Kinetics of Axial Ligand Exchange in Ruthenium(II) Tetraphenylporphyrin Complexes

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Variable-temperature ^{1}H n.m.r. lineshape analysis has been used to determine the kinetics of axial ligand exchange in 1-methylimidazole and 4-t-butylpyridine complexes of benzyl isocyanide(tetraphenylporphyrinato)ruthenium(II). The results are compared with those for other ruthenium(II) porphyrins and for ruthenium(II) complexes of simple amine ligands, and discussed in terms of π bonding and anti-symbiotic effects. The *cis* effect of tetraphenylporphyrin is much less in ruthenium(II) complexes than in their iron(II) analogues. This is considered as definite evidence for the formation of a high-spin intermediate in the latter case.

ALTHOUGH rates of substitution in ruthenium(II) complexes have been extensively investigated in recent years, the systems studied have tended to fall into the three groups represented by equations (1),[1-5], (2),[5-7] and (3) [8] where A = simple amine, L and X = neutral or anionic ligands (charges have been omitted for the sake of

$$[RuA_5(OH_2)] + X \rightleftharpoons [RuA_5X] + H_2O \quad (1)$$

$$[RuA_4L(OH_2)] + X \rightleftharpoons [RuA_4LX] + H_2O \quad (2)$$

$$[RuNO_xX_y(OH_2)_{6-x-y}] + H_2O \rightleftharpoons [RuNO_xX_{y-1}(OH_2)_{7-x-y}] + X^- \quad (3)$$

clarity). The one exception to this classification is the study by Eaton and co-workers [9-11] of axial substitution in carbonyl(heterocyclic amine)(porphyrinato)ruthenium complexes. Apart from their intrinsic interest as a new class of ruthenium(II) complexes, ruthenium(II) porphyrins have been considered as model systems for heme proteins.[12,13] Like their iron(II) analogues, ruthenium(II) porphyrins react reversibly with carbon monoxide and dioxygen *via* thermal and photochemical mechanisms;[14] however, they are much easier to handle because of their lower susceptibility to irreversible oxidation. In the course of previous work on a variety of iron(II) macrocyclic systems [15] it has been demonstrated that iron(II) porphyrin complexes undergo axial substitution at rates which are much greater than those for other iron(II) amine complexes. It is of interest to see whether this exceptional reactivity is also shown by the ruthenium(II) porphyrins. We have therefore used ^{1}H n.m.r. full lineshape analysis to measure the rates of ligand exchange for [Ru(tpp)($PhCH_2NC$)(Bu^t-py)] and [Ru(tpp)($PhCH_2NC$)(1Me-imH)].† We compare the results with those found for porphyrinato- and amino-complexes of ruthenium(II) and with those for iron(II) macrocyclic complexes.

† Abbreviations used in this paper: tpp = tetraphenylporphyrinate, tipp = tetra(*p*-isopropylphenyl)porphyrinate, dmetp = 7,12-diethyl-2,18-bis[2-(methoxycarbonyl)ethyl]-3,8,13,17-tetramethylporphyrinate, Bu^t-py = 4-t-butylpyridine, 1Me-imH = 1-methylimidazole, imH = imidazole, 4,5Me_2-imH = 4,5-dimethylimidazole, py = pyridine, pip = piperidine, pyz = pyrazine, phen = 1,10-phenanthroline, tttt = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene, H_2dmg = dimethylglyoxime, pc = phthalocyaninate(2−), ttch = tetrabenzo[*b,f,j,n*][1,5,9,13]tetra-azacyclohexadecine.

RESULTS AND DISCUSSION

N.M.R. Spectra and the Nature of the Complexes.—The room-temperature ^{1}H n.m.r. spectrum of a 1,1,2,2-tetrachloroethane solution of [Ru(tpp)($PhCH_2NC$)(Bu^t-py)] and excess Bu^t-py shows a complex of peaks in the mid- to low-field region; these were generally assigned to the tpp protons and the aromatic protons of $PhCH_2NC$ and of the free and complexed pyridine, and were not considered further. The spectrum contains only two peaks in the high-field region, a singlet at 1.26 p.p.m. and another at 0.38 p.p.m. [see Figure 1(*b*)]. The first was assigned to the methyl protons of free Bu^t-py; the chemical shift is in reasonable agreement with that given by Eaton *et al.*[9] The second was assigned to the corresponding resonance of [Ru(tpp)($PhCH_2NC$)(Bu^t-py)]. The chemical shift is comparable to that found for [Ru(tpp)(CO)(Bu^t-py)] and analogous complexes of substituted tetraphenylporphyrins,[9-11] although the upfield shift on complexation is somewhat smaller when $PhCH_2NC$ is the *trans* ligand. This appears to be a general phenomenon (see below).

