbitals to the empty $3d_\pi$ phosphorus orbitals. However, during the last decade, questions have been raised regarding this interpretation of metal–phosphorus bonding [42,43].

Quantum mechanical calculations [43] in free and coordinated PR_3 systems have suggested that the σ^* orbital of the P–R bond is the receptor for the nd_π electrons instead of the $3d_\pi$ phosphorus orbitals.

Most of the work to be described here has been carried out with phosphites and phosphines and offers the opportunity for comparing their chemical behaviour. This investigation has also been extended to triphenyl arsine and triphenyl stibine molecules.

B. SYNTHESES

(i) Synthesis of trans-[$Ru(NH_3)_4L_2$]X_2 compounds

With yields better than 70%, complexes *trans*-[$Ru(NH_3)_4(L)_2$]X_2, (where $L = P(OMe)_3$, $P(OEt)_3$, $P(OPr)_3$, $P(O^iPr)_3$, $P(OBut)_3$, $P(O^tBut)_3$, $P(O\phi)_3$, $P(OCH_2CH_2Cl)_3$, ETBP, DMMP, $P(But)_3$, and $X = PF_6^-$ or $CF_3SO_3^-$) have been isolated (see Table 1) from the reaction in acetone of the complexes [$Ru(NH_3)_5(H_2O)$]$(PF_6)_2$ or *trans*-[$Ru(NH_3)_4(SO_2)(H_2O)$]$(CF_3SO_3)_2$ with the desired phosphite [30,33–35,44] or phosphine [32,42,43] molecules as follows:

$$trans\text{-}[Ru(NH_3)_4Z(H_2O)]^{2+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4ZL]^{2+} + H_2O$$

$$trans\text{-}[Ru(NH_3)_4ZL]^{2+} + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4L_2]^{2+} + Z$$

where $Z = SO_2$ or NH_3.

The bisphosphite complexes have also been prepared [28,41] using [$Ru(NH_3)_5$-(H_2O)]$(CF_3SO_3)_3$ instead of [$Ru(NH_3)_5(H_2O)$]$(PF_6)_2$. In the first step, the phosphite molecule reduces the Ru(III) species to Ru(II) through an outer sphere mechanism [44] followed by the substitution of the remaining free $P(OR)_3$ in the metal coordination sphere.

The presence of the monosubstituted species *trans*-[$Ru(NH_3)_4$-$(P(OEt)_3)(H_2O)$]$^{2+}$ was not detected even in the presence of a 10 times excess of the starting Ru(II) salt with respect to the phosphane. When Ru(II) was in excess, the final products were always the bisphosphite species plus unreacted Ru(II) salt.

The experimental data accumulated on such systems suggest that $k_2 \gg k_1$; $k_{-2} \ll k_{-1}$. Kinematic data supporting this scheme will be discussed in the present paper.

(ii) Synthesis of trans-[$Ru(NH_3)_4L(H_2O)$]X_2 salts

The Ru(II), monophosphite [29,33–35] salts (*trans*-[$Ru(NH_3)_4L(H_2O)$]$(X)_2$), $X = PF_6^-$ or $CF_3SO_3^-$, have been isolated (see Table 1) with very good yields (higher than 90%) from aquation of the corresponding bisphosphite complexes according to the reaction:

TABLE 1

UV-visible spectra[a] and formal potentials[a] $E^{O'}_{RuIII/RuII}$ for *trans*-$[Ru(NH_3)_4LY]^{2+}$

L	Y	λ_{max} (nm)[b]	ε ($M^{-1}\,cm^{-1} \times 10^{-2}$)[b]	$E^{O'}$ (V vs. SCE)[b]	Ref.
$P(OMe)_3$	$P(OMe)_3$	294	3.5	+0.68	44
		262	5.1		
$P(OEt)_3$	$P(OEt)_3$	294	2.4	+0.65	29
		262	4.4		
$P(OPr)_3$	$P(OPr)_3$	294	2.3	+0.64	35
		262	4.2		
$P(O^iPr)_3$	$P(O^iPr)_3$	294	3.1	+0.63	44
		262	4.8		
$P(OBut)_3$	$P(OBut)_3$	294	2.3	+0.64	44
		262	4.1		
$P(O^tBut)_3$	$P(O^tBut)_3$			+0.60[c]	45
ETPB	ETPB			+0.79[c]	45
$P(OC_2H_4Cl)_3$	$P(OC_2H_4Cl)_3$	226[a]	36	+0.96[a,d]	45
		264	4.7		
		296	4.7		
DMPP	DMPP	230[a]	2.6×10^2	+0.63	45
		280[a]	1.9×10^2		
		410[a]	7.0		
$P(OEt)_3$	$P(OMe)_3$	294	2.7	+0.68	44
		262	4.7		
$P(OEt)_3$	$P(O^iPr)_3$	294	2.8	+0.63	44
		262	5.0		
$P(OEt)_3$	$P(OBut)_3$	294	2.6		44
		262	4.6		
$P(OEt)_3$	$P(O\phi)_3$	294	2.0		45
$P(OEt)_3$	$P(Et)_3$			+0.56	34
$P(Et)_3$	$P(Et)_3$			+0.47	45
$P(But)_3$	$P(But)_3$			+0.47[c]	45
H_2Pcy	H_2Pcy	216[a]	39	+0.62[d,e]	45
		252	33		
		338	5.2		
$As\phi_3$	NH_3	376	3.6	+0.42	46
$Sb\phi_3$	NH_3	393	4.2	+0.41	46
$As\phi_3$	H_2O	404	6.1	+0.37	46
$Sb\phi_3$	H_2O	420	6.6	+0.36	46
$P(OMe)_3$	H_2O	316	7.3	+0.50	33
$P(OEt)_3$	H_2O	316	6.5	+0.46	29
$P(OH)(OEt)_2$	H_2O	316	5.2	0.36	47
$P(OH)_3$	H_2O	316	5.3	0.41	47
$P(O)(OEt)_2^-$	H_2O	316	5	0.22	47
$P(O)(OH)_2^-$	H_2O	316	5	0.18	47
$P(OPr)_3$	H_2O	316	6.0	+0.45	34
$P(OC_2H_4Cl)_3$	H_2O	314	7.1	+0.61	45

TABLE 1. (*continued*)

L	Y	λ_{max} (nm)^b	ε (M^{-1} cm^{-1} $\times 10^{-2}$)^b	$E^{O'}$ (V vs. SCE)^b	Ref.
$P(O^iPr)_3$	H_2O	316	5.6	+0.44	33
$P(OBut)_3$	H_2O	316	5.4	+0.44	33
$P(O^tBut)_3$	H_2O	314	5.5	+0.44^c	45
$P(O\phi)_3$	H_2O	316	7.8	+0.66	45
ETPB	H_2O	314	3.6	+0.59^d	45
DMPP	H_2O	410	–	+0.44	45
$P(Et)_3$	H_2O			+0.33	34
$P(But)_3$	H_2O			0.30	34
$P(\phi)_3$	H_2O	386	7.3	0.48^d	34
dppe	H_2O	362	6.5	0.50	45
H_2Pcy	H_2O	354	6.7	+0.45^d	45
$P(OEt)_3$	NH_3	309	3.9		39
$P(OEt)_3$	CO	284	4.0	+1.1^c	48
$P(OEt)_3$	NO^+	264	8.9		49
$P(OEt)_3$	NO_2^-	334	18		49
$P\phi_3$	NO_2^-	362	24		49
PEt_3	L-hist	306	4.1		51
$P(OEt)_3$	Meime	302	1.2		51
$P(OEt)_3$	imN	303	5.2		29
$P(OEt)_3$	fu	314	3.2		51
$P(OEt)_3$	gly	304	5.5		51
$P(OEt)_3$	cys	312	3.8		51
$P(OEt)_3$	SO_2^{2-}	300	3.5		29
$P(OEt)_3$	$S_2O_3^{2-}$	322	3.2		51
$P(OEt)_3$	$CS_2N_3^-$	390			54
$P(OEt)_3$	CN^-	312	2.8		50
$P(OEt)_3$	N_3^-	323	7.0		50
$P(OEt)_3$	SCN^-	310	4.7		50
$P(OEt)_3$	isn	350	48		29
$P(OEt)_3$	nic	322	20		52
$P(OEt)_3$	nic	312	36		
$P(OEt)_3$	pyr	366	42	0.54	29
$P(OEt)_3$	Mepyr	525			29
$P(OEt)_3$	4-cp	360	29		52
$P(OEt)_3$	4-cpH$^+$	315	12		52
$P(OH)(OEt)_2$	pyr	375	24		45, 47
$P(O)(OEt)_2^-$	pyr	415	33		45, 47
$P(OH)_3$	pyr	365	36		45, 47
$P(O)(OH)^-$	pyr	415	30		45, 47
$P(OC_2H_4Cl)_3$	pyr	352	31		45
$P(OMe)_3$	pyr	365	57		33
$P(O^iPr)_3$	pyr	370	41		33
$P(OBut)_3$	pyr	365	40		33
$P(O^tBut)_3$	pyr	366	39		45
$P(O\phi)_3$	pyr	330	22		34

TABLE 1. (*continued*)

L	Y	λ_{max} (nm)^b	ε (M^{-1} cm^{-1} $\times 10^{-2}$)^b	$E^{O'}$ (V vs. SCE)^b	Ref.
ETPB	pyr	360	13		45
DMPP	pyr	410	48		45
$As\phi_3$	pyr	422	55	0.61	45
$Sb\phi_3$	pyr	425	46	0.59	45
$P(Et)_3$	pyr	410	45		34
$P(But)_3$	pyr	417	39		34
$P\phi_3$	pyr	393	30	0.77^e	34
H_2Pcy	pyr	406	46		45
dppe	pyr	392	22		45
$P(OMe)_3$	isn	370	45	0.57	35
$P(OPr)_3$	isn	370	47	0.53	35
$P(O^iPr)_3$	isn	370	44	0.49	35
$P(OBut)_3$	isn	370	39		35
$P(O^iBut)_3$	isn	373	30		45
$P(O\phi)_3$	isn	326	32		45
$P(Et)_3$	isn	410	42		45
$P(But)_3$	isn	407	43		45
dppe	isn	380	24		45
$P\phi_3$	isn	390	25		45
$As\phi_3$	isn	410	34		45
$Sb\phi_3$	isn	H_2O	35		45

[a] $u = 0.10$ ($NaCF_3COO/CF_3COOH$), $C_{H^+} = 10^{-2}$ to 10^{-4} M, 25 ± 2°C.

[b] Uncertainties: $\lambda_{max} \pm 2$ nm; $\varepsilon \pm 10\%$; $E^{O'} \pm 0.010$ V.