The ^{1}H n.m.r. spectrum of a mixture of [Ru(tpp)($PhCH_2NC$)(1Me-imH)] and 1Me-imH in $Cl_2CHCHCl_2$ at room temperature shows a complex of peaks in the low- and mid-field region corresponding to the tpp protons and the ring protons of $PhCH_2NC$. Again, these were not specifically assigned and were not considered further. The spectrum also shows singlets at 3.61 (A), 2.43 (B), 2.33 (C), 2.13 (D), and 2.11 (E) p.p.m., as indicated in Figure 2(*b*). The peak at 3.61 p.p.m. (A) was assigned to the methyl protons of free 1Me-imH; the chemical shift is in good agreement with the value of 3.69 p.p.m. found in CD_3CN solution.[15] Peak D was assigned to the corresponding resonance of [Ru(tpp)($PhCH_2NC$)(1Me-imH)]. Consistent with this assignment the difference in chemical shifts of peaks A and D is similar to that found for the resonance of the 5-methyl group of 3,5-dimethylpyrazole on complexation with [Ru(tipp)(CO)].[10] Peaks B and C were assigned to H^2 and H^4 of the 1Me-imH ring of [Ru(tpp)($PhCH_2NC$)(1Me-imH)]. Taking the chemical shifts of the corresponding resonances in free 1Me-imH as 7.43 and 7.00 p.p.m.,[15] the upfield changes in chemical shift on complexation with [Ru(tpp)($PhCH_2NC$)] are 5.0 and 4.9 p.p.m. for H^2 and H^4, respec-

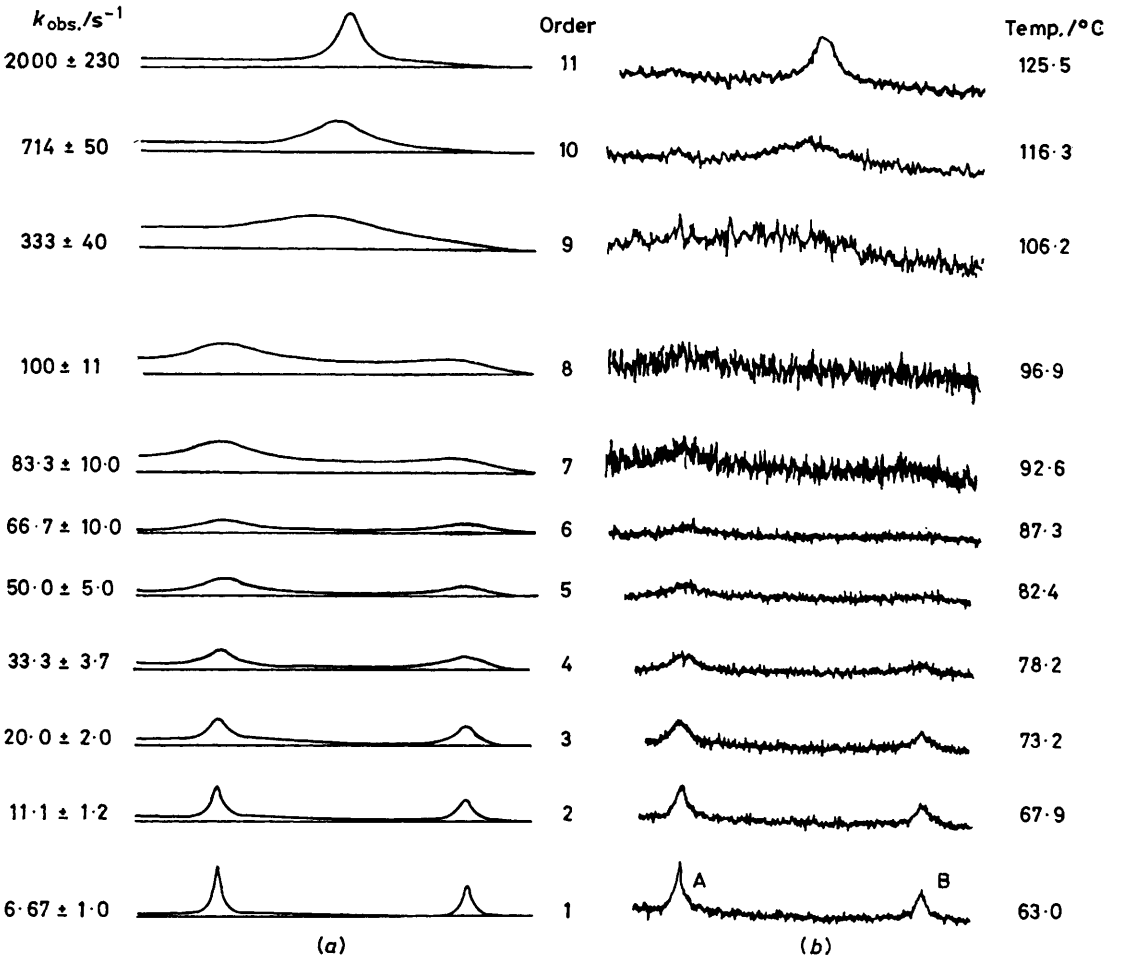
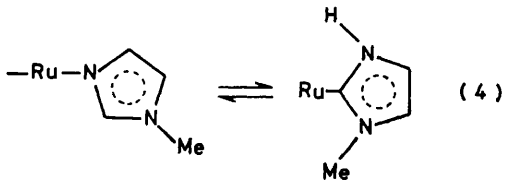


FIGURE 1 Calculated (*a*) and experimental (*b*) n.m.r. spectra for exchange of Bu^t-py with [Ru(tpp)(PhCH$_2$NC)(Bu^t-py)]

tively. These values are comparable with the changes of 6.45 and 6.46 p.p.m. found [16] for the corresponding resonances of imidazole on complexation with [Ru(dmetp)(CO)] but, as noted above, the changes are smaller for the PhCH$_2$NC complex. We cannot locate the H^5 resonance of complexed 1Me-imH, but following Faller and Sibert's [16] multiple resonance study on [Ru(dmetp)(CO)(imH)] we believe it to be hidden under the complex structure already assigned to the tpp and PhCH$_2$NC ring resonances. Peak B was assigned to the CH$_2$ protons of the co-ordinated PhCH$_2$NC.

The mode of binding of Bu^t-py in [Ru(tpp)(PhCH$_2$NC)(Bu^t-py)] is quite unambiguous, but there is some question about the site of binding in the 1Me-imH analogue. Co-ordination through the imidazole C^2 atom has been suggested [17] as an explanation for the observation [18] of apparent metal shuffling in [Ru(dmetp)(CO)(4,5Me$_2$-imH)]. However, if this complex does adopt such a structure it is almost certainly due to destabilisation of the *N*-bound isomer by steric hindrance between the porphyrin ring and the methyl groups α to the donor atom. (In the absence of such steric hindrance, *e.g.*, in [Ru(NH$_3$)$_5$(imH)]$^{2+}$, the *C*-bound isomer is intrinsically the least stable.[17]) For [Ru(tpp)(PhCH$_2$NC)(1Me-imH)] it is possible to write a rapid equilibrium (4) in which the observed properties are an average of those for the two



(4)

isomers. However, in this compound it is the *C*- and not the *N*-bound isomer which is subject to steric strain. We therefore believe that for [Ru(tpp)(PhCH$_2$NC)(1Me-imH)] any equilibrium of this type lies so far to the left that the contribution of the *C*-bound isomer to the observed properties is negligible.

Kinetics.—The effect on the ^{1}H n.m.r. spectrum of heating a sample of a mixture of [Ru(tpp)(PhCH$_2$NC)(Bu^t-py)] and Bu^t-py in Cl$_2$CHCHCl$_2$ is shown in Figure 1(*b*). The changes are consistent with exchange process (5). Using full lineshape analysis, the values of $k_{obs.}$ and

[Ru(tpp)(PhCH$_2$NC)(Bu^t-py)] + Bu^t-py* ⇌
[Ru(tpp)(PhCH$_2$NC)(Bu^t-py*)] + Bu^t-py (5)