[c] $u = 0.10$ ($NaCF_3COO/CF_3COOH$), 25 ± 2°C; 20/80 ethanol/water medium; uncertainty on $E^{O'} = \pm 0.020$ V.

[d] $u = 0.10$ ($NaCF_3COOH$), 25 ± 2°C, 20/80 acetone/water medium; uncertainty on $E^{O'} = 0.020$ V.

[e] Air; calculated on the basis of E_{Pa}.

$$\textit{trans}\text{-}[Ru(NH_3)_4P(OR)_3)_2]^{2+} + H_3O^+ \, L \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}}$$

$$\textit{trans}\text{-}[Ru(NH_3)_4(P(OR)_3)(H_2O)]^{2+} + P(OR)_3$$

To avoid back reaction, the solution was kept acidic, $C_{H^+} > 10^{-4}$ M. Under these conditions, the aquated phosphite molecule rapidly hydrolyzes [40,41] to the corresponding dialkylphosphite, which in its turn isomerizes to the phosphonate form. This phosphonate form, $P(O)(H)(OR)_2$, has no affinity for the $[Ru(NH_3)_4(P(OR)_3)]^{2+}$ moiety.

$$P(OR)_3 + H_2O \xrightarrow{\text{fast}} P(OH)(OR)_2 + ROH$$

$$P(OH)(OR)_2 \overset{\text{fast}}{\rightleftharpoons} P(O)(H)OR)_2$$

The monophosphine complexes have been obtained in a similar way to that of the monophosphite complexes [34,45,46]. In this case, the back reaction was avoided by phosphinoxide formation.

For $L = As\phi_3$, $Sb\phi_3$, the reaction of $[Ru(NH_3)_5(H_2O)](PF_6)_2$ with triphenyl arsine or triphenyl stibine leads [46], respectively, to the formation of $[Ru(NH_3)_5(As\phi_3)](PF_6)_2$ and $[Ru(NH_3)_5(Sb\phi_3)](PF_6)_2$.

The NH_3 ligand in the trans position to $As\phi_3$ and $Sb\phi_3$ is easily aquated [46] in acidic aqueous media, leading to *trans*-$[Ru(NH_3)_4(As\phi_3)(H_2O)](PF_6)_2$ and *trans*-$[Ru(NH_3)_4(Sb\phi_3)(H_2O)](PF_6)_2$, respectively, with yields higher than 90%.

If $L = P\phi_3$, the compound *trans*-$[Ru(NH_3)_4(P\phi_3)(H_2O)](PF_6)_2$ is obtained [45] directly from the reaction of $[Ru(NH_3)_5(H_2O)](PF_6)_2$ with $P\phi_3$. The reaction of $P(OH)(OEt)_2$ and $P(OH)_3$ with $[Ru(NH_3)_5(H_2O)]^{2+}$ leads [47], respectively, to the monosubstituted species *trans*-$[Ru(NH_3)_4(P(OH)_3)(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(OH)(OEt)_2)H_2O]^{2+}$.

(iii) Synthesis of trans-[$Ru(NH_3)_4LY$]X_2, $Y \neq H_2O$ and $L = P(R)_3$, POR_3, $Sb\phi_3$ and $As\phi_3$

The ligand L stabilizes the ruthenium(II) centre with respect to oxidation and at the same time labilizes the coordinated water molecule.

With yields better than 60%, *trans*-$[Ru(NH_3)_4LY]X_2$ derivatives (see Table 1) have been prepared [29,34,35,44–51] by reacting the desired *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ complex in aqueous medium with excess of the chosen ligand Y.

$$trans\text{-}[Ru(NH_3)_4L(H_2O)]^{2+} + Y \rightarrow trans\text{-}[Ru(NH_3)_4LY]^{2+} + H_2O$$

The compounds *trans*-$[Ru(NH_3)_4(P(OEt)_3)CO](PF_6)_2$ and *trans*-$[Ru(NH_3)_4(P(OEt)_3)NO](PF_6)_3$ have been prepared [48,49] by bubbling CO and NO, respectively, at 1 atm through acidic aqueous solutions containing the *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)](PF_6)_2$ complex.

The mixed species *trans*-$[Ru(NH_3)_4(P(OEt)_3)Y](PF_6)_2$, where $Y = P(OMe)_3$, $P(OBut)_3$, $P(O^iPr)_3$, $P(O\phi)_3$ and PMe_3, have been obtained [44] by reacting the *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ complex in acetone with the selected phosphane.

C. CHARACTERIZATION

(i) Electronic, voltammetric, and infrared spectra and X-ray data

As expected for d^6 ions with low spin configuration, and D_{4h} symmetry [48], two absorption bands were observed [29,33,34,44,45] in the electronic spectra of the species *trans*-$[Ru(NH_3)_4(P(OR_1)_3)(P(OR_2)_3)]^{2+}$ ($R_1 = R_2$, $R_1 \neq R_2$). These bands at 294 and 260 nm (see Table 1), attributed to ligand field (LF) transitions, have been assigned to ${}^1A_g \rightarrow {}^1A_{2g}, {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}, {}^1E_g$ transitions, respectively. When R =

$P(O\phi)_3$, the ligand field band at higher energy is enveloped by the more intense π–π^* intraligand transition (IT).

For the *trans*-$[Ru(NH_3)_4(P(OR)_3)Y]^{2+,1+,0}$ ions, only one well-defined absorption peak is observed in the UV spectra and is attributed to the LF transition ${}^1A_1 \rightarrow {}^1E$, consistent with C_{4v} symmetry (see Table 1). The λ_{max} for the *trans*-$[Ru(NH_3)_4(P(OR)_3)(H_2O)]^{2+}$ complex ions [29,33–35,45,47–52] are all in the same region of the spectrum, at 316 ± 2 nm. Since the microsymmetry is maintained and the ligand field strength of the $P(OR)_3$ ligands is very similar, small differences in the energy of the LF bands are very difficult to differentiate in experiments at room temperature.

The preceding arguments could also account for the electronic spectra of the *trans*-$[Ru(NH_3)_4(P(OR_1)_3)(P(OR_2)_3)]^{2+}$ ions, although in this case the λ_{max} for the two LF transitions are not so well defined as for the monophosphite complexes.

However, if $Y \neq H_2O$, the changes in energy for the LF transitions, according to the ligand field strength of L, are more easily identified [49,50] ($\lambda_{max} = 264$ and 323 nm for $Y = NO^+$ and N_3^-, respectively).

The bands at 334 and 362 nm exhibited [49] by the complex ions *trans*-$[Ru(NH_3)_4(P(OEt)_3)NO_2]^+$ and *trans*-$[Ru(NH_3)_4P\phi_3NO_2]^+$, respectively, have been tentatively attributed to LF transitions. However, their molar absorption coefficients are too high [53] for a ligand field transition (1.8 and $2.4 \times 10^3\ M^{-1}\ cm^{-1}$ for $Y = P(OEt)_3$ and $P\phi_3$, respectively), and probably could be better assigned to MLCT transitions.

For ions *trans*-$[Ru(NH_3)_4PR_3(H_2O)]^{2+}$, the LF transitions could be observed [34,45,46] at lower energies than that exhibited for the corresponding phosphite complexes. This is consistent with the higher ligand field strength of phosphites with respect to their analogous phosphine ligands.

Values of λ_{max} for $[Ru(NH_3)_5L]^{2+}$ and *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ ($L = As\phi_3$ and $Sb\phi_3$) are observed [46] at wavelengths higher than 375 nm.

Taking into account the energy of the LF transition for the *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ complexes, the following spectrochemical series can be written: $P(OH)_3 \Leftrightarrow P(O)(OH)_2^- \Leftrightarrow P(OMe)_3 \Leftrightarrow P(OEt)_3 \Leftrightarrow P(O)(OEt)_2^- \Leftrightarrow P(OH)(OEt)_2 \Leftrightarrow P(OPr)_3 \Leftrightarrow P(O^iPr)_3\ P(OBut)_3 \Leftrightarrow P(O\phi)_3 \Leftrightarrow ETPB \Leftrightarrow P(OC_2H_4Cl)_3 > PEt_3 > P(But)_3 > P\phi_3 > As\phi_3 > Sb\phi_3$.

In general, the ligand field absorption band is difficult to observe for species containing heterocycles in the coordination sphere [29,33–35,45–52]. In such systems, an intense MLCT transition ($4d_\pi \rightarrow \pi^*$) is observed in the visible region of the spectrum and the LF band is obscured by intense intraligand π–π^* transitions.

MLCT bands for Ru(II) species are attributed [29–32] to the process:

$$Ru^{II}\text{–}Y \xrightarrow{h\nu} [Ru^{III}, Y^-]$$

and, as expected, a relationship is observed between the energy of the band and the formal potential $E^{O'}_{Ru(III)/Ru(II)}$ for the corresponding aquo species *trans*-

$[\mathrm{Ru(NH_3)_4L(H_2O)}]^{3+/2+}$, where L = P(III), As(III) and Sb(III). The more positive the numerical value of $E^{\mathrm{O'}}_{\mathrm{Ru(III)/Ru(II)}}$, the more resistant will the Ru(II) centre be towards oxidation to Ru(III), and therefore the higher the energy of the corresponding MLCT band.

With the substitution of one or both of the water molecules in *trans*-$[\mathrm{Ru(NH_3)_4(H_2O)_2}]^{2+}$ species for P(III), As(III) or Sb(III) ligands, the Ru(II) oxidation state is stabilized with respect to Ru(III). This stabilization is reflected in the $E^{\mathrm{O'}}$ value for the Ru(III)/Ru(II) couple in these complexes with respect to the *trans*-$[\mathrm{Ru(NH_3)_4(H_2O)_2}]^{2+}$ species and could be [46] as high as +0.96 V for *trans*-$[\mathrm{Ru(NH_3)_4(P(III))_2}]^{2+}$, P(III) = $\mathrm{P(OC_2H_4Cl)_3}$, and +0.66 V [34,35] for *trans*-$[\mathrm{Ru(NH_3)_4P(III)(H_2O)}]^{2+}$ ions, P(III) = $\mathrm{P(OC_2H_4Cl)_3}$ and $\mathrm{P(O\phi)_3}$.

It is well accepted [30–32] that Ru(II) is a strong π base and a rather weak σ acid, whereas Ru(III) is a strong σ acid and a weak π acid. Therefore, the shift to more positive values in $E^{\mathrm{O'}}_{\mathrm{Ru(III)/Ru(II)}}$ for a series of related complexes *trans*-$[\mathrm{Ru(NH_3)_4L(H_2O)}]^{3+/2+}$ is a parameter indicative of the degree of back bonding between the Ru(II) centre and the ligand L and therefore of the ligand π-acidity. Accordingly, from the $E^{\mathrm{O'}}_{\mathrm{Ru(III)/Ru(II)}}$ values for the *trans*-$[\mathrm{Ru(NH_3)_4L(H_2O)}]^{3+/2+}$ species (see Table 1), the following series for $\mathrm{L}\pi^-$ acidity increase can be written: $\mathrm{P(O)(OH_2)^-} < \mathrm{P(O(OEt_2)^-} < \mathrm{P(But)_3} < \mathrm{P(Et)_3} < \mathrm{P(OH)(OEt)_2} \Leftrightarrow \mathrm{Sb\phi_3} < \mathrm{As\phi_3} < \mathrm{P(OH)_3} < \mathrm{DMPP} < \mathrm{P(O^iBut)_3} \Leftrightarrow \mathrm{P(OBut)_3} \Leftrightarrow \mathrm{P(O^iPr)_3} < \mathrm{H_2Pcy} \Leftrightarrow \mathrm{P(OPr)_3} < \mathrm{P\phi_3} \Leftrightarrow \mathrm{P(OEt)_3} \leqslant \mathrm{dppe} \Leftrightarrow \mathrm{P(OMe)_3} < \mathrm{ETPB} < \mathrm{P(OC_2H_4Cl)_3} \Leftrightarrow \mathrm{P(O\phi)_3}$.

The heterocyclic ligands Y in *trans*-$[\mathrm{Ru(NH_3)_4(P(III))Y}]^{2+}$ aquate quickly and therefore an excess of ligand is required to assure a reasonable equilibrium concentration of the complex. Under these experimental conditions for the strong σ base ligands, the medium hydrogen ion concentration reaction decreases and disproportionation reactions occur [51,55] following the electrochemical oxidation of Ru(II) to Ru(III). Therefore, in these systems the cyclic voltammograms frequently do not exhibit the cathodic component, displaying an irreversible behaviour.

The anodic process [48] for the aquation of the *trans*-$[\mathrm{Ru(NH_3)_4(P(OEt)_3)CO}]^{2+}$ complex involves the ligand and metal centre oxidation.

$$\textit{trans}\text{-}[\mathrm{Ru(NH_3)_4(P(OEt)_3)CO}]^{2+} + 2\mathrm{H_2O} \xrightarrow{-3e}$$

$$\textit{trans}\text{-}[\mathrm{Ru(NH_3)_4(P(OEt)_3)(H_2O)}]^{3+} + \mathrm{CO_2} + 2\mathrm{H^+}$$

As a consequence, the cathodic component is not observed.

The IR spectra [28,30–33,43,44] of the *trans*-$[\mathrm{Ru(NH_3)_4L_2}]\mathrm{X_2}$ complexes, in the 4000–600 $\mathrm{cm^{-1}}$ range are the sum of the bands present in the phosphane and the ruthenium ammine moieties; for the *trans*-$[\mathrm{Ru(NH_3)_4LY}]$ ($\mathrm{Y = H_2O}$ or $\mathrm{Y \neq H_2O}$), the bands of Y were also identified [29,33–35,44–52]. The full interpretation of the spectrum is complicated by the large number of bands observed. Therefore the IR spectra are used only for identification purposes.

Table 2 summarizes a selected group of frequencies for ruthenium(II) complexes.

TABLE 2

Selected infrared group frequencies[a]

Compound	Stretching frequencies (cm^{-1})		Ref.
trans-$[Ru(NH_3)_4P(OEt)_3CO](PF_6)_2$	ν(CO)	1995	48
trans-$[Ru(NH_3)_4(P\phi_3)CO](PF_6)_2$	ν(CO)	1931	48
trans-$[Ru(NH_3)_4(P(OEt)_3)NO](PF_6)_3$	ν(NO)	1907	49
trans-$[Ru(NH_3)_4(P(\phi)_3)NO](PF_6)_3$	ν(NO)	1842	49
trans-$[Ru(NH_3)_4(P(OEt)_3)(C_2H_2)](PF_6)_2$	ν(C≡C)	1972	59
trans-$[Ru(NH_3)_4(P(OEt)_3)CN]PF_6$	ν(C≡N)	2071	50, 52

[a] Recorded on KBr pellets and nujol.

The ν(CO) values [48] for the phosphane complexes in Table 2 are lower than those observed for the free CO molecule (2100 cm^{-1}) but higher than those for ν(CO) in $[Ru(NH_3)_5CO]Cl_2$ (1930–1916 cm^{-1}), being consistent with the different extension of the Ru(II) → CO back-bonding in these complexes [56–58].

Electrochemical and spectroscopic data and studies [49] on the reactivity of the coordinated NO support the formulation $Ru(II){-}NO^+$ for the nitrosyl complexes of Table 2. The ν(NO) value in the triphenylphosphine complex is consistent with values observed for ruthenium ammine nitrosyl complexes. However, the ν(NO) value in *trans*-$[Ru(NH_3)_4(P(OEt)_3)NO](PF_6)_3$ is about 50 cm^{-1} higher than any other reported value for related ruthenium tetraammine complexes.

The ν(CN) and ν(C≡C) frequency data [52,59] for complexes *trans*-$[Ru(NH_3)_4(P(OEt)_3)(CN)]PF_6$ and *trans*-$[Ru(NH_3)_4(P(OEt)_3)(C_2H_2)](PF_6)_2$ are very close to the values reported for the corresponding group frequencies [60] in NaCN and C_2H_2. These observations suggest that the coordination to the monophosphite complex induces only a small change in the electron distribution of these two ligands.

(ii) Symmetry and bond distances

The X-ray crystallographic data for *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_3$ [61] show the $P(OEt)_3$ molecule coordinated to the Ru(II) centre through the phosphorus atom. The compound crystallizes in the orthorhombic system with cell dimensions $a = 14.807(7)$, $b = 21.065(5)$, $c = 13.466(5)$ Å, Pbca with four molecules per unity cell. The microsymmetry around the metal centre $Ru(N_4)(P_2)$ is D_{4h}. The four NH_3 ligands are in the same plane and the two phosphites are in the trans position. The bond distances are: Ru–P = 2·366 Å, $Ru{-}N_1 = 2.100$ Å and $Ru{-}N_2 = 2.244$ Å.

We have assumed trans instead of cis configuration for complexes $[Ru(NH_3)_4(P_1(III))(P_2(III))]^{2+}$ and $[Ru(NH_3)_4(P_1(III))(H_2O)]^{2+}$ by taking into account the similarities between the chemical properties, the electronic. voltammetric and ^{1}H NMR spectra of the above compounds and those for the ions *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$, respectively.

D. REACTIVITY

(i) *Aquation studies*

The aquation reactions of the complex ions *trans*-$[Ru(NH_3)_4(P_1(III))(P_2(III))]^{2+}$, (with $P_1(III) = P_2(III)$, and $P_1(III) \neq P_2(III)$ where $P_1(III)$ and $P_2(III)$ are phosphite or phosphine), have been studied [33–35,45,62] and experimental data are summarized in Table 3.

The specific rate constants k_{-1} for phosphites are independent of the hydrogen ion concentration if $C_{H^+} > 10^{-4}$ M. At lower hydrogen ion concentrations, the conversion of $P(OR)_3$ into $P(O)(H)(OR)_2$ becomes slower [40,41] and the aquated phosphite molecule can substitute again [29,33] into the coordination sphere of the

TABLE 3

Rates of aquation and activation parameters for *trans*-$[Ru(NH_3)_4(P_1(III))(P_2(III))]^{2+}$

$P_1(III)$	$P_2(III)$	$k_1 \times 10^{5\,a}$	$\Delta H^{\neq\,b}_{-1}$ (kcal mol^{-1})	$\Delta S^{\neq\,b}_{-1}$ (cal deg^{-1} mol^{-1})	Ref.
$P(OMe)_3$	$P(OMe)_3$	2.4	30.3	22.0	33
$P(OEt)_3$	$P(OEt)_3$	2.2	28.2	15	29
$P(OPr)_3$	$P(OPr)_3$	1.2	26.0	6.5	45
$P(O^iPr)_3$	$P(O^iPr)_3$	8.4	23.0	0.50	33
$P(OBut)^c$	$P(OBut)_3$	1.9	26.3	8.30	33
$P(O^tBut)_3{}^d$	$P(O^tBut)_3$	1.3			45
ETPB	ETPB	0.2			45
$P(OCH_2H_4Cl)_3$	$P(OCH_2H_4Cl)_3$	4.5	27	12.5	45
$DMPP^e$	DMPP	2.6	22.7	−3.5	45
H_2PCy^e	H_2PCy	2.8	25.6	6.7	45
$P(OMe)_3{}^c$	$P(OEt)_3$	2.3	30.0	20.5	33
$P(O^iPr)_3{}^c$	$P(OEt)_3$	9.2	21.6	−4.7	33
$P(OBut)_3{}^c$	$P(OEt)_3$	1.7	27	11	33
$P(Et)_3$	$P(OEt)_3$	2.2			34
$P(Et)_3$	$P(Et)_3$	2.3			45
$P(But)_3{}^f$	$P(But)_3$	2.8			45

[a] 25°C ± 0.1°C, $\mu = 0.10$ ($NaCF_3COO/CF_3COOH$); $C_{H^+} = 1.0 \times 10^{-3}$ M Uncertainties ± 5%, $C_{Ru(II)} = 1.0 \times 10^{-3}$ M.
[b] Uncertainties: $\Delta H^{\neq}_{-1} \pm 1$ kcal mol^{-1}; $\Delta S^{\neq}_{-1} \pm 2$ kcal mol^{-1} deg^{-1}, calculated for T = 25°C.
[c] Ethanol/water medium: 50/50. $C_{Ru(II)} = 1.0 \times 10^{-5}$ M.
[d] Ethanol/water medium: 45/55.
[e] Acetone/water medium: 10/90. $C_{Ru(II)} = 1.0 \times 10^{-4}$ M, $C_{H^+} = 1.0 \times 10^{-2}$ M.
[f] Ethanol/water medium: 7/93. $C_{Ru(II)} = 5.0 \times 10^{-5}$ M.

aquoruthenium complex. As a consequence, small values are observed for phosphite aquation rates when $C_{H^+} < 10^{-4}$ M. However, if the aquation in basic medium is carried out in the presence of a large excess of an auxiliary ligand X ($X = SO_3^{2-}$ or imidazole), stable *trans*-$[Ru(NH_3)_4(P(OR)_3)X]^{2-,0}$ species are formed and good agreement [45] is obtained between aquation rates measured in acidic and alkaline media.

For phosphine complexes, the reactions were studied in acidic media using pyrazine as a competitor ligand.