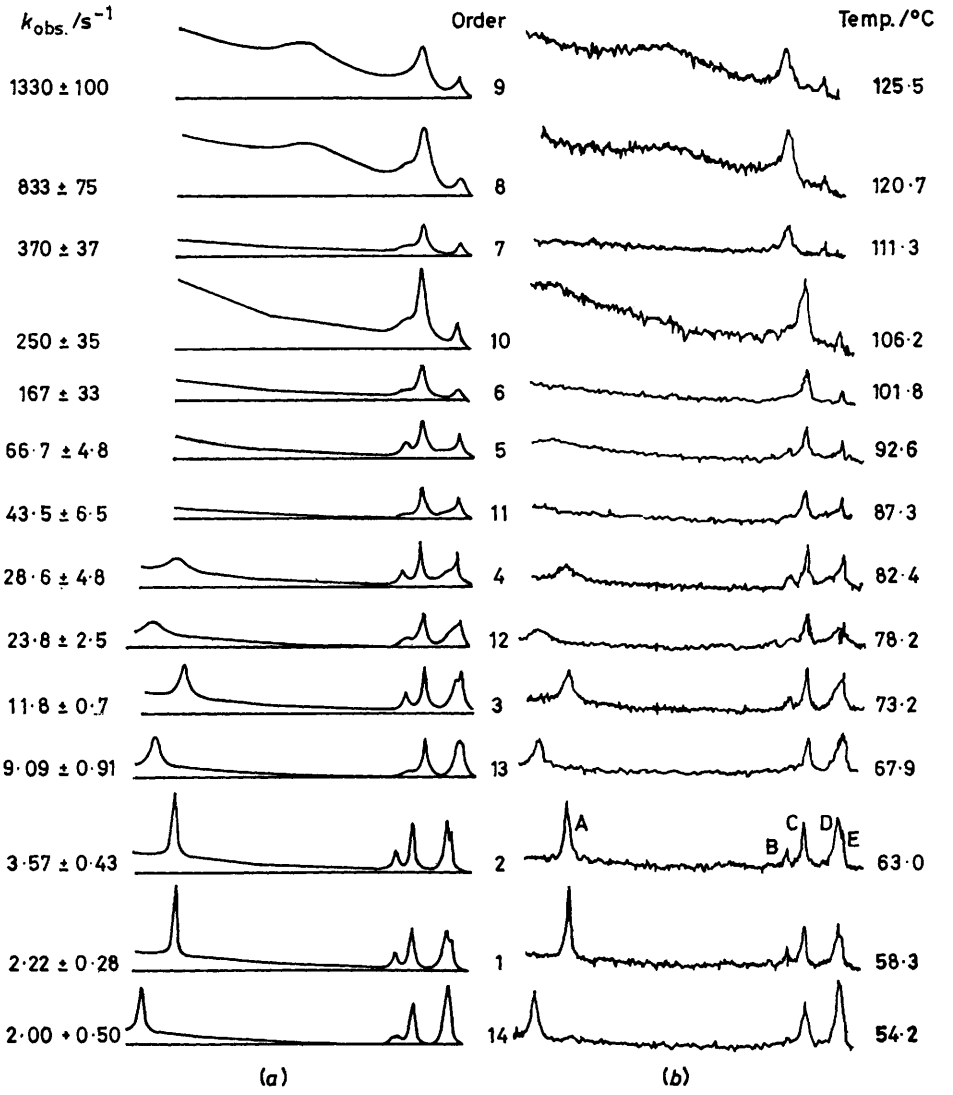


FIGURE 2 Calculated (*a*) and experimental (*b*) n.m.r. spectra for exchange of 1Me-imH with [Ru(tpp)($PhCH_2NC$)(1Me-imH)]

the simulated spectra shown in Figure 1(*a*) were obtained.

The effect on the ^1H n.m.r. spectrum of heating a mixture of [Ru(tpp)($PhCH_2NC$)(1Me-imH)] and 1Me-imH is shown in Figure 2(*b*); the changes are consistent with exchange process (6). This exchange should lead to

$$[Ru(tpp)(PhCH_2NC)(1Me\text{-}imH)] + 1Me\text{-}imH^* \rightleftharpoons [Ru(tpp)(PhCH_2NC)(1Me\text{-}imH^*)] + 1Me\text{-}imH \quad (6)$$

coalescence of corresponding resonances of the free and co-ordinated 1Me-imH. However, over the temperature range studied only the methyl resonances show much change; this is because their separation is smaller than that of the ring resonances. The latter would in any case be less suitable for the lineshape analysis because the free ligand peaks overlap with the more intense porphyrin resonances. Thus only the behaviour of the methyl resonances was considered in the lineshape analysis; corrections for small variations in peaks B, C, and E were made as discussed in the Experimental section. The simulated spectra, together with the values of $k_{obs.}$ calculated for reaction (6), are shown in Figure 2(*a*).

The enthalpy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ of activation for reaction (5) were found to be 93.4 ± 3.7 kJ mol^{-1} and 48 ± 10 J K^{-1} mol^{-1}, respectively, with a 23% uncertainty in $k_{obs.}$. For reaction (6), $\Delta H^{\ddagger}$ was 97.0 ± 1.8 kJ mol^{-1} and $\Delta S^{\ddagger}$ 55 ± 5 J K^{-1} mol^{-1}, with a 15% uncertainty in $k_{obs.}$. The large uncertainties in $k_{obs.}$ for both systems reflect a scatter of the points about the least-squares line and not systematic deviation from the Eyring equation. The scatter is due to the inherent uncertainty of the lineshape analytical method and to extra difficulties caused by the accumulation during the run of small amounts of paramagnetic products of decomposition.

It is currently accepted [1-11] that substitution reactions of octahedral ruthenium(II) complexes are dissociative in nature, and they are usually discussed in terms of an S_N1(lim.) mechanism. Accordingly, we interpret our results in terms of the formation of a five-co-ordinate

intermediate, equations (7) and (8). For the reactions

$$[Ru(tpp)LX] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(tpp)L] + X \quad (7)$$

$$[Ru(tpp)L] + Y \xrightarrow{k_2} [Ru(tpp)LY] \quad (8)$$

studied here, X and Y are identical so that $k_{-1} = k_2$, and $k_{obs.} = k_1$, the rate constant for dissociative loss of X from the substrate. The results found here are compared to results found for other ruthenium(II) porphines, for simple ruthenium(II) amine complexes, and for iron(II) complexes of macrocyclic ligands. Relevant kinetic data are collected in Table 1.

However, in [Ru(tpp)($PhCH_2NC$)X], Bu^t-py is, if anything, a slightly better leaving group than 1Me-imH. Rates of substitution in [Ru(tipp)(CO)X], where X is a heterocyclic amine, show a similar insensitivity to the electronic properties of the leaving group.[10] These results can be explained by considering the nature of the other ligands bound to ruthenium(II) in these complexes. In both [Ru(tpp)($PhCH_2NC$)X] and [Ru(tipp)(CO)X] the ligand *trans* to X is a strong π-acceptor;[26] Srivastava[12] has also suggested that porphyrins have π-acid properties. The presence of other π-acid ligands in the molecule reduces π bonding to X by the anti-symbiotic

TABLE 1

Kinetic data for axial substitution in ruthenium(II) and iron(II) complexes *trans*-[MA_4LX]