The kinetic data obtained in acidic media [29,33,45] are in agreement with the rate law

$$\frac{d[trans\text{-}[Ru(NH_3)_4(P_1(III))(H_2O)]]}{dt} = k_{-1}[trans\text{-}[Ru(NH_3)_4(P_1(III))(P_2(III))]^{2+}]$$

where $P_1(III) = P_2(III)$ or $P_1(III) \neq P_2(III)$.

In the mixed species, $P_1(III) \neq P_2(III)$, the aquation product is always the more stable monophosphane complex *trans*-$[Ru(NH_3)_4(P(III))(H_2O)]^{2+}$ [44]. This selectivity reflects the competition between the two trans phosphorus ligands for the $4d_\pi$ electrons of the Ru(II) centre. As a result of this, the stronger Ru(II)—P(III) bond in the reactant is maintained in the product.

The aquation of the $P(OBu)_3$ ligand from the complex ion *trans*-$[Ru(NH_3)_4P(OBu)_3)_2]^{2+}$ has been studied in aqueous ethanolic medium and the specific rate k_{-1} showed very little sensitivity to the changes in the water concentration.

The experimental data for the mononuclear systems [29,33,45] and for the binuclear complex μ-TEPP-*trans*-bis$[(P(OEt)_3)Ru(NH_3)_4]_2^{4+}$ [62], show unequivocally that the ligand does not undergo hydrolysis while coordinated to the metal centre. Similar chemical inertness with respect to oxidation reactions is observed for coordinated phosphites [29,33,34,45,62–64] and phosphines [34,46]. This behaviour is noticeable, in contrast to the well-known reactivity of the non-coordinated phosphites and phosphines [40,41] or the phosphanes when coordinated to cobaloximes [14,63].

A very good linear relationship was found between the $\Delta H^{\ne}_{-1}$ and $\Delta S^{\ne}_{-1}$ data of Table 3, suggesting that these compounds undergo aquation reactions which follow the same mechanism [65]. The free energy of activation, $\Delta G^{\ne}_{-1}$, for the series of compounds studied is in the range of 24 ± 1 kcal mol^{-1} and the isokinetic temperature is 55°C.

The accumulated experimental data strongly suggest that aquation reactions of 18-electron *trans*-$[Ru(NH_3)_4(P_1(III))(P_2(III))]^{2+}$ complexes [20,42] are governed by a dissociative activation mechanism [29,33,45]. As judged from the kinetic data (Table 3), the energy necessary to break the $Ru(II) \rightarrow P_2(III)$ bond in the complexes *trans*-$[Ru(NH_3)_4P_1(III)P_2(III)]^{2+}$ depends on the nature of $P_1(III)$ and $P_2(III)$ and is about 25 ± 6 kcal mol^{-1}.

The bistriphenylphosphite complex aquates very quickly at room temperature [66] yielding *trans*-$[Ru(NH_3)_4(P(O\phi)_3)(H_2O)]^{2+}$ with the *trans*-$[Ru(NH_3)_4(P\phi_3)(H_2O)]^{2+}$ complex is the only product isolated [46] from the reaction of $[Ru(NH_3)_5(H_2O)]^{2+}$ with large excess of $P\phi_3$ in acetone. Space filling C.P.K. models, suggest that the second $P\phi_3$ and the $P(O\phi)_3$ ligands, respectively, should be quite labile due to steric hindrance.

No straightforward relationship has been obtained by plotting $\log k_{-1}$ versus $E^{O'}$ for the Ru(III)/Ru(II) couple or $\log k_{-1}$ versus the cone angle values of P_1(III) or P_2(III) in the *trans*-$[Ru(NH_3)_4P_1(III)P_2(III)]^{3+/2+}$ complexes.

(ii) The triethyl, diethyl and phosphorous acid systems

The equilibrium constant [29] for the reaction

$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} + P(OEt)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4(P(OEt)_3)_2]^{2+} + H_2O$$

is $(k_1/k_{-1}) = 7.5 \times 10^{-1}\ M^{-1}\ s^{-1}/2.2 \times 10^{-5}\ s^{-1} = 3.3 \times 10^4\ M^{-1}$ at 25°C.

By combining the values of the $E^O_{Ru(III)/Ru(II)}$ couples in the complex ions *trans*-$[Ru(NH_3)_4P(OEt)_3)_2]^{3+/2+}$ and *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+/2+}$ with the equilibrium constant for the above reaction, it was possible to calculate [29] the equilibrium constant for

$$trans\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+} + P(OEt)_3 \rightleftharpoons trans\text{-}[Ru(NH_3)_4(P(OEt)_3)_2]^{3+} + H_2O$$

as $30\ M^{-1}$ at 25°C. This value is not accessible experimentally since the Ru(III) complex ion oxidizes the free phosphite molecule through an outer sphere mechanism before the substitution reaction occurs [44].

Combining the values of $E^{O'}_{Ru(III)/Ru(II)}$ for *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+/2+}$ and for *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+/2+}$, the affinity [29] of Ru(II) in *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ for $P(OEt)_3$ is calculated to be 3×10^{11} times greater than that of Ru(III) in *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+}$.

The equilibrium

$$trans\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + NH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4P(OEt)_3NH_3]^{2+} + H_2O$$

has been studied [51] in aqueous medium at 25°C and $\mu = 0.10$ ($NaCF_3COO$). The values for k_1, k_{-1} and K_{eq} are respectively, $3.1 \pm 0.1\ M^{-1}\ s^{-1}$, $(5.5 \pm 0.3) \times 10^{-3}\ s^{-1}$ and $5.6 \times 10^2\ M^{-1}$.

The specific rate value for NH_3 aquation in *trans*-$[Ru(NH_3)_5P(OEt)_3]^{2+}$ is 350 times higher than in $[Ru(NH_3)_6]^{2+}$ [30–32] but only about half of the value observed for $[Ru(NH_3)_5SO_3]$.

In the absence of light and oxygen, aqueous acidic solutions [29] (1.0×10^{-3} M CF_3COOH) of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ and other monosphosphane complexes [33,34,44,45] are stable for more than a week. The complex ion $[Ru(NH_3)_5(H_2O)]^{2+}$ under the same experimental conditions undergoes aquation of the cis NH_3 ligands [30–32] in a time scale of hours. Therefore the cis delabilizing effect exhibited by $P(OR)_3$ over the cis NH_3 ligands is noticeable in *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ complexes [29,33,45].

Phosphorous acid and the diethyl phosphite molecule, P(III), exist in tautomeric equilibrium with their respective phosphonate [40,41] forms, P(IV):

$$P(OR)_3 \rightleftharpoons P(O)(H)(OR)_2$$

For diethyl phosphite, the concentration of the phosphonate form is about 20 times greater [67] than that of $P(OH)(OEt)_2$.

The substitution of $P(OH)(OEt)_2$ into $[Ru(NH_3)_5(H_2O)]^{2+}$ is first order in the phosphite concentration and independent [47] of the hydrogen ion concentration of the medium in the 10^{-1} to 10^{-3} M range.

$$trans\text{-}[Ru(NH_3)_5(H_2O)]^{2+} + P(OH)(OEt)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_5(P(OH)(OEt)_2)]^{2+} + H_2O$$

$$trans\text{-}[Ru(NH_3)_5(P(OH)(OEt)_2)]^{2+} + H_2O \xrightarrow{k_{-2}} trans\text{-}[Ru(NH_3)_4(P(OH)(OEt)_2)(H_2O)]^{2+} + NH_3$$

Assuming that the $P(OH)(OEt)_2$ concentration [67] is only 5% of the total $P(O)(H)(OEt)_2$, the second-order specific rate constant, k_1, has been computed to be $0.24 \pm 0.02\ M^{-1}\ s^{-1}$, $\Delta H_1^{\neq} = 11 \pm 2$ kcal mol^{-1} and the upper limit for $\Delta S_1^{\neq}$ is estimated to be -24.6 cal K^{-1} M^{-1}.

The second-order specific rate constant for the substitution of $P(OEt)_3$ in $[Ru(NH_3)_5(H_2O)]^{2+}$ has not been measured but should be of the same order of magnitude as the one determined for the coordination of $P(OH)(OEt)_2$ in $[Ru(NH_3)_5(H_2O)]^{2+}$ since both ligands are quite similar. The same arguments hold for the comparison of the specific rate constant for the aquation of the NH_3 molecule in the *trans*-$[Ru(NH_3)_5(P(OH)(OEt)_2)]^{2+}$ and *trans*-$[Ru(NH_3)_5P(OEt)_3]^{2+}$ ions.

Experimental data [29,47,51] relative to the title complexes suggest the following scheme for the reaction between $P(OR)_3$ and $[Ru(NH_3)_5(H_2O)]^{2+}$.

$$[Ru(NH_3)_5(H_2O)]^{2+} + P(OR)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(NH_3)_5P(OR)_3]^{2+} + H_2O$$

$$[Ru(NH_3)_5P(OR)_3]^{2+} + H_2O \xrightarrow{k_{-2}} trans\text{-}[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+} + NH_3$$

$$trans\text{-}[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+} + P(OR)_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}$$
$$trans\text{-}[Ru(NH_3)_4(P(OR)_3)_2]^{2+} + H_2O$$

The second phosphite molecule is substituted faster than the first in the Ru(II) coordination sphere. The rate-determining step in the above scheme is the specific rate constant k_{-2} for the aquation of the NH_3 ligand in the position trans to the coordinated phosphite.

As pointed out earlier in this paper, the aquomonophosphite species is the only phosphite complex formed in the reaction of $P(OH)(OEt)_2$ and $P(OH)_3$, respectively, with $[Ru(NH_3)_5(H_2O)]^{2+}$. This behaviour seems to be general for phosporus ligands that exhibit the tautomeric equilibrium $P(III) \rightleftharpoons P(V)$.

P(III) is biphilic [40,41], a good σ base and π acid. In the P(V) form of the phosphonate, the phosphorus and the oxygen atom are bonded through phosphoryl bond P=O, where a quite strong back-bonding interaction already exists [40,41]: $2p_\pi(O) \rightarrow 3d_\pi(P)$. Considering these two forms, phosphite and phosphonate, only the first has empty orbitals to accommodate the $4d_\pi$ electrons from the metal centre and consequently is able to coordinate to Ru(II).

The ability of the Ru(II) centre to stabilize the phosphite [47] form and the inertness of the coordinated phosphite molecules to undergo oxidation [29,62] and hydrolysis [29,33,62] reactions were used to compare the extent of the Ru(II) → P(III) and the O(II) → P(III) back-bonding interactions.

After the coordination of the first $P(OH)_3$ or $P(OH)(OEt)_2$ molecule to the Ru(II) centre, the availability of the $4d_\pi$ electrons is greatly reduced and the metal centre is not able to shift the phosphonate → phosphite equilibrium anymore. The fact that $P(OH)(OR)_2$ ($R = H$ or Et) does not react [29,47] with *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ while the biphilic ligands [44,45,66] $P(OR)_3$ ($R =$ Me, Et, Pr, ^{i}Pr, But, PO) do gives experimental support to the above considerations.

Deprotonation of the coordinated water molecule in *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ occurs [29,63] at $C_{H^+} < 10^{-10}\ M^{-1}$. However, for $C_{H^+} > 10^{-5}$ M, it is possible to observe [47] the acid dissociation

$$trans\text{-}[Ru(NH_3)_4(P(OR)_2(OH))(H_2O)]^{2+} + H_2O \rightleftharpoons$$
$$trans\text{-}[Ru(NH_3)_4P(OR)_2(O)(H_2O)]^{1+} + H_3O^+$$

The pK_a values for the acids *trans*-$[Ru(NH_3)_4(P(OR)_2(OH))(H_2O)]^{2+}$ are [47] 3.7

and 4.7 (25°C, $\mu = 1.0$ $NaCF_3COO$) for R = Et and H, respectively. For the corresponding Ru(III) acids, *trans*-$[Ru(NH_3)_4(P(OR)_2(OH))(H_2O)]^{3+}$, the pK_a values under the same experimental conditions are 1.5 and 1.0 for R = Et and H, respectively. The *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)(OEt)(H_2O)]^{2+}$ ions are [47] less acidic than phosphoric acid [41] by 2.6 and 1.6 pK_a units, respectively, and the corresponding Ru(III) complexes are more acidic by 1.1 and 0.6 pK_a units.

Inductive effects have been invoked [47] to explain such behaviour. In Ru(II) complexes, (Ru(II) → P(III)) back-bonding is more intense than O(II) → P(III), and will increase the electron density on the P(III) atom, making the proton less acidic than in H_3PO_4. Contrasting with the Ru(II) behaviour, the Ru(III) centre will act as a Lewis acid and therefore the O—H bond will be more easily broken than in H_3PO_4 where O(II) → P(III) back-bonding is operative [40,41]. The coordinated phosphite molecules $P(OH)_3$ and $P(OH)(OEt)_2$, similar to the phosphoric acid, assume a tetrahedral configuration with the metal centre at the corner of the tetrahedron. Therefore, upon coordination, the phosphorus atom undergoes an oxidative addition and exhibits the reactivity character of P(V).

(iii) Substitution reactions in trans-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$

Substitution of the coordinated water molecule in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ has been studied using a large variety of entering ligands [29,33–35,45,49–52], as may be seen in Tables 4 and 5.

It has been observed that substitution of the NH_3 molecule in the trans position to the water ligand for $P(OEt)_3$ drastically changes the thermodynamic and kinetic behaviour of the Ru(II) centre. This effect can be evaluated by comparing the affinities of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ for ligands of different donor–acceptor abilities. The affinity of the Ru(II) centre in the monophosphite complex for NH_3, imN and pyr, in terms of K_{eq}, is respectively 16, 1.8×10^3 and 10^{10} times smaller than that observed for the pentaammine moiety [30–32].

The affinity of the complex ion *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ expressed in terms of K_{eq}, for pyridinic nitrogen atoms [51] in six-membered heterocyclic molecules (containing 1 or 2 nitrogen atoms) is within 15 (py) and 36 M^{-1} (isn) while for five-membered rings (imN and derivatives) K_{eq} is in the 1.1×10^2 (1-Meime) to 1.5×10^3 (imN) range. The high affinity of $[Ru(NH_3)_5(H_2O)]^{2+}$ for N-heterocycles is well known [30–32,67] and therefore the behaviour exhibited by the monophosphite complex is quite noticeable.

The major change observed is due to the loss of affinity of the metal centre for typical π-acid ligands. This behaviour has been interpreted as the result of competition for the $4d_\pi$ electrons of the metal centre between the $P(OEt)_3$ and the π-acid ligands. In *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$, the $4d_\pi$ electrons of the Ru(II) centre are not freely available for coordination to an incoming ligand as they are in

TABLE 4

Specific rates for equilibrium constant data for the substitution reactions

$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} + Y^{n\pm} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4(P(OEt)_3)Y]^{(2\pm n)+} + H_2O$$

Y	k_1 [a] ($M^{-1}\,s^{-1}$)	$k_{-1} \times 10^2$ [a] (s^{-1})	K_{eq} (M^{-1})	Ref.
nic	3.0	14	19	52
nic^-	5.7	12	48	52
4-cp [b]	2.0	15	13	52
$4\text{-}cpH^+$ [c]	21	860	2.4	52
py	0.79	5.4	15	51
pic	0.91	4.2	22	51
pyr	3.8	20	20	29
isn	2.2	6.4	36	29
$Mepyr^+$ [b]	57	610	9.3	29
1-Meime	3.4	2.7	1.3×10^2	51
imN	15.2	0.99	1.5×10^3	29
L-hist	1.3	0.38	3.2×10^2	51
gly	11	63	17	51
fu	–	–	27 [g]	51
NH_3	3.1	0.55	5.7×10^2	51
N_3^- [b]	1.7×10^2	1.8×10^3	10	50
CN^- [b]	3.1×10^2	12	2.6×10^3	50
SCN^- [b]	1.4×10^2	2.8×10^3	4.8	50
$CS_2N_3^-$ [b]	1.3×10^2	45	2.8×10^2	54
SO_3^{2-} [b]	5.9×10^2	0.75	7.9×10^4	29
$S_2O_3^{2-}$ [b]	1.9×10^2	2.5×10^2	75	51
NO_2^- [d]	3.8×10^2	5.1×10^2	76	49
NO^+ [e]		7.2×10^{-3}		49
CO	3.11	2.6×10^{-3}	1.2×10^5	48
$P(OEt)_3$ [f]	0.75	1.1×10^{-5}	6.7×10^4	29

[a] 25 ± 0.2°C, $\mu = 0.10$ $NaCF_3COO/CF_3COOH$; $C_{Ru} = 2 \times 10^{-3}$ to 5×10^{-5} M; uncertainties ± 6%.

[b] $\mu = 1.0$ ($CF_3COOH/NaCF_3COO$).

[c] $\mu = 1.0$ (CF_3COOH).

[d] $C_{H^+} = 10^{-11}$ M, $\mu = 0.30$ $NaCF_3COO$.

[e] $C_{H^+} = 10^{-1.4}$; $\mu = 0.30$ ($NaCF_3COO/CF_3COOH$).

[f] k_{-1} because the statistical factor has been divided by two.

[g] Upper limit.

$[Ru(NH_3)_5(H_2O)]^{2+}$ due to the high π-acidity of the phosphane. The fact that $[Ru(NH_3)_5(H_2O)]^{2+}$ binds strongly to N_2 and SO_2 molecules [30–32] and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ does not clearly illustrate the above considerations [29].

Nevertheless, the Ru(II) centre in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ still ex-

TABLE 5

Activation parameters for the substitution reactions[a]

$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} + Y^{n+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4(P(OEt)_3)Y]^{(2\pm n)+} + H_2O$$

Y	$\Delta H_1^{\neq}$ (kcal mol^{-1})	$\Delta S_1^{\neq}$ (cal deg^{-1} mol^{-1})	$\Delta H_{-1}^{\neq}$ (kcal mol^{-1})	$\Delta S_{-1}^{\neq}$ (cal deg^{-1} mol^{-1})	Ref.
Py	9.2	10.2	15.4	15	50
Pyr	19.5	9.4	20.8	0.4	29
isn	17.5	1.7	23.5	14.6	29
imN	16.1	0.2	20.7	1.7	29
nic	14.0	−8.6	24.0	18.2	52
4-CP[b]	12.2	−16.2	18.3	−0.9	52
$4\text{-}CPH^{+}$ [b]	6.5	−32	9.1	−25	52
$CS_2N_3^-$ [b]	8.7	−19.4	10.3	−26.3	54
N_3^- [b]	3.4	37	6.0	−32	50
CO			18	−18	48
NO_2^- [c]	7.6	−21.2	9.2	−24.4	49

[a] $\mu = 0.10$ ($CF_3COOH/NaCF_3COO$), $\Delta S_1^{\neq}$ and $\Delta S_{-1}^{\neq}$ calculated for $T = 25°C$, uncertainties, $\Delta H_1^{\neq}$, $\Delta H_{-1}^{\neq}$ ± 1.5 kcal mol^{-1}; $\Delta S_1^{\neq}$, $\Delta S_{-1}^{\neq}$ ± 2 cal deg^{-1} mol^{-1}.

[b] $\mu = 1.0$ ($CF_3COOH/NaCF_3COO$).

[c] $\mu = 0.30$ ($CF_3COOH/NaCF_3COO$).

hibits [29,48,52] a strong affinity for $P(OEt)_3$, SO_3^{2-}, CN^- and CO. The monophosphite complex selectivity towards biphilic ligands is under investigation in our laboratory for analytical purposes. This class of ligand, good π acids which at the same time exhibit σ base characteristics, interacts quite strongly with the monophosphite complex. A synergism between the σ and π components of the $Ru-P(OEt)_3$ and Ru–Y bonds along the $Y-Ru-P(OEt)_3$ axis, strengthening the Ru–Y bond, should be operative when Y is a biphilic ligand. For ligands such as N_2 and SO_2, which are not biphilic, this synergistic interaction would be absent.

A borderline situation is observed for the acetylene molecule [59]. This unsaturated hydrocarbon binds strongly [68] to $[Ru(NH_3)_5(H_2O)]^{2+}$ but a very weak association has been observed [59] between *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ and C_2H_2.

The plots of K_{obs} versus [Y] for substitution of the water molecule in *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ exhibit different profiles [34,35,45,49,50–52] according to the nature of Y. For electrophilic substituents such as nic, nic^-, 4-Cp, $4\text{-}CpH^+$, pyr, $Mepyr^+$ and py, a clear tendency for rate saturation has been observed at ligand concentrations higher than 0.10 M. However, for nucleophilic substituents such as L-hist, gly, NH_3, imM, Meime, N_3^-, SCN^-, CN^-, SO_3^{2-}, $S_2O_3^{2-}$ and $CS_2N_3^-$, no such tendency has been observed. The dependence of K_{obs} upon [Y] should exhibit first-order behaviour in all ranges of [Y] studied.