Complex	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$10^3 k_{298}$/s^{-1}	Ref.
[Ru(tpp)($PhCH_2NC$)(Bu^t-py)]	93.4 ± 3.7	48 ± 10	83	This work
[Ru(tpp)($PhCH_2NC$)(1Me-imH)]	97.0 ± 1.8	55 ± 5	46	This work
[Ru(tpp)($PhCH_2NC$)$_2$]	110.4 ± 1.1	64 ± 4	0.65	35
[Ru(tpp)(CO)(Bu^t-py)]	88.7 ± 4.2	29 ± 10	62	11
[$Ru(NH_3)_6$]$^{2+}$			0.0016 [a]	4
[$Ru(NH_3)_5(N_2)$]$^{2+}$	115.9 ± 3.3	33 ± 13	0.0020	2*b*
[$Ru(NH_3)_5(TeMe_2)$]$^{2+}$			0.12	5
[$Ru(NH_3)_5(SO_3)$]			9.6	7*a*
[$Ru(NH_3)_4(SO_3)$(imH)]			3.7	7*b*
[$Ru(NH_3)_4(SO_3)$(1Me-imH)]			<1	7*b*
[$Ru(NH_3)_4(SO_3)$(pyz)]	107.9 ± 4.2	73 ± 14	4.5	7*a*
[Fe(tpp)(1Me-imH)$_2$]	65 [b]	31 [b]	1.14 × 10^6	*c*
[Fe(tpp)(py)$_2$]	67 [b]	61 [b]	1.88 × 10^7	*c*
[Fe(tpp)(pip)$_2$]	55 [b]	15 [b]	6.94 × 10^6	*c*
[Fe(tttt)(1Me-imH)$_2$]$^{2+}$	74.9 ± 2.9	0 ± 8	450	15
[Fe(tttt)(imH)$_2$]$^{2+}$	90.0 ± 2.1	46 ± 8	270	15
[Fe(ttch)(1Me-imH)$_2$]$^{2+}$	109.6	82	6.9	*d*
[Fe(dmg)(1Me-imH)$_2$]			0.69 [e]	*f*
[Fe(pc)(1Me-imH)$_2$]	118 ± 4	96 ± 14	1.3 [g]	*h*
[Fe(phen)$_3$]$^{2+}$	131.8 ± 2.1	117 ± 8	0.070	*i*
[Fe(phen)]$^{2+}$	50.1	−67	2 200	*j*

[a] Divided by 6 to correct for statistical factors. [b] Calculated by the authors of this paper as indicated in the text. [c] D. Lavalette, C. Tetreau, and M. Momenteau, *J. Am. Chem. Soc.*, 1979, **101**, 5395. [d] I. W. Pang and D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 2192. [e] Determined at 10 °C. [f] I. W. Pang and D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 590. [g] Determined at 23 °C. [h] D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 1170. [i] F. Basolo, J. C. Haynes, and H. M. Neumann, *J. Am. Chem. Soc.*, 1954, **76**, 3807. [j] R. S. Bell and N. Sutin, *Inorg. Chem.*, 1962, **1**, 359.

The ease of loss of X from [Ru(tpp)($PhCH_2NC$)X] increases in the order X = $PhCH_2NC$ ≪ 1Me-imH ~ Bu^t-py, whether this is judged by relative rate constants or enthalpies of activation. The position of $PhCH_2NC$ in the series correlates with the presumed high ground-state strength of the $PhCH_2NC$–Ru bond. The affinity of ruthenium(II) for π-acids is well documented [19-24] and $PhCH_2NC$, being by far the best π-bonding ligand, would be expected to form the strongest bonds to this metal. Quantitatively, the series cannot be explained by such simplistic arguments, however. The enthalpy change $\Delta H^{\ominus}$ associated with reaction (9) is 65.3 kJ mol^{-1} more favourable when X is MeNC than when X is py,[19] but

$$[Ru(NH_3)_5(OH_2)]^{2+} + X(g) \longrightarrow [Ru(NH_3)_5X]^{2+} + H_2O \quad (9)$$

$\Delta H^{\ddagger}$ for reaction (10) is only 17.0 kJ mol^{-1} lower when X

$$[Ru(tpp)(PhCH_2NC)X] \longrightarrow [Ru(tpp)(PhCH_2NC)] + X \quad (10)$$

is Bu^t-py than when X is $PhCH_2NC$. Similarly, pyridines are better π-acceptors than imidazoles [25] and form stronger bonds to ruthenium(II) in simple amines.[1c,17] effect.[27] This weakens the Ru–X bond in the ground state and the polarisability inherent in the π system provides a dynamic response to compensate for loss of X in the transition state. The kinetics are therefore less sensitive to the π-acidity of the leaving group than might have been expected.

The kinetics show a similar insensitivity to the π-acidity of the ligand *trans* to the leaving group. $\Delta H^{\ominus}$ for reaction (9) is −151.0 kJ mol^{-1} when X is CO and −107.9 kJ mol^{-1} when X is MeNC,[19] most of the difference being due to the greater π-acidity of CO.[28] Despite this, the rates and values of $\Delta H^{\ddagger}$ for loss of Bu^t-py from from [Ru(tpp)(CO)(Bu^t-py)] and [Ru(tpp)($PhCH_2NC$)-(Bu^t-py)] are within experimental error the same. The anti-symbiotic effect is again responsible.