The treatment of the experimental data according to an SN_1 mechanism

$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} \rightleftarrows trans\text{-}[Ru(NH_3)_4P(OEt)_3]^{2+} + H_2O$$

$$trans\text{-}[Ru(NH_3)_4P(OEt)_3]^{2+} + Y \rightarrow trans\text{-}[Ru(NH_3)_4(P(OEt)_3)Y]^{2+}$$

leads to different limiting rates for each of the entering ligands at high values of [Y]. Furthermore, the value of k_{obs} for ligands [29,49,50] as SO_3^{2-}, N_3^-, CN^-, SCN^- and NO_2^-, even at $[Y] \leqslant 0.1$ M, exceeds the observed limiting rate for $Mepyr^+$. Therefore, the experimental data cannot be explained by an SN_1 limit mechanism.

An interchange mechanism has been proposed [29,49] to explain such behaviour:

$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} + Y \xrightarrow{K_{obs}}$$
$$trans\text{-}[[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} \ldots Y]$$

$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} \ldots Y] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$$
$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)Y]^{2+} + H_2O$$

Analysis of the experimental data [70–73] according to the relations

$$\frac{1}{k_{obs} - k'_{-1}} = \frac{1}{k'_1} + \frac{1}{k'_1 K_{obs}[Y]}$$

suggests that bond making [29–50] is not important for electrophilic substituents but should be relevant when Y is a nucleophile.

The aquation rates, k_{-1}, of the ligand $trans\text{-}[Ru(NH_3)_4(P(OEt)_3)Y]^{2\pm n}$ are invariably slower than the rates for anation, k_1. The activation parameters and corresponding aquation rates are strongly dependent on the nature of the leaving group but independent of the nature of substituent X, where $X \neq H_2O$.

Isokinetic plots of $\Delta H_1^{\neq}$ versus $\Delta S_1^{\neq}$ and $\Delta H_{-1}^{\neq}$ versus $\Delta S_{-1}^{\neq}$ are linear [65]; $\Delta G_1^{\neq} = 16.4 \pm 1$ and $\Delta G_{-1}^{\neq} = 18.5 \pm 1$ kcal mol^{-1}.

A linear relationship [68–71] was found between $\log k_1$ versus $\log K_{eq}$ and $\log k_{-1}$ versus $\log(1/K_{eq})$, with the experimental data of Table 3, for several nucleophiles. The slope is about 0 for the anation reaction, suggesting the existence of a transition state that resembles the reactants [65,70–73]. For the aquation reaction, the slope is close to 1, which implies that the transition state resembles the products [65,70–73].

For substitution reactions in the $trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]$ system, an activated complex containing one metal complex and one ligand with some degree of bond making has been proposed [29–52].

In summary, the studies of substitution reactions in $trans\text{-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ clearly illustrate how perturbations of a chemical system (changes in the properties of the entering ligand) will affect the position of the preferred mechanistic pathway in a mechanistic continuum [73].

(iv) Trans-effect and trans-influence series

An extensive study [29,33–35, 45–47, 75] has been carried out on the substitution reactions:

$$trans\text{-}[\mathrm{Ru(NH_3)_4L(H_2O)}]^{2+} + \mathrm{Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[\mathrm{Ru(NH_3)_4LY}]^{2+} + \mathrm{H_2O}$$

where L = P(III), As(III), Sb(III) ligands and Y = pyr or isn (see Table 6).

The plots of k_{obs} versus [Y] for these reactions exhibit the same profile as was described in the preceding section for the reaction of *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{2+}$ complex ion with electrophilic ligands. For $[\mathrm{Y}] > 0.1$ M, the rates become independent of the substituting ligand concentration.

A linear relationship was observed for the plots of $\Delta H_1^{\neq}$ versus $\Delta S_1^{\neq}$ and $\Delta H_{-1}^{\neq}$ versus $\Delta S_{-1}^{\neq}$, respectively; $\Delta G_1^{\neq} = 16.7 \pm 1$ and $\Delta G_{-1}^{\neq} = 18.8 \pm 1$ kcal mol^{-1} (see Table 7).

If a mechanism governed mainly by dissociative activation is assumed to be operative in the above reaction [70–74,76], the specific rate constant for substitution of the coordinated water molecule by Y, k_1, has been proposed as a relative measure of the lability of the water ligand and therefore as a parameter [29,33,35,45–47,75] for the relative measurement of the trans-effect of Y.

Based on the k_1 data of Table 6, the following order [33,34,44,45] of increasing trans-effect can be written for Y = pyr: $\mathrm{Sb\phi_3} < \mathrm{As\phi_3} < \mathrm{ETPB} \simeq \mathrm{P(O\phi)_3} < \mathrm{P(OC_2H_4Cl)_3} \leqslant \mathrm{P\phi_3} < \mathrm{dppe} \Leftrightarrow \mathrm{H_2PCy} \Leftrightarrow \mathrm{P(OMe)_3} < \mathrm{P(OEt)_3} < \mathrm{DMPP} < \mathrm{P(O^tBut)_3} \Leftrightarrow \mathrm{P(O^iPr)_3} \leqslant \mathrm{P(OBut)_3} < \mathrm{P(OH)(OEt)_2} \Leftrightarrow \mathrm{P(OH)_3} < \mathrm{P(But)_3} < \mathrm{P(Et)_3} < \mathrm{P(OH)_2O^-} < \mathrm{P(OEt)_2O^-}$.

The same tendency for increasing trans-effect of Y was observed [35,45] if isn ($\mathrm{p}K_{\mathrm{a}} = 3.5$) is used instead of pyr ($\mathrm{p}K_{\mathrm{a}} = 0.50$): $\mathrm{Sb\phi_3} < \mathrm{As\phi_3} < \mathrm{P(O\phi)_3} < \mathrm{P\phi_3} \Leftrightarrow \mathrm{P(OMe)_3} < \mathrm{dppe} < \mathrm{P(OEt)_3} \Leftrightarrow \mathrm{P(OPr)_3} \Leftrightarrow \mathrm{P(O^tBut)_3} \Leftrightarrow \mathrm{P(OBut)_3} \Leftrightarrow \mathrm{P(O^iPr)_3} < \mathrm{P(But)_3}$.

Despite the recognized [77] relevance of steric effects on substitution reactions of complexes with P(III), As(III), and S(III) donor ligands, there have been unfruitful attempts to correlate [33–35,44,45,47] k_1 or $\log k_1$ data with the corresponding pnictide ligands cone angles [4].

A good linear relationship is observed for phosphanes by plotting $E^{\mathrm{O}'}_{\mathrm{Ru(III)/Ru(II)}}$ in *trans*-$[\mathrm{Ru(NH_3)_4(P(III))(H_2O)}]^{3+/2+}$ versus $\log k_1$.

The so-called trans-effect for ligands of Table 6 has been interpreted [29,33,35,45–47,75] as being due more to electronic than steric effects in nature. The stronger the back-bonding of Ru(II)–L, the more the ruthenium centre exhibits a Ru(III) character. As a consequence, the metal centre undergoes a slower substitution reaction [76]. In other words, the ligand that back-bonds more strongly to Ru(II)

TABLE 6

Specific rates and equilibrium data for the substitution reactions[a]

$$trans\text{-}[\mathrm{Ru(NH_3)_4L(H_2O)}]^{2+} + \mathrm{Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[\mathrm{Ru(NH_3)_4LY}]^{2+} + \mathrm{H_2O}$$

L	Y	k_1 ($M^{-1}s^{-1}$)	k_{-1} (s^{-1})	K_{eq} (M^{-1})	Ref.
$P(Et)_3$	pyr	51.0	0.45	1.1×10^2	34
$PBut_3$	pyr	34.0	0.51	68	34
$P\phi_3$	pyr	1.1	0.039	30	34
dppe	pyr	1.8	0.056	32	45
H_2Pcy	pyr	1.8	0.026	69	45
$P(OMe)_3$	pyr	2.2	0.24	16	45
$P(OEt)_3$	pyr	3.8	0.20	19	29
$P(OC_2H_4Cl)_3$	pyr	1.0	0.11	9.0	45
$P(OH)_3$	pyr	15.4	0.82	19	45
$P(OH)_2O^-$	pyr	5.0×10^2	11.0	45	45
$P(OH)(OEt)_2$	pyr	15.4	0.87	18	45
$P(OEt)_2O^-$	pyr	5.6×10^2	11.0	52	45
$P(O^iPr)_3$	pyr	8.5	0.42	21	45
$P(OBut)_3$	pyr	9.8	0.33	30	34
$P(O^tBut)_3$	pyr	8.3	0.39	21	45
$P(O\phi)_3$	pyr	0.15	0.042	3.6	34
ETPB	pyr	0.15	0.023	6.5	45
DMPP	pyr	4.1	0.051	80	45
$As\phi_3$	pyr	5.6×10^{-2}	9.2×10^{-5}	6×10^2	45
$Sb\phi_3$	pyr	4.6×10^{-2}	4.8×10^{-5}	9.6×10^2	45
$P(But)_3$	isn	21	22×10^{-2}	95	45
$P\phi_3$	isn	1.2	1.6×10^{-2}	75	46
dppe	isn	1.7	2.0×10^{-2}	85	45
$P(OMe)_3$	isn	1.2	5.2×10^{-2}	22	35
$P(OEt)_3$	isn	2.2	6.4×10^{-2}	36	29
$P(OPr)_3$	isn	2.3	5.9×10^{-2}	39	35
$P(O^iPr)_3$	isn	7.4	3.4×10^{-1}	22	35
$P(OBut)_3$	isn	8.1	2.0×10^{-1}	40	35
$P(O^tBut)_3$	isn	6.0	3.0×10^{-1}	20	45
$P(O\phi)_3$	isn	8.0×10^{-2}	5.6×10^{-3}	14	45
$As\phi_3$	isn	6.3×10^{-2}	4.4×10^{-5}	1.4×10^3	46
$Sb\phi_3$	isn	3.8×10^{-2}	2.1×10^{-5}	1.8×10^3	46

[a] $\mu = 0.10$ ($NaCF_3COO/CF_3COOH$), 25.0 ± 0.2°C; uncertainty on rate values are lower than 10%.

exhibits higher crystal field parameters. Consequently, the complex reaction is slower. This argument would explain why phosphites always exhibit a smaller trans-effect than the corresponding phosphines.

The trans-influence of L in the *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ complex ions was related to the weakening of the bond Ru(II)—Y in terms of ΔG_{eq}. The following order of increasing trans-influence of L on the basis of $1/k_{eq}$ for Y = pyr may be written: $\mathrm{Sb\phi_3} < \mathrm{As\phi_3} < \mathrm{P(Et)_3} <$ DMPP $< \mathrm{H_2Pcy} \Leftrightarrow \mathrm{P(But)_3} < \mathrm{P(OEt)_2O^-} < \mathrm{P(OH)_2O^-} <$ dppe $\Leftrightarrow \mathrm{P\phi_3} \Leftrightarrow \mathrm{P(OBut)_3} < \mathrm{P(O^tBut)_3} \Leftrightarrow \mathrm{P(O^i(Pr)_3} \Leftrightarrow \mathrm{P(OEt)_3} \Leftrightarrow \mathrm{P(OH)_3} \Leftrightarrow \mathrm{P(OH)(OEt)_2} \Leftrightarrow \mathrm{P(OMe)_3} < \mathrm{P(OC_2H_4Cl)_3} <$ ETPB $< \mathrm{P(O\phi)_3}$.

As observed for the trans-effect series, the tendency for increasing trans-influence is not altered when Y is changed from pyr to isn: $\mathrm{Sb\phi_3} < \mathrm{As\phi_3} < \mathrm{P(But)_3} <$ dppe $\leqslant \mathrm{P\phi_3} < \mathrm{P(OBut)_3} < \mathrm{P(OPr)_3} < \mathrm{P(OEt)_3} < \mathrm{P(OMe)_3} \Leftrightarrow \mathrm{P(O^iPr)_3} \Leftrightarrow \mathrm{P(O^tBut)_3} < \mathrm{P(O\phi)_3}$.

For phosphanes, the positions of the same ligand in the trans-effect and trans-influence series are not the same. In general, phosphanes that exhibit a low trans-effect, i.e. ETPB, $\mathrm{P(O\phi)_3}$, $\mathrm{P(OC_2H_4Cl)_3}$, exhibit a high trans-influence.

Phosphites exhibit a stronger trans-influence than the corresponding phosphines. No straightforward correlation seems to come out of an analysis of Y cone angles [4,34] and their trans-influence. Indeed, phosphites with smaller cone angles than those of analogous phosphines exhibit a stronger trans-influence, therefore electronic effects seem to play the major role in the ligands trans-influence.

A plot of $E^{O'}_{\mathrm{Ru(III)/Ru(II)}}$ for *trans*-$[\mathrm{Ru(NH_3)_4L_1(H_2O)}]^{3+/2+}$ ions versus K_{eq} for the corresponding *trans*-$[\mathrm{Ru(NH_3)_4L_1L_2}]^{2+}$ complexes exhibits a linear tendency. As the formal potential for the aquo species becomes more positive, the more stable becomes Ru(II) with respect to Ru(III), and less available will be the $4d_\pi$ electrons of the $[\mathrm{Ru(NH_3)_4L}]^{2+}$ moiety to interact with ligand Y. As a consequence, the trans-influence of L will be stronger.

The position of pnictides [29,33–35,45,50] in the series of ligands arranged

TABLE 7

Activation parameters for the substitution reaction[a]

$$trans\text{-}[\mathrm{Ru(NH_3)_4L_1(H_2O)}]^{2+} + \mathrm{Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[\mathrm{Ru(NH_3)_4LY}]^{2+} + \mathrm{H_2O}$$

L	Y	$\Delta H_1^{\neq}$ (kcal mol^{-1})	$\Delta S_1^{\neq}$ (cal deg^{-1} mol^{-1})	$\Delta H_{-1}^{\neq}$ (kcal mol^{-1})	$\Delta S_{-1}^{\neq}$ (cal deg^{-1} mol^{-1})	Ref.
$\mathrm{P(But)_3}$	isn	8.6	−23.4	14.3	−13.4	45
$\mathrm{P(OMe)_3}$	isn	17.9	2.0	23	12.5	35
$\mathrm{P(OEt)_3}$	isn	17.5	1.7	23.5	14.6	35
$\mathrm{P(OPr)_3}$	isn	16.4	−1.8	21.5	8.5	35
$\mathrm{P(O^iPr)_3}$	isn	11.4	−16.4	18.4	1.0	35
$\mathrm{P(OBut)_3}$	isn	9.8	−21.6	15.9	−8.3	35
$\mathrm{P(OMe)_3}$	pyr	16.0	−0.7	20	4.2	34
$\mathrm{P(OEt)_3}$	pyr	19.5	9.4	20.8	0.4	34
$\mathrm{P(O^iPr)_3}$	pyr	10.8	−18	14.6	−11.3	34
$\mathrm{P(OH)(OEt)_2}$	pyr	7.65	−27	12.2	17.5	45

[a] Uncertainties: $\Delta H_1^{\neq}$ and $\Delta H_{-1}^{\neq} \pm 1$ kcal mol^{-1}; $\Delta S_1^{\neq}$ and $\Delta S_{-1}^{\neq} = 2$ cal deg^{-1} mol^{-1}.

in order of increasing trans-labilizing [29,68,76,78] effect in *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$, considering the second-order specific rate of the replacement of water by isn, is: $CO \leqslant N_2 < isn < py < As\phi_3 < Sb\phi_3 < P(O\phi)_3 < NH_3 \leqslant imN < OH^- < P\phi_3 \Leftrightarrow P(OMe)_3 < dppe < P(OEt)_3 \Leftrightarrow P(OPr)_3 < P(O^iPr)_3 \Leftrightarrow CN^- \Leftrightarrow P(O^tBut)_3 \Leftrightarrow P(OBut)_3 < P(But)_3 < SO_3^{2-} < imC$. Unfortunately there are insufficient data available in the literature [6,28,43] to write a similar trans-influence series with Y = pyr.

However, a similar series [29,31,43,76] can be drawn for the trans-influence of pnictides ligands when Y is isn: $NH_3 < SO_3^{2-} < Sb\phi_3 < As\phi_3 < imC < P(But)_3 < dppe < P\phi_3 \leqslant P(OBut)_3 \Leftrightarrow P(OPr)_3 \Leftrightarrow P(OEt)_3 < P(OMe)_3 \Leftrightarrow P(O^iPr)_3 \Leftrightarrow P(O^tBut)_3 < P(O\phi)_3$.

As pointed out previously [76], the observed ligand ordering in the trans-effect and trans-influence series for octahedral Ru(II) and square planar Pt(II) complexes [8,28] is not the same.

The versatility of pnictide ligands, mainly phosphanes, can be easily envisaged from their position in the above trans-effect and trans-influence series. In principle, only by change of the radical attached to the pnictide atom, e.g. P(III), is it possible to achieve a desired kinetic or thermodynamic effect, therefore making these ligands very attractive for the design of new catalysts [2–4,79].

(v) Ruthenium(III) phosphites

The *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)](X_3)_3$ salt ($X^- = PF_6^-$ and CF_3SO_3) has been isolated [63] from the chemical or electrochemical oxidation of the *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)](X)_2$ salt. These Ru(III) species absorb at 285 nm ($\varepsilon = 8.1 \pm 0.3 \times 10^{-3}\ M^{-1}\ cm^{-1}$) and 390 nm ($\varepsilon = 9 \pm 1 \times 10\ M^{-1}\ cm^{-1}$). The EPR spectrum of solid *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)](X)_3$ is consistent with axial symmetry C_{4v} ($g_\perp = 2.429$ and $g_\parallel = 1.675$) and with the electronic spectrum. The *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{3+}$ ion decomposes in aqueous solution according to:

$$4Ru(III) \rightleftarrows 3Ru(II) + Ru(IV)$$

The decay rate of the Ru(III) species is inversely proportional to the solution hydrogen ion concentration of the solution, ($C_{H^+} = 1.0 \times 10^{-1}$ M, $k_{obs} = 4 \times 10^{-5}\ s^{-1}$; $C_{H^+} = 10^{-12}$ M, $k_{obs} = 3.3\ s^{-1}$, 25°C, $\mu = 0.3$ $NaCF_3COO$).

The addition of pyrazine or isonicotinamide to aqueous acid solutions of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{3+}$ leads [80] to heterocycle oxidation and ruthenium centre reduction. The specific rates for $Ru(III) + Y \rightarrow Ru(II) + Y_{ox}$ have been estimated as $7\ M^{-1}\ s^{-1}$ and $6 \times 10^{-5}\ M^{-1}\ s^{-1}$ for Y = pyr and isn, respectively, (25°C, $C_{H^+} = 10^{-3}$ M, $\mu = 0.30$ $NaCF_3COO$, CF_3COOH). The use of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{3+}$ for the catalytic oxidation of N-heterocycles has been proposed.

(vi) Other d^6 systems studied

These studies have been extended [81] to the $[Ru(CN)_5(H_2O)]^{3-}$, $[Os(NH_3)_5(H_2O)]^{2+}$ and $[Fe(CN)_5(H_2O)]^{3-}$ systems.

The complex ions *trans*-$[Ru(CN)_4(P(OEt)_3)_2]^{2-}$ and *trans*-$[Os(NH_3)_4(P(OEt)_3)_2]^{2+}$ have been identified in solution by cyclic voltammetry and spectroscopic techniques (UV-visible and NMR (^1H, ^{13}C)). The *trans*-$[Ru(CN)_4(P(OEt)_3)_2]^{2-}$ ions undergo aquation reactions yielding the aquo monophosphite species *trans*-$[Ru(CN)_4P(OEt)_3)(H_2O)]^{2-}$, $k_{-1} = 1.6 \pm 0.1 \times 10^{-5}\ s^{-1}$ at 25°C, $\mu = 0.10$. The osmium(II) complex does not undergo aquation reaction in a time scale of days under the same experimental conditions as those described above.

$Na_3[(Fe(CN)_5P(OEt)_3]H_2O$ has been isolated and characterized by microanalysis, IR, UV-visible, NMR (^1H, ^{13}C) and Mössbauer spectroscopies. The phosphite substitutes in $[Fe(CN)_5(H_2O)]^{3-}$ with the specific rate constant k_1 equal to $1.4 \pm 0.1\ s^{-1}$ at 25°C, $\mu = 0.10$. The corresponding Fe(III) species were isolated from chemical or electrochemical oxidation of the corresponding Fe(II) complexes. The Fe(III) and Fe(II) phosphite complexes do not undergo aquation reaction in the time scale of a week.

From the accumulated data on the phosphite complexes of Os(II), Ru(II), and Fe(II) systems the following order of decreasing back-bonding, $M(II) \rightarrow P(III)$, has been proposed: $[Os(NH_3)_4(P(OEt)_3)_2]^{2+} > [Fe(CN)_5P(OEt)_3]^{3-} > [Ru(NH_3)_4(P(OEt)_3)_2]^{2+} > [Ru(CN)_4(P(OEt)_3)_2]^{2-}$.

E. SUMMARY

Information has been accumulated regarding the fundamental chemistry of pnictides as ligands in mononuclear octahedral d^6 and d^5 low-spin systems. Most of the results refer to substitution reactions. Trans-effect and trans-influence and reaction mechanisms have been evaluated. In this field, some activation volume measurements are in course of measurement. Attempts are in progress to achieve a better evaluation of the trans-effect and trans-influence series for the pnictide ligands using imN and SO_3^{2-} rather than pyr and isn as substrates.