Apart from the differences implied above, it is hard to compare the *cis* effect of the porphyrin ring directly with that of four amine ligands, since there is no information available on the *trans* $PhCH_2NC$ tetra-amines. Nevertheless, comparison with the kinetics of reactions (11)—(16) which involve loss of a nitrogen-donor ligand suggests

$$[Ru(NH_3)_5(N_2)]^{2+} + H_2O \longrightarrow [Ru(NH_3)_5(OH_2)]^{2+} + N_2 \quad (11)$$

$$[Ru(NH_3)_6]^{2+} + H_2O \longrightarrow [Ru(NH_3)_5(OH_2)]^{2+} + NH_3 \quad (12)$$

$$[Ru(NH_3)_5(TeMe_2)]^{2+} + H_2O \longrightarrow trans\text{-}[Ru(NH_3)_4(TeMe_2)(OH_2)]^{2+} + NH_3 \quad (13)$$

$$[Ru(NH_3)_5(SO_3)] + H_2O \longrightarrow trans\text{-}[Ru(NH_3)_4(SO_3)(OH_2)] + NH_3 \quad (14)$$

$$trans\text{-}[Ru(NH_3)_4(SO_3)(imH)] + H_2O \longrightarrow trans\text{-}[Ru(NH_3)_4(SO_3)(OH_2)] + imH \quad (15)$$

$$trans\text{-}[Ru(NH_3)_4(SO_3)(pyz)] + H_2O \longrightarrow trans\text{-}[Ru(NH_3)_4(SO_3)(OH_2)] + pyz \quad (16)$$

some trends. Assuming lability parallels thermodynamic stability of the substrate, the kinetics of reactions (12)—(15) are directly comparable with those for reactions (5) and (6). Since N_2 is predicted to lie between $PhCH_2NC$ and Bu^t-py in effectiveness as a leaving group,[19] we compare the data for reaction (11) with those for a hypothetical complex, [Ru(tpp)($PhCH_2NC$)X], whose kinetic parameters are the average of those for [Ru(tpp)($PhCH_2NC$)$_2$] and [Ru(tpp)($PhCH_2NC$)(Bu^t-py)]; *i.e.*, $\Delta H^{\ddagger} = 101.9$ kJ mol^{-1}, $\Delta S^{\ddagger} = 56$ J K^{-1} mol^{-1}, and $10^3 k_{298} = 7.3$ s^{-1}. Based on the data [2b,4] for reactions (11) and (12), the tpp complexes are a factor of 10^3—10^4 times more reactive than the tetra-amines. However, this difference is to some extent a consequence of the low *trans* effect of the hard,[29] pure σ-donor NH_3 in $[Ru(NH_3)_5X]^{2+}$ compared to that of $PhCH_2NC$ in [Ru(tpp)($PhCH_2NC$)X]. If the *trans* NH_3 group is replaced by the more polarisable $TeMe_2$,[5] the gap between the rates of substitution in $[Ru(NH_3)_4LX]$ and [Ru(tpp)($PhCH_2NC$)X] narrows, and when a good π-acceptor such as SO_3^{2-} is present,[7] the rates at 298 K differ by only a factor of ten.* The *cis* effect of tpp in ruthenium(II) complexes is thus greater than that of NH_3, but only moderately so. We ascribe the greater *cis* effect of tpp to its π-acidity which enables it to affect leaving-group bonding in the ground and transition states by the anti-symbiotic and polarisability mechanisms discussed earlier.

The moderate *cis* effect found for tpp in ruthenium(II) complexes contrasts sharply with the large *cis* effect [15,30,†] of tpp in iron(II) complexes. Rates of axial substitution in the iron(II) porphyrins are also much greater than in their ruthenium analogues; rates of 1Me-imH exchange in [Ru(tpp)($PhCH_2NC$)(1Me-imH)] and [Fe(tpp)(1Me-imH)$_2$] differ by a factor of *ca.* 10^5. Qualitative observations indicate 1Me-imH exchange in [Ru(tpp)(1Me-imH)$_2$] is several orders of magnitude slower than in [Ru(tpp)(1Me-imH)X], where X = CO or $PhCH_2NC$. Thus the difference in the lability of 1Me-imH in [Fe(tpp)(1Me-imH)$_2$] and [Ru(tpp)(1Me-imH)$_2$] is a factor of 10^8 or greater. Unfortunately, no accurate activation parameters are available for the iron(II) porphyrins, but for reaction (17) values of $\Delta H^{\ddagger} = 65$ kJ mol^{-1}, $\Delta S^{\ddagger} =$