Polynuclear systems and oxidation reduction reactions in the title complexes are also being explored [80].

For selected compounds, X-ray studies are in progress. From bond distance data for these systems we expect to obtain information regarding the phosphane orbitals involved in $Ru(II) \rightarrow P(III)$ back-bonding.

The functionalization of silica gel with phosphorus groups as aminopropyldiphenylphosphine and diphenylphosphinoethyl could offer a unique opportunity to compare the chemical behaviour of the supported phosphane complexes with that of their analogues in solution [82]. This is also being investigated.

For mono- and bisphosphito complexes, the LF bands are well defined. These are therefore interesting compounds for photosubstitution studies [83]. Furthermore, photochemical studies can offer a unique opportunity to develop a synthetic route for the cis derivatives since the phosphite exhibits strong cis delabilizing effect.

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REFERENCES

1 C. Masters, Homogeneous Transition-Metal Catalysis, Chapman and Hall, London, 1981.
2 L.H. Pignolet, Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, 1983.
3 E.C. Alyea and D.W. Meek, Adv. Chem. Ser., 196 (1982) 195.
4 C.A. Tolman, Chem. Rev., 77 (1977) 44.
5 J. Halpern, Phosphorus Sulfur, 18 (1983) 307.
6 M.L. Tobe, in G. Wilkinson, R.D. Gillard and J.A. McLeverty (Eds.), Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987, Chap. 7.1.
7 S.D. Robinson, in M.J. Mays (Ed.), MTP International Review of Science, Ser. 2, Vol. 6, Part 2, Butterworths, London, 1975, Chap. 3.
8 T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
9 A. Pidcock, in C.A. McAuliffe (Ed.), Aspects of Inorganic Chemistry, Halsted Press, New York, 1973, pp. 1–29.
10 C.A. McAuliffe and W. Levason, Phosphine, Arsine and Stibine Complexes of the Transition Elements, Elsevier, Amsterdam, 1979.
11 P.G. Douglas and B.L. Shaw, J. Chem. Soc. A, (1970) 1556.
12 D.A. Couch and S. Robinson, Inorg. Nucl. Chem. Lett., 9 (1973) 1079.
13 D.A. Couch and S.D. Robinson, Inorg. Chim. Acta, 9 (1974) 39.
14 R.C. Stewart and L.G. Marzilli, J. Am. Chem. Soc., 100 (1978) 817.
15 L.G. Marzilli, P.J. Toscano, J.H. Ramsden, L. Randaccio and N.B. Pahor, in E.C. Alyea and D.W. Meek (Eds.), Catalytic Aspects of Metal Phosphine Complexes, American Chemical Society, Washington, DC, 1982, pp. 85–99.
16 R.D. Garlatti and G. Tauzher, Inorg. Chim. Acta, 142 (1988) 263.
17 D.J. Darensbourg and B.J. Baldwin-Zuschke, Inorg. Chem., 20 (1981) 3846.
18 J.R. Burdett and T.A. Albright, Inorg. Chem., 18 (1979) 2112.
19 B. Olgemöller and W. Beck, Inorg. Chem., 22 (1983) 997.
20 J.A.S. Howell and P.M. Burkinshaw, Chem. Rev., 83 (1983) 557.
21 S.P. Modi and J.D. Atwood, Inorg. Chem., 22 (1983) 26 and references cited therein.
22 H.E. Bryndza, P.J. Domaille, R.A. Paciello and J.E. Bercaw, Organometallics, 8 (1989) 379.
23 T.S. Repinskaya, V.A. Gindin and A.M. Popov, Zh. Obshch. Khim., 56 (1986) 2415; Chem. Abstr., 106 (1987) 187774c.
24 R. Vac, J.H. Nelson, E.B. Milosavljevic and L. Solujic, Inorg. Chem., 28 (1989) 3831.
25 M.M. Rahman, H.Y. Liu, A. Prock and W.P. Giering, Organometallics, 6 (1987) 650.

26 D.W. Krassowski, J.H. Nelson, K.R. Brower, D. Hauenstein, R.A. Jacobson, Inorg. Chem., 27 (1988) 4294.
27 Md. Rahman, H.Y. Liu, K. Eriks, A. Prock and W.P. Giering, Organometallics, 8 (1989) 1.
28 Z. Lin and M.B. Hall, Inorg. Chem., 30 (1991) 646 and references cited therein.
29 D.W. Franco and H. Taube, Inorg. Chem., 17 (1978) 571.
30 H. Taube, Surv. Prog. Chem., 6 (1973) 1.
31 H. Taube, Comments Inorg. Chem., 1 (1981) 17.
32 P.C. Ford, Coord. Chem. Rev., 5 (1970) 75.
33 D.W. Franco, Inorg. Chim. Acta, 48 (1981) 1.
34 J.C. Nascimento Filho, J.M. de Rezende, B.S. Lima Neto and D.W. Franco, Inorg. Chim. Acta, 145 (1988) 111.
35 J.C. Nascimento Filho and D.W. Franco, Inorg. Chim. Acta, 113 (1986) 55.
36 A.G. Sharpe, The Chemistry of Cyano Complexes of the Transition Metals, Academic Press, London, 1976.
37 D.H. Macartney, Rev. Inorg. Chem., 9 (1988) 101.
38 C.R. Johnson and R.E. Sheperd, Inorg. Chem., 22 (1983) 2439.
39 E.A. Seddon and K.R. Seddon, in R.J.H. Clark (Ed.), The Chemistry of Ruthenium, Elsevier, Amsterdam, 1984.
40 W. Gerrard and H.R. Hudson, in G.M. Kosolapoff and L. Maier (Eds.), Organic Phosphorus Compounds, Vol. 5, Wiley-Interscience, New York, 1975, pp. 21–302.
41 D.E.C. Corbridge, Phosphorus, Elsevier, Amsterdam, 1978.
42 R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley, New York, 1988, pp. 71–74.
43 C.A. McAuliffe, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon, Oxford, 1987, Chap. 14.4 and references cited therein.
44 D.W. Franco, Inorg. Chim. Acta, 32 (1979) 273.
45 J.C. Nascimento Filho, J.M. de Rezende, B.S. Lima Neto, J.B. Lima and D.W. Franco, in preparation.
46 J.M. de Rezende and D.W. Franco, Transition Met. Chem., 12 (1987) 267.
47 R.L. Sernaglia and D.W. Franco, Inorg. Chem., 28 (1989) 3485.
48 L.M.A. Plicas and D.W. Franco, Inorg. Chim. Acta, 134 (1987) 265.
49 L.S. Santos, S.I. Klein, C.U. Davanzo, M. Tabak, E. Dradi and D.W. Franco, Proceedings of the XXVIII International Conference on Coordination Chemistry, Gera, Germany, 1990, Vol. 2, 7–10. Full paper in preparation.
50 S.M.C. Neiva, L.S. Santos, S.B. Araujo, J.C. Nascimento Filho and D.W. Franco, Can. J. Chem., 65 (1987) 372.
51 S.M.C. Neiva, L.S. Santos and D.W. Franco, in preparation.
52 S.B. Araujo and D.W. Franco, in preparation.
53 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 2nd edn., 1984.
54 E. Trabuco and D.W. Franco, Polyhedron, 5 (1986) 1503.
55 S.C. Martins and D.W. Franco, in preparation.
56 C.H. Campbell, A.R. Dias, M.L.H. Green, T. Saito, M.G. Swanwick, J. Organomet. Chem., 14 (1969) 349.
57 J.A. Stanko and T.W. Starinshak, Inorg. Chem., 8 (1969) 2156.
58 A.D. Allen, T. Eliades, R.O. Harris and B. Reinslau, Can. J. Chem., 47 (1969) 1605.
59 A.K. Okura and D.W. Franco, in preparation.
60 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 3rd edn., 1978.

61 R.H.P. Francisco, J.C. Nascimento Filho and D.W. Franco, in preparation.
62 M.S. Galhiane and D.W. Franco, J. Coord. Chem., 13 (1984) 315.
63 N.M.S. Rezende, S.C. Martins, L.A. Marinho, J.A.V. Santos, M. Tabak, J.R. Perussi and D.W. Franco, Inorg. Chim. Acta, 182 (1991) 87.
64 W.C. Trogler, L.A. Epps and L.G. Marzilli, Inorg. Chem., 14 (1975) 2748.
65 J.R. Chipperfileld, in N.B. Chapman and J. Shorter (Eds.), Advances in Linear Free Energy Relationships, Plenum Press, London, 1972, p. 321 and references cited therein.
66 D.W. Franco, unpublished results.
67 P.R. Hammond, J. Chem. Soc., (1962) 1365 and references cited therein.
68 R.E. Shepherd and H. Taube, Inorg. Chem., 12 (1973) 1392.
69 J.C. Nascimento Filho, L.M.A. Plicas and D.W. Franco, in preparation.
70 R.G. Wilkins, The Study of Kinetics and Mechanisms of Transition Metal Complexes, Allyn and Bacon, Boston, 1974.
71 J.H. Espenson, Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, New York, 1981.
72 C.H. Langford and H.B. Gray, Ligand Substitution Process, Benjamin, New York, 1965.
73 J.D. Atwood, Inorganic and Organometallic Reaction Mechanisms, Books/Cole, Monterey, 1985.
74 P.A. Lay, Coord. Chem. Rev., 110 (1991) 213 and references cited therein.
75 B.S. Lima Neto and D.W. Franco, in preparation.
76 S.S. Isied and H. Taube, Inorg. Chem., 15 (1976) 3070.
77 L. Chen and A.J. Poë, Inorg. Chem., 28 (1989) 3641.
78 J.A. Marchant, T. Matsubara and P.C. Ford, Inorg. Chem., 16 (1977) 2160 and references cited therein.
79 L.L. Hegedus (Ed.), Catalyst Design, Wiley, New York, 1987.
80 J.A.V. Santos, L.A. Marinho, S.C. Martins, N.M.S. Rezende and D.W. Franco, Proceedings of the Seventh International Symposium on Homogeneous Catalysis, Lyon-Villeurbanne, France, 1990, P-76. Full paper in preparation.
81 L.C.G. Vasconcellos, E. Tfouni, L.M.A. Plicas, A.A. Batista, K.S.M. Ferreira and D.W. Franco, in preparation.
82 S.M.C. Neiva, M.R. Martins, M.T. Hoffman and D.W. Franco, Proceedings of the Chemically Modified Surfaces Symposium, Chadds Ford, Pennsylvania, 1991.
83 S.E. Mazzetto, L.M.A. Plicas, E. Tfouni and D.W. Franco, Inorg. Chem., 31 (1992) 516.