$$[Fe(tpp)L_2] \longrightarrow [Fe(tpp)L] + L \quad (17)$$

31 J K^{-1} mol^{-1} (L = 1Me-imH); $\Delta H^{\ddagger} = 67$ kJ mol^{-1}, $\Delta S^{\ddagger} = 61$ J K^{-1} mol^{-1} (L = py); and $\Delta H^{\ddagger} = 55$ kJ mol^{-1}, $\Delta S^{\ddagger} = 15$ J K^{-1} mol^{-1} (L = pip) can be obtained by combining the rate constants of Weschler *et al.*[30] for dichloromethane solutions at −79 °C with those of Lavalette *et al.*† for toluene solutions at 25 °C. (It is unlikely that solvation effects differ greatly in the two solvents.) These values of $\Delta H^{\ddagger}$ are much lower than those for other low-spin iron(II) complexes, being within 16 kJ mol^{-1} of that for loss of phen from *high-spin* [Fe(phen)]$^{2+}$. The values of $\Delta S^{\ddagger}$ for reaction (17) are also considerably more negative than the values for substitution reactions of most other low-spin iron(II) complexes. Again, this is a trend towards the value for the high-spin complex, although the effect is less marked than for the $\Delta H^{\ddagger}$ values. These results reinforce the suggestion of Stynes and James,[31] based on somewhat different arguments, that the high reactivity of the iron–tpp complexes is due to a low-energy pathway involving an axially distorted high-spin intermediate. Production of such a species is facilitated by the poor fit of the low-spin Fe^{2+} ion in the over-sized porphyrin ring, which gives a low effective ligand field for the porphyrin ligand. A similar pathway is not available for the ruthenium(II) analogues because the larger Ru^{2+} ion fits the porphyrin ring better, and because *d*-orbital splittings are larger for a second transition-series ion.[32] Both factors give tpp a higher effective ligand-field strength in the ruthenium complex and render a high-spin intermediate inaccessible. As a result, the *cis* effect of tpp in the ruthenium(II) series is due only to its π-acidity, and is much less than in the iron(II) analogues.

EXPERIMENTAL

Synthesis of Compounds.—The starting material [Ru(tpp)(CO)$_2$] was prepared using the method of Tsutsui *et al.*,[18a] using a 1 : 2 mol ratio of $[Ru_3(CO)_{12}]$: tpp and refluxing under nitrogen for 22 h. The tpp was synthesized according to the method of Adler *et al.*[33]

[Ru(tpp)($PhCH_2NC$)$_2$] was prepared by a method analogous to that of Eaton,[34] giving purple crystals of [Ru(tpp)($PhCH_2NC$)$_2$]·$CHCl_3$ in 77% yield (Found: C, 68.85; H, 4.65; N, 7.45. Calc. for $C_{61}H_{43}Cl_3N_6Ru$: C, 68.65; H, 4.05; N, 7.85%).

[Ru(tpp)($PhCH_2NC$)(py)] and [Ru(tpp)($PhCH_2NC$)(Bu^t-py)] were prepared by heating a chloroform solution of [Ru(tpp)($PhCH_2NC$)$_2$] (0.19 mmol) with 5 cm^3 (*ca.* 50-fold excess) of the appropriate pyridine at 65 °C for 35 min. Kinetic experiments [35] indicate production of the mono-

* This factor is somewhat higher when 1Me-imH is the leaving group, due to anomalously low rates of substitution in [Ru(NH_3)$_4$(SO_3)(1Me-imH)] compared to those in the analogous complexes of other heterocyclic amines. The explanation for this is unclear, but it may be due to hydrogen-bonding effects in the aqueous solutions used for the studies on $[Ru(NH_3)_4(SO_3)X]$. Alternatively, it may reflect the difficulty of measuring rates of aquation as small intercepts in the plots of $k_{obs.}$ *versus* [entering group] for anation reactions.

† D. Lavalette, C. Tetreau, and M. Momenteau, *J. Am. Chem. Soc.*, 1979, **101**, 5395. Values of the rate constant for reaction (17) were calculated from these authors' values of the rate and equilibrium constants for the reverse reaction. For [Fe(tpp)(pip)$_2$] the equilibrium constant used was that of the complex [Fe(tpp–py)(pip)] in which the pyridine ligand is bound to the tetraphenylporphyrin ring; the equilibrium constants for the chelated and unchelated complexes are very similar for both the 1Me-imH and the py systems.

pyridine complex occurs cleanly and quantitatively with a half-life of *ca.* 5 s under these conditions. (Formation of the bis complex requires prolonged boiling at 130 °C and/or photolysis of the initial monopyridine product.) After cooling and filtering the reactant solution, the monopyridine complex was precipitated and washed with hexane and dried *in vacuo*. The n.m.r. peak positions and intensities of the product are entirely consistent with its assignment as a pure monopyridine complex.

[Ru(tpp)($PhCH_2NC$)(1Me-imH)] was prepared from [Ru(tpp)($PhCH_2CN$)(py)] by a substitution reaction using a 50-fold excess of 1Me-imH in dichloromethane solution. Again, kinetic experiments [35] indicate the reaction to give the mono(1Me-imH) complex is quantitative. The complex was precipitated and washed with hexane and dried *in vacuo*. N.m.r. spectra support the characterisation of the product as a pure mono(1-methylimidazole) complex.

All reactions were carried out under a nitrogen atmosphere to exclude oxygen.

N.M.R. Spectra.—Spectra of 1,1,2,2-tetrachloroethane solutions, degassed by bubbling with nitrogen, were recorded on a Varian HA-100 spectrometer using the solvent ^1H resonance as the lock signal. Because the complexes slowly decompose to paramagnetic species in the presence of added amines, spectra were recorded immediately after sample preparation. For the kinetic measurements the spectrometer was equipped with a Varian V-4341/V-6057 variable-temperature accessory. Temperatures were measured using the difference in chemical shifts of the ethylene glycol ^1H resonances.[36] Observed n.m.r. spectra and calculated overlays are available as Supplementary Publication No. SUP 23184 (14 pp.).*

Kinetics.—Lineshape analysis was performed on a Hewlett-Packard 2100 minicomputer using a Fortran program based on the approach of Johnson and Moreland,[37] but with modifications noted earlier.[15] To deal with specific problems in the systems studied here the program included the following features. (1) The curving baseline caused by proximity of the weak 1Me-imH and Bu^t-py resonances to the strong solvent resonance was simulated by applying increasing linear-drift corrections over successive small portions of the spectrum. (2) The imidazole ring resonances (C and E) and the $PhCH_2NC$ peak (B) in the 1Me-imH system were simulated using their observed linewidths and chemical shifts and assuming negligibly slow exchange with ' dummy ' peaks located at arbitrary positions outside the plotting and calculation ranges.† (3) Despite degassing with nitrogen, some decomposition to paramagnetic species occurred at the high temperatures needed to effect exchange. Room-temperature spectra were recorded before and after the runs and systematic corrections (depending on the temperature and time of exposure of the sample) made to the chemical shifts and linewidths characteristic of the slow-exchange limit. Corrections for variations in T_2 (spin–spin relaxation time) and chemical shift values with temperature were not made since measurements [9] on similar complexes suggested these were much less than the corrections for the accumulation of paramagnetic decomposition products. The large separation of the exchanging peaks here also means that this neglect has a smaller effect than in systems [38] where it has been found to be significant. The parameters used in the spectral simulations are given in Table 2.

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† This is simply a device to allow us to circumvent the input limitations of our program which at present allow us to include several different exchange processes occurring at different rates (including the negligibly small) but not peaks which do not undergo any exchange at all.

TABLE 2
Parameters used for lineshape simulation

(*a*) [Ru(tpp)($PhCH_2NC$)(1Me-imH)] + 1Me-imH

		Exchanging peaks			
		Chemical shift/Hz		T_2/s	
Order	Temp./°C	Free	Complexed	Free	Complexed
	Room temp.[a]	362	213.5	0.15	0.12
1	58.3	362.5	213.5	0.22	0.09
2	63.0	362.5	213.5	0.22	0.12
3	73.2	362.5	213.5	0.20	0.12
4	82.4	363	213.5	0.20	0.12
5	92.6	365	213.5	0.17	0.12
6	101.8	367	213.5	0.13	0.12
7	111.3	371	213.5	0.12	0.12
8	120.7	376	213.5	0.12	0.12
9	125.5	382	213.5	0.11	0.12
10	106.2	383	213.5	0.11	0.12
11	87.3	382	213.5	0.10	0.12
12	78.2	378	213.5	0.10	0.12
13	67.9	379.5	213.5	0.12	0.12
14	54.2	380.5	213.5	0.10	0.12
	Room temp.[b]	384		0.10	0.15

(*b*) [Ru(tpp)($PhCH_2NC$)(Bu^t-py)] + Bu^t-py

		Exchanging peaks			
		Chemical shift/Hz		T_2/s	
Order	Temp./°C	Free	Complexed	Free	Complexed
	Room temp.[a]	125.5	37.5	0.26	0.14
1	63.0	125.5	37.5	0.26	0.14
2	67.9	125	37.5	0.26	0.14
3	73.2	125	37.5	0.26	0.12
4	78.2	125	37.5	0.26	0.10
5	82.4	125	37.5	0.26	0.08
6	87.3	127	37.5	0.26	0.05
7	92.6	129	37.5	0.26	0.03
8	96.9	129	37.5	0.26	0.03
9	106.2	132	37.5	0.26	0.04
10	116.3	134	37.5	0.26	0.05
11	125.5	134	37.5	0.26	0.06
	Room temp.[b]	135.5	37.5	0.26	0.07

[a] Before run. [b] After run.

The data were analysed by systematically varying τ, the lifetime of the *complexed amine*, and plotting the theoretical spectrum. Visual inspection of observed and calculated spectra allowed the choice of the highest (τ_U) and lowest (τ_L) values of τ which gave acceptable fits to the data. The final value of τ was taken as $\bar{\tau}$, the arithmetic mean of τ_U and τ_L, and the range $\bar{\tau}$—τ_L (or τ_U—$\bar{\tau}$) was used as a measure of the uncertainty in $\bar{\tau}$. Values of $k_{obs.}$ were given by the reciprocals of $\bar{\tau}$ and are listed in Figures 1 and 2, together with the uncertainties in $k_{obs.}$ generated by the range $\bar{\tau}$—$\bar{\tau}_L$. Activation parameters were obtained from an unweighted least-squares dependence of $\log(k_{obs.}/T)$ on $(1/T)$. Such an analysis assumes a constant percentage error in $k_{obs.}$ which is calculated in the analysis. In accordance with the Berkson model,[39] all the error associated with a given point is assumed to lie in the ordinate; the uncertainty in the temperature is therefore subsumed in that of $k_{obs.}$. Uncertainties in $k_{obs.}$ calculated by this second method are larger and, we feel, more realistic than those given in Figures 1 and 2, and it is the former which are quoted in the text.

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